

N.N. Semenov Institute of Chemical Physics RAS  
Association of Composite Materials of France  
Saint Petersburg Research Center RAS  
Institute of Fluid and Solid Mechanics — Strasbourg  
Department of Chemistry and Material Sciences RAS  
Scientific Council on High-Molecular Compounds RAS  
Holding Company "COMPOSITE"  
Institute of Macromolecular Compounds RAS  
The Joint Scientific Council on Problems of Mechanics,  
Strength, and Materials Science RAS

# ***Russian-French Symposium on Composite Materials***



**Book of abstracts**

**JULY 10-13, 2012  
Saint Petersburg, RUSSIA**

## Foreword

Dear Colleagues,

On behalf of the Organizing Committees we are pleased to welcome you at the first **Russian-French Symposium on Composite Materials**, which will be held on July 10-13, 2012 in Saint Petersburg, the north capital of Russian Federation.

Our both countries achieved the significant progress in development, research, and production of composite materials for various industrial and practical applications. Further progress of this important area of national economies calls for the intensification of research activities focused on development of new generations of composite materials based on the advanced organic and inorganic matrices and fillers. An important step toward this goal is a cooperation of leading experts, scientists, and engineers of Russia and France working in this promising area. We do hope that this first Symposium, will serve as a reliable platform for bilateral cooperation, comprehensive discussion of the current trends in research, technology, and optimization of mechanical properties and operating characteristics of engineering composite materials.

The Symposium program comprises various topics of research and application of modern composite materials. They include investigations in manufacture technology and processing of polymeric and inorganic composites, “green” composites, theory and modeling of their physical-mechanical properties<sup>†</sup>.

We wish you a fruitful and enjoyable stay in Saint Petersburg.

Alexander BERLIN, Yves REMOND, and Stanislav PATLAZHAN

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<sup>†</sup> Material presented in this book has been supplied by the authors and has not been corrected by the Editors.

# Committees

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The Organizing Committee of the first Russian-French Symposium on Composite Materials expresses sincere gratitude to the following sponsoring organizations:



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The Organizing Committee thanks the MONOMAX Service Agency and Congress service of the University of Strasbourg for the helpful assistance in organization of this meeting.

## Symposium Timetable

Date	MORNING SESSIONS			Lunch	AFTERNOON SESSIONS	Social Events	
10 <sup>th</sup> July	Registration		Opening		13 <sup>30</sup> – 15 <sup>00</sup>	Session 3	
	8 <sup>00</sup> – 9 <sup>00</sup>		9 <sup>00</sup> – 9 <sup>30</sup>			15 <sup>00</sup> – 17 <sup>00</sup>	
	Session 1	Coffee break	Session 2			Poster Session	Welcome party
	9 <sup>30</sup> – 11 <sup>00</sup>	11 <sup>00</sup> – 11 <sup>30</sup>	11 <sup>30</sup> – 13 <sup>30</sup>			17 <sup>00</sup> – 18 <sup>30</sup>	19 <sup>00</sup> – 22 <sup>30</sup>
11 <sup>th</sup> July	Session 4	Coffee break	Session 5		13 <sup>40</sup> – 15 <sup>00</sup>	Session 6	Conference Dinner
	9 <sup>00</sup> – 11 <sup>00</sup>	11 <sup>00</sup> – 11 <sup>30</sup>	11 <sup>30</sup> – 13 <sup>40</sup>			15 <sup>00</sup> – 18 <sup>00</sup>	19 <sup>30</sup>
12 <sup>th</sup> July	Session 7	Coffee break	Session 8		13 <sup>30</sup> – 15 <sup>00</sup>	Round Table	Hermitage
	9 <sup>00</sup> – 11 <sup>00</sup>	11 <sup>00</sup> – 11 <sup>30</sup>	11 <sup>30</sup> – 13 <sup>30</sup>			15 <sup>00</sup> – 17 <sup>00</sup>	17 <sup>30</sup> – 20 <sup>00</sup>
13 <sup>th</sup> July	Session 9	Coffee break	Session 14		13 <sup>20</sup> – 14 <sup>30</sup>		Goodbye party
	9 <sup>00</sup> – 10 <sup>50</sup>	10 <sup>50</sup> – 11 <sup>30</sup>	11 <sup>30</sup> – 13 <sup>00</sup>			14 <sup>30</sup> – 21 <sup>30</sup>	

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# PROGRAM OF PLENARY AND ORAL PRESENTATIONS

## MONDAY, 9<sup>th</sup> JULY 2012

15-00 – 19-00 Registration

19-30 – 22-00 *Bus city tour "The Parade St. Petersburg"*  
(optional)  
Meeting point near the SPB Research Center

## TUESDAY, 10<sup>th</sup> JULY

08-00 – 09-00 Registration

09-00 – 09-30 **OPENING CEREMONY**

### SESSION 1

Chairs: A.A. BERLIN and S.A. PATLAZHAN

09-30 – 10-00 **Y. REMOND** *"General survey of research activity and development of composite materials in France"*  
(PL)

10-00 – 10-20 **A.N. TROFIMOV**, L.V. PLESHKOV  
*"Composites based on hollow glass microspheres"*

10-20 – 10-40 **V. BELLENGER**, B. ESMAEILLOU, P. FERREIRA, A. TCHARKHTCHI *"Oxidation effect on fatigue behavior of a PA66/glass fibers composite material"*

10-40 – 11-00 **B.A. YARTSEV** *"Internal friction in composite structures"*

11-00 – 11-30 *Coffee break*

### SESSION 2

Chairs: Ph.A. OLIVIER and P.A. STOROZHENKO

11-30 – 12-00 **O.N. KOMISSAR**, A.K. KHMELNITSKIY  
(PL) *"Russian competence centre for aerospace polymer composite structures development and production"*

12-00 – 12-30 **J.Y. COGNARD** *"Analysis of the mechanical behaviour of composites and their bonded assemblies under out-of-plane loads using a modified ARCAN apparatus"*  
(PL)

- 12-30 – 12-50 A.A. BERLIN, A.Yu. SHAULOV “*Inorganic-organic blends. New method for preparation of polymer composites*”
- 12-50 – 13-10 P. VIOT, S. DENNEULIN, C. FROUSTEY, J.L. LATAILLADE, F. LEONARDI “*Study of the damage to composite structures by low-velocity perforation*”
- 13-10 – 13-30 S. TEREKHINA, M. MILLE, B. FAYOLLE, X. COLIN “*Changes in thermomechanical properties during the thermal ageing of a thermostable epoxy matrix*”
- 13-30 – 15-00 **LUNCH**

### SESSION 3

- Chairs:** A.A. KULKOV and Y. REMOND
- 15-00 – 15-30 (PL) V.G. KULICHKHIN, A.V. SEMAKOV, S.O. ILYIN, M.V. MIRONOVA “*Novel approaches to preparation of PAN precursors of high quality*”
- 15-30 – 16-00 (PL) R. MULLER, J. RONDIN, M. BOUQUEY, P. SONNTAG, G. MARTIN “*Elaboration of PP/EPDM blends using an elongational flow mixer: dispersive efficiency and impact on the (co)-continuity development*”
- 16-00 – 16-20 S.V. KOTOMIN, V.G. KULICHIKHIN “*Matrix-free aramid plastics and molecular composites*”
- 16-20 – 16-40 E. BESSARD, O. DE ALMEIDA, G. BERNHART “*Processing parameter optimization of C/PEEK composites using fast thermo-compression technology*”
- 16-40 – 17-00 Yu.N. SMIRNOV, A.I. EFREMOVA, V.A. LESNICHAYA, T.E. SHATSKAYA, V.I. NATRUSOV “*Development of binary prepreg technique for forming high-tenacity composite materials*”



## **POSTER SESSION**

**17-00 – 18-30** **Poster 1 to Poster 37**

**19-00 – 22-30** ***Welcome cocktail on boat along Neva river***  
Meeting point near the SPB Research Center

**WEDNESDAY, 11<sup>th</sup> JULY 2012**

## **SESSION 4**

**Chairs: O.N. KOMISSAR and F. TOUCHARD**

**09-00 – 09-30** **E.F. KHARCHENKO** *“High-strength organic-reinforced plastics and their application in load-bearing structures”*  
(PL)

**09-30 – 10-00** **M.F. ARIF, F. MERAGHNI, N. SAINTIER, J. FITOUSSI, G. ROBERT** *“Experimental fatigue damage investigation in short glass fiber reinforced polyamide composites: application to automotive industry”*  
(PL)

**10-00 – 10-20** **N.V. PIMENOV, Yu.V. ANTIPOV, A.A. KULKOV, A.M. KUPERMAN** *“Organic-reinforced plastics based on aramid fibrous materials”*

**10-20 – 10-40** **B. GENTILLEAU, F. TOUCHARD, J.-C. GRANDIDIER** *“A coupled thermal and damage model for high pressure hydrogen storage vessel”*

**10-40 – 11-00** **V.E. YUDIN, V.M. SVELTICHNYI** *“Viscoelasticity and fracture toughness of fibers reinforced composites based on thermally stable polymer matrices”*

**11-00 – 11-30** ***Coffee break***

## **SESSION 5**

**Chairs: J.Y. COGNARD and E.F. KHARCHENKO**

**11-30 – 12-00** **S.T. MILEIKO** *“Prospects of composites with metal- and intermetallic matrices”*  
(PL)

- 12-00 – 12-30 (PL) V.G. DEGTYAR, S.T. KALASHNIKOV, G.A. KRECHKA, V.N. SAVELIEV “*Experience in development and commercial application of carbon-carbon composites*”
- 12-30 – 12-50 A.N. TIMOFEEV, P.A. STOROZHENKO “*The CVI and PIP methods to obtain ceramic composite matrices*”
- 12-50 – 13-10 I.V. KALEDINA, A.B. MITKEVICH, A.A. KULKOV “*Simulation of shells of revolution from spiral reinforced carbon-carbon material*”
- 13-10 – 13-25 A.N. ASTAPOV, V.S. TERENTIEVA “*New heat-proof coatings for carbon-carbon composite materials protection from high-temperature gas corrosion and erosion*”
- 13-25 – 13-40 A.N. SOLOVYEV, O.A. SAVVATEEVA, A.E. SHUMOV, N.G. ALEXANDROV, I.G. OLENIN “*Perspective fuel tank design development. experimental research of modified carbon composites*”
- 13-40 – 15-00 **LUNCH**

### SESSION 6

- Chairs:** F. CHINESTA and V.G. KULICHIKHIN
- 15-00 – 15-30 (PL) S.N. CHVALUN “*Nanocomposites based on polysaccharides. Following nature*”
- 15-30 – 16-00 (PL) Ph.A. OLIVIER, P. DEMONT, I. EL SAWI, Ch. LAURENT, A. PEIGNEY “*Effects of double-walled carbon nanotubes upon some mechanical properties of T700 carbon fibres / RTM6 epoxy composites*”
- 16-00 – 16-20 E.R. BADAMSHINA, M.A. ZAVERKINA, Yu.A. OL’KHOV, Yu.N. SMIRNOV, Ya.I. ESTRIN “*The influence of ultrasmall additives of single-wall carbon nanotubes on the properties of polymer binders and of composite materials*”

- 16-20 – 16-40 **M.-L. SABOUNGI**, S. BHATTACHARYYA, D. ROY “*Protein functionalized carbon nanotube-polymer composites*”
- 16-40 – 17-00 **A.V. KRESTININ**, G.I. ZVEREVA, O.A. SAVVATEEVA, A.E. SHUMOV “*Production and application of single-walled carbon nanotubes (SWCNTs) as nanomodifiers for polymeric binders*”
- 17-00 – 17-20 A. MARTONE, A. PETRICCIONE, M.R. RICCIARDI, V. ANTONUCCI, **M. ZARRELLI**, M. GIORDANO “*Insight of carbon nanotubes loading in polymer matrix for advanced composite*”
- 17-20 – 17-40 K. WANG, **N. BARTH**, S. AHZI, R. MATADI-BOUMBIMBA, N. BAHLOULI, Y. REMOND “*On the micromechanical modeling of the thermomechanical behavior of semi-crystalline polymers and polymer nanocomposites*”
- 17-40 – 18-00 **V.A. BERSHTEIN** “*Thermostable polycyanurate-poss hybrid nanocomposites: synthesis, structure, dynamics, and properties*”

19-30 *Conference Dinner in the restaurant "Ресторанъ"*

Meeting point at SPB Research Center at 19-00

**THURSDAY, 12<sup>th</sup> JULY 2012**

**SESSION 7**

**Chairs: F. MERAGHNI and S.T. MILEIKO**

09-00 – 09-30 **A. POITOU** “*How to model processing for composite materials?*”  
(PL)

09-30 – 10-00 **F. CHINESTA**, A. LEYGUE, F. BORDEU, S. CHATEL “*Recent advances and new challenges in model order reduction for the modeling and simulation of composite materials, processes and structures*”  
(PL)

- 10-00 – 10-20 **S.V. LYULIN**, S.V. LARIN, V.M. NAZARYCHEV, A.A. GURTOVENKO, N.V. LUKASHEVA, A.V. YAKIMANSKY, V.E. YUDIN, I.V. GOFMAN, V.M. SVETLICHNYI “*Computer simulation of polyimides and heat-resistant nanocomposites*”
- 10-20 – 10-40 **A.V. OSTRIK**, V.N. BAKULIN “*Model of temperature-nonequilibrium elementary cell for heterogeneous materials with a disperse microspherical filler*”
- 10-40 – 11-00 **A.L. SVISTKOV**, V.V. SHADRIN, K.W. STOCKELHUBER, B. LAUKE, G. HEINRICH “*A two-level phenomenological model of rubber compounds*”
- 11-00 – 11-30 ***Coffee break***

### **SESSION 8**

**Chairs:** S.N. CHVALUN and M.-L. SABOUNGI

- 11-30 – 12-00 **Eduard AKIM** “*Scientific basis of a cellulosic composite materials and advances in technology for their production*”  
(PL)
- 12-00 – 12-30 **D. VASCONCELLOS**, C. BONNAFOUS, **F. TOUCHARD**, L. CHOCINSKI-ARNAULT “*Static and fatigue damage mechanisms in woven hemp/epoxy composites*”  
(PL)
- 12-30 – 12-50 **T. BUDTOVA**, A. LE DUC, A. ABDENNADHER, B. VERGNES “*Natural fiber reinforced composites: mechanisms of fibre breakage under processing and final properties*”
- 12-50 – 13-10 **A. LE DUIGOU**, C. BALEY “*Why LCA is an important tool for biocomposites development?*”
- 13-10 – 13-30 **C. BALEY**, A. LE DUIGOU, A. BOURMAUD, P. DAVIES “*Interfaces in biocomposites reinforced by flax fibres*”
- 13-30 – 15-00 ***LUNCH***

## ROUND TABLE

**15-00 – 17-00** **Russian-French collaboration in research and development of composite materials**

**17-30 – 20-00** *Evening promenade at the Hermitage*  
Meeting point near the SPB Research Center

**FRIDAY, 13<sup>th</sup> JULY 2012**

## SESSION 9

**Chairs:** **A. POITOU and A.N. TIMOFEEV**

**09-00 – 09-30** **G.I. SHAIUROVA**, S.A. LOBKOVSKIY, D.S. LOBKOVSKIY, M.S. FEDOSEYEV “*Structural features of aramid fibers and outlook of their application with the newest binders*”  
(PL)

**09-30 – 09-50** K. WANG, **N. BAHLOULI**, F. ADDIEGO, S. AHZI, Y. REMOND, R. MULLER “*Effect of recycling on polypropylene / ethylene octene rubber blends and polypropylene / talc composites used in automotive applications*”

**09-50 – 10-10** **M.A. VANIEV**, I.A. NOVAKOV “*Composites based on polymer-monomer systems*”

**10-10 – 10-30** **O.V. VASILEVA**, T.V. PESKOV, T.Yu. YURANOVA, L.V. MUKHAMEDZYANOVA, D.V. MASAYLO “*Magnetic shields technology of nanocrystalline soft magnetic alloys based on Fe and Co*”

**10-30 – 10-50** **D.A. SAPOZHNIKOV**, O.N. ZABEGAEVA, A.A. SAKHAROVA, T.V. VOLKOVA, V.A. KOTEL'NIKOV, E.V. VOLKOVA, “*Modification of poly(methyl methacrylate) and polycaproamide by polyimides and nanoparticles*”

**10-50 – 11-30** *Coffee break*

## **SESSION 10**

- Chair:** **R. MULLER and A.N. TROFIMOV**
- 11-30 – 12-00 (PL)** **BAKULIN V.N.** “*Investigation of stressed-strained state of composite materials and layered shell constructions made from IT*”
- 12-00 – 12-20** **V.V. REPINSKII**, V.N. BAKULIN “*Calculation of composite three-layer shells with cutouts*”
- 12-20 – 12-40** **N.N. FEDONYUK**, I.V. SLOVTSOV “*Numerical modeling of processes involved in damage accumulation and failure of multiaxial fiberglass composite materials*”
- 12-40 – 13-00** **P.V. KOMAROV**, I.V. MIKHAILOV, Y.-T. CHIU, S.-M. CHEN “*The effect of surface modifier on the interphase structure of polyimide/SiO<sub>2</sub> composites: atomistic simulation*”
- 13-00 – 13-20** ***CLOSING CEREMONY***
- 13-20 – 14-30** ***LUNCH***
- 14-30 – 21-30** ***Goodbye party – tour to Peterhof on boat (optional)***  
Meeting point near the SPB Research Center

## **SATURDAY, 14<sup>th</sup> JULY 2012**

- 10-00 – 18-00** ***The post-symposium full day tour to Pushkin and to Pavlovsk – the residences of the Russian Emperors (optional)***  
Meeting point at the entrances of Sokos Hotels

## PROGRAM OF POSTER PRESENTATIONS

1. **O.N. ABRAMOV**, P.A. STOROZHENKO, D.V. SIDOROV, T.L. MOVCHAN, A.V. ORESHINA “*Graphitized carbon fiber preparation from oilstock*”
2. **V.N. BAKULIN**, A.V. ARTEMIEV “*Applying of polymeric composite materials and modern technologies of it’s processing in constructions of vertical-axial wind power plants of low and middle power*”
3. **A.K. BERKOVICH**, G.S. CHEBOTAeva, D.A. ALENTIEV, V.G. SERGEYEV “*Effect of MWCNTS on PAN thermal stabilization: FTIR studies*”
4. **V.A. BERSHTEIN**, P.N. YAKUSHEV, V.M. GUN’KO, L.M. EGOROVA., Z. WANG, M. ILLSLEY, E.F. VORONIN, G.P. PRIKHOD’KO, R. LEBODA, J. SKUBISZEWSKA-ZIEBA, S.V. MIKHALOVSKY “*Poly(vinyl alcohol) nanocomposite films for biomedical applications: dynamics, thermal behavior, and elastic properties*”
5. **M.Ch. BLOKHINA**, G.I. SHCHERBAKOVA, P.A. STOROZHENKO, D.V. ZHIGALOV, D.V. SIDOROV, I.A. TIMOFEEV, P.A. TIMOFEEV “*Carbon-carbon composite modifiers*”
6. **G.S. CHEBOTAeva**, A.K. BERKOVICH, A.N. OZERIN, V.G. SERGEYEV “*Structure and properties of polyacrylonitrile/multi wall carbon nanotube composites*”
7. **A.A. DALINKEVICH**, Yu.V. ANTIPOV, A.A. KULKOV, A.A. FILIPENKO, K.Z. GUMARGALIEVA “*Macrokinetic model of heat and humidity aging of aramide organoplasts*”
8. **A.Y. DANILOV**, I.V. PLATONOVA, S.D. KHIZHNYAK, P.M. PAKHOMOV “*Study of morphology and piezoelectric properties of composite materials based on matrix from polyvinylidene fluoride and polyamidebenzimidazole*”
9. **T.R. DEBERDEEV**, N.V. ULITIN, AL.AL. BERLIN, A.A. KULKOV, R.Ya. DEBERDEEV “*Mathematical formalism for prediction of electromagnetic and mechanical properties of epoxyamine polymers for composite materials*”

10. **S.E. EVLAMPIEVA**, V.V. MOSHEV “*Triboelastic modeling of time-dependence of nano-structural elastomeric composites*”
11. **I.Z. FAYZULLIN**, I.N. MUSIN, S.I. VOLFSO, R.B. YUFEREV “*Assessment of efficiency of technological additives in the wood flour–plastic composites*”
12. **M. GOMINA** “*Thermally drained composite panels for the more electric aircraft*”
13. **K.Z. GUMARGALIEVA**, A.A. BERLIN, A.A. DALINKEVICH, A.A. KULKOV, S.S. MARAKHOVSKY, A.V. SUKHANOV “*Modern basalt fibers and basalt fibrous polymeric composites*”
14. V.N. BAKULIN, **E.L. GUSEV** “*Mathematical methods of the numerical analysis and optimum synthesis inhomogeneous composite structures with the required complex of the properties at the wave influences*”
15. **V.A. IGNATJEV**, T.A. KISELEVA, N.I. KOLCOV “*Influence hydroxyethyl replaced urea on properties of polyurethane compositions*”
16. V.N. BAKULIN, **V.V. INFYANSKAS** “*Calculation of composite materials constructions by finite elements method*”
17. **A.N. IVANOVA**, S.I. KUCHANOV, Sh.A. SHAGINYAN, L.I. MANEVITCH “*Application of Galerkin’s method for description of microphase separation of compressible polydisperse Markovian copolymers*”
18. **V.O. KALEDIN**, A.A. KULKOV, V.L. STRAKHOV “*A new generation of fire protection on the basis of dispersed and fibrous materials*”
19. **V.O. KHARLAMOV**, A.V. KROKHALEV, S.V. KUZ’MIN, V.I. LYSAK “*Obtaining of anti-friction Cr<sub>3</sub>C<sub>2</sub>-Ti hard alloys using explosive stressing*”
20. **P.V. KOMAROV**, S.V. ZABLOTSKY, J.-P. CHEN, Y.-T. CHIU, V.A. IVANOV, V.G. SERGEEV, A.R. KHOKHLOV “*The effect of filler and solvent on the internal structure and physical properties of PAN based nanocomposites*”



21. **L.A. KOMAR**, B. LAUKE, G. HEINRICH “*Modeling of pair interaction between rigid inclusions surrounded by an interfacial layer in a polymer matrix subjected to high uniaxial loading*”
22. **L.A. KOMAR**, I.A. MOROZOV “*Simulation of the behavior of rigid particle-filled elastomer under high uniaxial loading in the framework of the pair interaction problem taking into account the interphase layer*”
23. V.D. BORMAN, V.Ya. VARSHAVSKIY, **A.L. KVANIN**, Yu.Yu. LEBEDINSKII, M.A. PUSHKIN, I.V. TRONIN, V.N. TRONIN, V.I. TROYAN “*Correlation analyzing of strength and defects of carbon fibers using stable distributions*”
24. **M.A. MAKAROVA**, V.V. TERESHATOV, V.Yu. SENICHEV, S.V. KRASNOSELSKIKH, E.R. VOLKOVA, Zh.A. VNUTSKIY, A.I. SLOBODINYUK “*Ecologically clear high-density thermoplastic composites for protection against radiation*”
25. **G.A. NIKOLAYCHUK**, E.A. TSVETKOVA, O.Y. MOROZ “*The study of microwave absorbing covers based on hydrogenated carbon thin films with ferromagnetic nanoparticles*”
26. **O.G. RYZHOVA**, S.V. ZHUKOVA, P.A. STOROZHENKO, A.N. POLIVANOV, A.I. DRACHEV, I.A. TIMOFEEV “*Oligoelementorganosilazanes – precursors for silicon nitride nanoceramics, self reinforced by nanotubes*”
27. **E.A. TATARINOVA**, D.A. MIGULIN, A.M. MUZAFAROV “*Phenyl substituted MQ-resins as binder for polymer composite materials*”
28. **V.I. VETTEGREN**, A.V. SAVITSKII, M.A. SUSLOV “*Temperature dependences of the tensile strengths of a carbon fiber and a three-dimensional reinforced carbon-carbon composite*”
29. **P. VIOT**, L. MAHEO, D. BERNARD, A. CHIRAZI, G. CEGLIA, V. SCHMITT, O. MONDAIN-MONVAL “*Study of the mechanical behavior of multi-scale open-cell foams*”

30. **E.R. VOLKOVA**, V.V. TERESHATOV, V.I. KARMANOV  
*“The structure and physic-mechanical properties of hard polyurethanes as influenced upon by the curing rate”*
31. **E.R. VOLKOVA**, V.V. TERESHATOV, J.A. VNUTSKIKH, M.A. MAKAROVA, A.I. SLOBODINYUK, V.Yu. SENICHEV, I.L. TUTUBALINA, M.S. FEDOSEEV  
*“High-strength low-temperature quickly curing polyurethanes: design, structure and properties”*
32. **P.N. YAKUSHEV**, V.A. BERSHTEIN, V.M. GUN’KO., L.V. KARABANOVA, T.E. SUKHANOVA, L.M. EGOROVA, A.A. TUROVA, V.I. ZARKO, E.M. PAKHLOV, M.E. VYLEGZHANINA, S.V. MIKHALOVSKY  
*“Biocompatible hybrid polyurethane-poly(2-hydroxyethyl methacrylate) semi-iph-oxide nanocomposites: structure, interfacial behavior, dynamics, and properties”*
33. **A. BASKAR**, M. ANTHONY XAVIOR  
*“Reducing the total material processing time using the concept of dummy machines in cds heuristics”*
34. **S. JAMINION**, J.P. CHAMBARDE, C. BOSQUET, F. HILD, S. ROUX  
*“Displacement and strain field measurement by digital stereo-correlation”*
35. **V.P. RYBALKO**, A.I. NIKITSIUK, E.I. PISARENKO, P.B. D’YACHENKO, V.V. KIREEV  
*“Structural composites based on methyl methacrylate”*
36. **M.A. SAIBALAJI**, K. KALAICHELVAN, M. SREENIVASAN  
*“Optimization of organic fibers % (kevlar / arocel / acrylic fibers) in a friction composite – its effect on thermal stability and friction characteristics”*
37. **M.A. SAIBALAJI**, K. KALAICHELVAN, M. SREENIVASAN  
*“Optimization of alkyl benzene modified phenolic resin matrix% in a semi metallic brake PAD formulation – effect on friction and wear performance”*
38. **V.I. VETTEGREN**, A.V. SAVITSKII  
*“Studying the kinetics of formation the PAN gel-fiber by measuring the electrochemical potentials”*

# PLENARY LECTURES

# **EXPERIMENTAL FATIGUE DAMAGE INVESTIGATION IN SHORT GLASS FIBRE REINFORCED POLYAMIDE COMPOSITES: APPLICATION TO AUTOMOTIVE INDUSTRY**

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Polyamide reinforced short glass fiber composites are widely used in automotive industry. Such materials are extensively employed for automotive components (e.g. air intake manifolds, pedal clutch, etc.). During service life time, these components are subjected to a repeated loading (e.g. engine and chassis vibration) which may induce a progressive damage of the material. The damage itself can be quantified by the stiffness reduction method.

In the present work, the damage quantification based on the decrease of dynamic modulus is discussed. Load-controlled fatigue tests to the injection molded polyamide-66 reinforced with 30%wt short glass fiber (PA66-GF30) specimens with relative humidity of 0% at frequency of 3Hz and stress ratio of 0.1 have been chosen as the experimental protocol. The dynamic moduli are calculated by considering the slope of the hysteresis curve. This method provides the best damage indicator despite the existence of complex interaction between the damage, the viscoelastic of matrix and the heat dissipation inside the material. The infrared thermography and X-Ray microtomography (figure 1) techniques have been used to investigate the damage mechanisms in the studied polyamide composite. The results by X-Ray microtomography showed that the void and defects exists at fiber ends and at the fiber matrix interface. These defects then grow during the fatigue loading. The rigorous analysis of X-Ray microtomography at low and high cycles of fatigue loading at different percentage of fatigue lifetime will be presented.

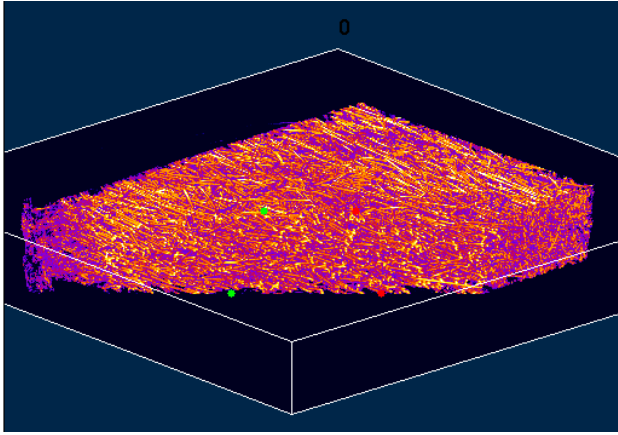


Figure 1. An example of an overall view obtained by tomography 3-D reconstruction.

# INVESTIGATION OF STRESSED-STRAINED STATE OF COMPOSITE MATERIALS AND LAYERED SHELL CONSTRUCTIONS MADE FROM IT

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Currently at creation of constructions of very wide range of purposes in different areas of national economy, wide application are being found for composite materials (CM). Adoption of CM with high specific characteristics (strength, rigidity) and others required for important product properties such as radio-transparency, corrosion stability etc., and also possibility of adjustment of mechanical and physical characteristics in wide ranges, allows creation of multi-functional high-effective constructions with set parameters.

At the same time, at creation of composite elements of constructions with set complex of properties more correct is to make projection of construction and composite material from which that construction should be made, simultaneously.

Rising demands to composite constructions necessitate constant improvement of methods of investigation of stressed strained state (SSS) and deformation of CM and CM constructions.

Applying for calculation SSS of CM and CM constructions various mathematical methods leads to definite difficulties at usage of results of calculation of SSS of CM for investigation of stressed strained state and deformation of composite construction. Such difficulties do not arise in case of applying for calculation of SSS of CM and CM constructions the same mathematical methods.

In presented work the approach is being offered for construction of effective finite elements models (FEM) for adjusted investigation of SSS of CM and especially constructions from CM, including layered shells with account of their peculiarities (heterogeneity, transversal deformation, anisotropy of properties etc.).

Offered approach and created effective adjusted mathematical models resulted in a row of specialized calculating programs, and also in application package (AP) "Composite", intended for solving of wide range of problems of mechanics of CM and CM constructions. One of the first versions of created AP "Composite"

and examples solutions of different problems of mechanics of CM, plates, shells and CM constructions are indicated in monograph [2] and other publications. With the help of AP “Composite” was investigated the SSS and deformation of CM and CM constructions with different rate of detailed elaboration the material itself as well as CM constructions.

Created models, methods, AP allows making investigations on all constructional levels, starting from material (fibre, matrix) of elements of constructions to separate units and products in whole.

Important results of experimental and calculating-experimental investigation of composites and constructions from it were received with help of improved high-accuracy methods of holographic and spec-interferometry [3].

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# RECENT ADVANCES AND NEW CHALLENGES IN MODEL ORDER REDUCTION FOR THE MODELING AND SIMULATION OF COMPOSITE MATERIALS, PROCESSES AND STRUCTURES

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Composite materials and their related manufacturing processes involves many modeling issues, mainly related to their multi-physics and multi-scale nature, to the strong couplings and the complex geometries. Simulations of such materials, manufacturing processes and resulting structures involve many difficulties. Model order reduction –MOR- is an appealing alternative for addressing the efficient solution of such models. We proved in some of our works that MOR allows (i) solving models defined in highly dimensional models as the ones encountered in the kinetic theory description of molecular systems circumventing the so-called curse of dimensionality; (ii) solving transient models in a non-incremental way; (iii) solving model defined in degenerated domains as the ones encountered in plate and shell laminates; (iv) solving materials, processes and shape optimization; (v) perform simulation based real time control; (vi) simulating complex coupling and multi-scale analysis for addressing microstructure development, ...



# NANOCOMPOSITES BASED ON POLYSACCHARIDES. FOLLOWING NATURE

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Structure of natural composite materials and methods of fabrication of cellulose and chitin nanofibers will be analyzed. A novel concept for creation of nanocomposites based on polyacrylic acid and  $\beta$ -chitin will be presented as well.

Nanocomposites are not a human invention; Nature repeatedly uses such approach to create materials, which often contain rigid organic and inorganic substances as fillers. Examples of natural composites are wood and exoskeletons of arthropods. In both cases, matrix is a soft polymer and filler is presented by nanofibrills of polysaccharide with high storage modulus. Such structure gives the material hardness without fragility, allowing supportive and protective functions.

The report reviews current trends in the science of nanocomposites based on natural polysaccharides. Structure of natural composite materials and methods for synthesis of cellulose and chitin nanofibers were investigated.

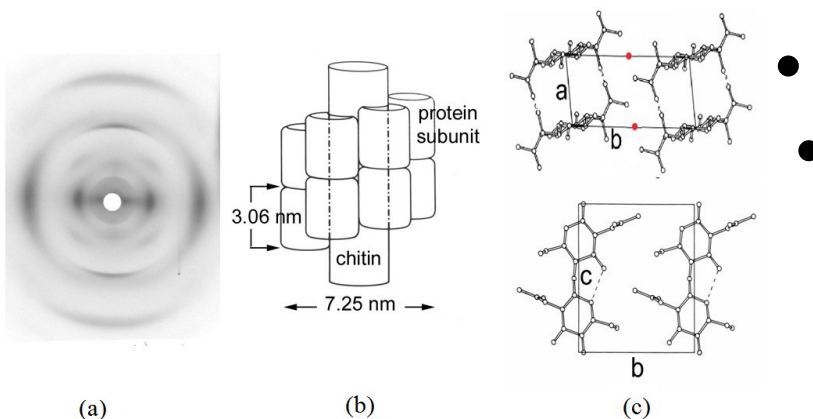


Fig. 1. Structure of  $\beta$ -chitin, (a) – WAXS of squid gladius; (b) – scheme of chitin/protein complex; (c) – crystal structure, black dots indicate water molecules.

Studies carried out allowed us to propose a new method for production of the synthetic composite materials with polysaccharides as fillers. It is known that polysaccharides can form complexes with water – hydrates, herewith water molecules incorporated into the crystal lattice of the polymer. Formation of the monohydrate is accompanied by substantial increase of lattice parameter  $b$  from 9.3 Å to 10.3 Å. When complex formed, water molecule can be substituted by a molecule that could participate in the process of polymerization. This allows the use of such systems for the creation of new nanocomposites by *in situ* polymerization. We found that acrylic acid can be integrated into the crystal lattice of  $\beta$ -chitin. During the process of polymerization of acrylic acid, regularity of the structure along the  $b$  axis of the chitin crystal structure disappears i.e. exfoliation occurs. Composites synthesized reveal unique mechanical properties

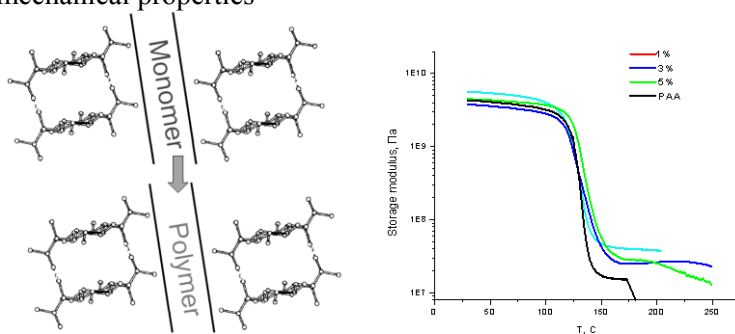


Fig. 2. Synthesis scheme (left) and dependence of the storage modulus with temperature.

# **ANALYSIS OF THE MECHANICAL BEHAVIOUR OF COMPOSITES AND THEIR BONDED ASSEMBLIES UNDER OUT-OF-PLANE LOADS USING A MODIFIED ARCAN APPARATUS**

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The use of composite materials is a key element in energy reduction strategies, particularly in all areas of transportation. Therefore, the study of the behaviour of assemblies of composites and connections between composites and metallic structures, including bonded assemblies, is of great importance. Complex 3D loadings are needed to analyse the response of both the assemblies and the composites. Moreover, failure in bonded assemblies involving composites is often associated with crack initiation in the adhesive or delamination of the composite plies close to the adhesive joint caused by interlaminar or through-thickness stresses [1-2]. Unfortunately, few experimental devices are proposed in the literature to characterize the mechanical behavior of composites under out-of-plane loadings; and those which are available often use thick composite specimens, not representative of the application, or require special geometries [3]. For such thick composite specimens, the geometry of the specimen, the fixing system, and damage generated by machining can result in stress concentrations and subsequent large scatter in the experimental results. Ideally, to obtain experimental results representative of industrial applications, it is interesting to use composite plates with quite low thicknesses [4], which are easy to manufacture.

This paper describes the possibilities of an experimental device, using a modified Arcan apparatus, and optimized hybrid bonded assemblies, which limit the influence of edge effects in order to obtain reliable experimental results [5]. Different numerical studies have been performed in order to analyze and optimize the design of such a system (geometry of the composite plate, geometry of the substrates, fixing system, etc). This test allows the mechanical behaviour of both composites and hybrid metal/composite bonded assemblies to be analyzed under a large range of proportional tensile-

shear out-of-plane loadings. Moreover, it is important to note that failure can occur in the composite, in the adhesive joint or at the composite-adhesive interface according to the tensile-shear loading ratio. An optimization of the adhesive must be performed, especially under shear loadings, as the shear strength of the composite can be higher than that of the adhesive. Experimental results show that the fibre orientations, the characteristics of different plies, and the surface preparation all have an influence on the out-of-plane strength of composites and of hybrid bonded assemblies. Test results, showing the potential of the approach, are presented in the form of failure envelope plots for radial out-of-plane loadings. This study makes it possible to optimize the strength of hybrid bonded assemblies. Moreover, inverse procedures are under development in order to characterize the damage evolution in the composite under out-of-plane loadings.

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# EXPERIENCE IN DEVELOPMENT AND COMMERCIAL APPLICATION OF CARBON-CARBON COMPOSITES

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New class carbon-carbon composites have come into development in the country since the end of the seventies last due to increasing requirements to thermomechanical and thermochemical durability of composites.

The first domestic carbon-carbon material developed by the efforts of several institutes and companies, including OAO "Compozit", under the statement of work and direct participation of OAO "Makeyev GRTs" is a composite material of KIMF type comprising of a braided carbon body of 3-D orthogonal structure saturated with pyrolyzed carbon. The material has been widely studied, introduced into serial production and used until the present time in heat-stressed units of different equipment.

At the same time OAO "Makeyev GRTs" performed activities on developing bodies with different reinforcing patterns from carbon-filled plastic rods. For this purpose, a laboratory setup was designed and fabricated to try out technologies of producing rods from carbon one-, two- and three-fold fibers. A great amount of work was performed on searching and testing of both rod technique and bonding for the specified purposes. As a result, the rod technique by forming a previously coated carbon fiber in the extrusion nozzle of the specified diameter was chosen and tried out. For these purposes the bonding was chosen as aqua solution of polyvinyl alcohol with the advantages of satisfactory adhesion to the fiber and pitch used for the body impregnation, low graphitizable carbon residual and not least nontoxicity. At present the given rod technique is widely used by companies dealing with the development of carbon-carbon composites.

Bodies of the original four-direction structure with three directions in a horizontal plane and one perpendicular to them were developed for the first time in the country at the experimental facilities of OAO

"Makeyev GRTs" on the basis of carbon-filled plastic rods from domestic carbon one-, two- and three-fold fibers.

The C-C composites developed in cooperation with OAO "NIIgrafit" on the basis of the specified bodies were studied and the composite based on bodies from three-fold fibers was chosen for introduction into serial production because of the operational characteristics and labor cost of material production.

This material is applied by some Russian companies for components operating under high-temperature and high-pressure conditions.

At present GRTs has completed activities on developing bodies of finer structure based on one-fold fibers for further improvement of the material properties. The pilot lot of bodies produced at the GRTs experimental facilities was used to manufacture a set of C-C composite half-finished products. The researches of physico-mechanical and thermal characteristics of the material are currently performing and will be completed in the nearest future.

# HIGH-STRENGTH ORGANIC-REINFORCED PLASTICS AND THEIR APPLICATION IN LOAD- BEARING STRUCTURES

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High-strength organic-reinforced plastics have a set of properties which allow them to be used in the very diverse objects. However, the most effective application of the organic plastics was found in two areas. The former concerns structures working under static tension conditions, for example, in rocket-engine cases, and the latter is bound up with structures which work under lateral dynamic compression conditions in various kinds of armor materials and products on their basis (armored helmets, armored vests, shields and others).

In the first case, their use seems quite logical and clear, since organic plastics have record strength in the direction of reinforcement that is conditioned by unique strength of reinforcing fibers. In addition, we succeed in obtaining structural materials with ultimate volumetric filling with fibers – up to 0.95 ... 0.99, using organic plastics based on the Russian fibers with amorphous-crystalline structure. This effect is reached by thermoprofiling the fibers from round into prismatic in closed molds. Such ultimately reinforced organic fiber composites have also and ultimate properties: strength up to 4.0 GPa and elastic modulus up to 130 GPa.

In the case of lateral compression, it was considered as a weakest link, since strength of fibers themselves in the crosswise direction (in tension) is, according to the assessment of A. S. Andreyev, one of the first researchers of this matter, not more than 40 MPa, i.e. is lower than axial strength more than by 2 orders. And then the efficiency of layered organic-reinforced composites in crosswise direction under dynamic impact seems almost mysterious phenomenon.

The study conducted allowed us to establish that the residual longitudinal strength of fabrics is practically not changed up to certain, quite high, level of lateral pressure of the order of 1.2 GPa ... 1.3 GPa – see a curve in Figure 1. Analogous curves are also determined and for organic fabric reinforced composites based on

these fabrics. This material is failed only under high pressure with forming a hole presented in a photo inside the graph. In the case of acting a bullet on the fabric obstacle, we have similar phenomena that are seen in a photo outside the graph.

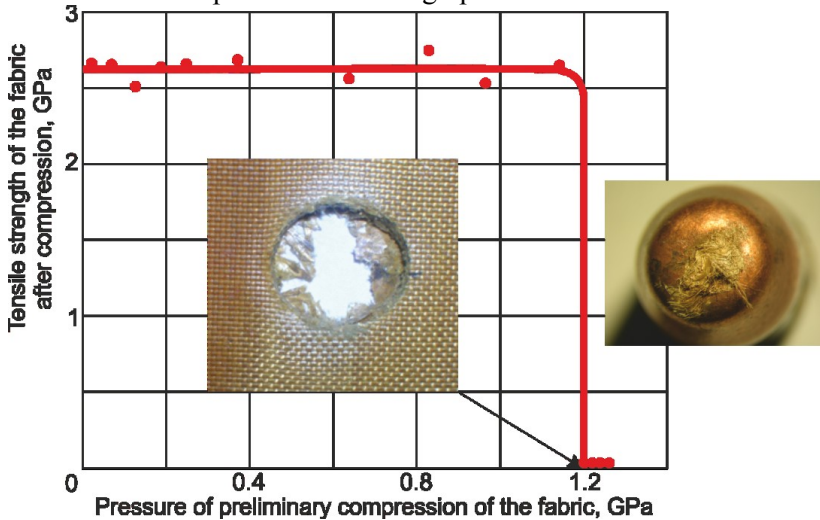


Figure 1. Tensile strength of the aramid fabric as a function of preliminary lateral compression pressure. In a photo: a place of puncture made by cylindrical rod, and a bullet after impact on the fabric obstacle.

Found regularities allow us to explain the high efficiency of application of organic fiber plastics and composites on their basis in ballistic protection means when the material is loaded across its layers.



# **RUSSIAN COMPETENCE CENTRE FOR AEROSPACE POLYMER COMPOSITE STRUCTURES DEVELOPMENT AND PRODUCTION**

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At present, the amount of polymer composites being used has become one of the major competitive advantages enhancing the advanced aircraft performance unattainable with the use of metals.

OJSC “ORPE “Technologiya”, a member of the holding company OJSC “RT-Chemcomposite” of the state corporation “Rostekhnologii”, is currently a unique for the business life in Russia Competence Centre incorporating the State Research Centre of the Russian Federation, carrying out fundamental, advanced research and applied developments, and up-to-date batch production. The Enterprise has at its disposal a weighty, sustainable scientific and technical backlog; research and production capacities; technological capabilities; the unique special-purpose equipment; highly-qualified scientific personnel, production engineers and designers; the experience of the development, experimental verification and introduction of technologies and batch production of polymer composite aggregates for home-produced passenger and military aircraft, launchers, and space vehicles.

Research and Development performed under collaboration of various experts at the boundary of several fields of knowledge allows to create radically new technologies of materials and products to be introduced into batch production.

The complex approach used for the development of polymer composite products includes research and development in the field of materials science and design engineering, testing and batch production of unique products which are in demand at the Russian and foreign markets. The scope of delivery of polymer composite products is increasing annually by no less than 30 %, particularly due to the development and production of science-intensive products of a new range. It has reached more than 25 tons of carbon fiber-reinforced plastic structures a year.

The Obninsk Competence Center has a wide, more-than-thirty years' experience on carbon fiber-reinforced plastic structures for aircraft and rocket-and-space engineering: from the spacecraft Buran to the advanced airliner MS-21 and aircraft engine Sam-146. In accordance with the Decree of the Government of the Russian Federation of 23 April 2012 № 615-P, OJSC «ORPE «Technologiya» maintains the status of the National Science Center of the Russian Federation. The high quality of the products being developed and batch-produced is determined by the stagewise modernization of production and improvement of the quality management system for the compliance with EN 9100:2003, the international standard for aerospace enterprises.

# NOVEL APPROACHES TO PREPARATION OF PAN PRECURSORS OF HIGH QUALITY

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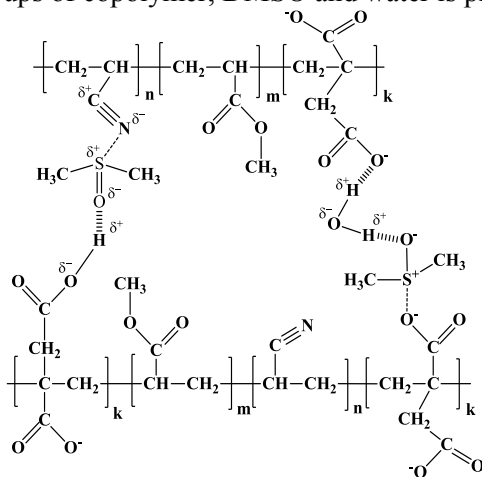
The traditional method of spinning PAN fibers is so-called wet, i.e., spinneret with dopes is immersed in liquid coagulation bath and interdiffusion interaction between elongated solution jets and bath takes place leading to formation as-spun fibers. The further treatments (orientation extension, thermal action, surface coating, etc.) lead to preparing final fibers. But except wet method of spinning, so-called dry-wet method exists, according to that liquid jets pass through air gap of definite length before being immersed to a coagulation bath. In this method, the important meaning has the phase state and rheological behavior of polymer solutions at extension strain. We have drawn our attention on these features of dry-wet process on an example of spinning of PAN fibers from solutions in DMSO.

First of all, the phase diagrams for polymer-solvent and polymer-solvent-coagulant systems were constructed using microinterference and turbidity methods. For PAN-DMSO(water) the amorphous phase equilibrium takes place with UCST around 70°C. That is why, in addition to wet method where interdiffusion prevails, the thermotropic method based on cooling solution jets below line of the phase equilibrium (binodal) can be realized. For PAN-DMSO system this results in phase decomposition of solution on two amorphous phases (high concentrated solution neighboring with very dilute solution, in a limit pure solvent, and such heterogeneous dope is immersed to coagulation bath. Actually, the diffusion processes will be intensified since more concentrated phase interacts with coagulant, and structure of fibers will be changed.

The other version of the dry-wet process for this system consist in realization of so-called mechanotropic spinning when due to extremely high extension of liquid jet the structure and the mechanism of phase decomposition is drastically modified. Due to extending and orientation of macromolecules, the condensed polymer phase forms, and drops of solvent exudes on the solidified

fibers surface. Actually, this is similar to the phase diagram deformation, i.e., to decreasing UCST to ambient temperatures. So, as-spun fibers with unique structure are forming just in the air gap. The liquid bath is needed for fixation of created at extension orientation and removing a residual solvent. In developed version of the spinning stand the tensile force can be measured during jet extension controlling transition solution-fiber.

The essential influence in phase state and rheological behavior causes the water content in solvent and copolymer chemical composition. Because of this influence two concentration regions of solutions exists with yield behavior with a border of 12% of PAN. The tentative scheme of non-covalent interactions between functional groups of copolymer, DMSO and water is proposed:



Actually, fibers obtained by this way (without immersing into coagulation bath) have mechanical properties in excess of corresponding properties of as-spun fibers processed by traditional wet-spinning process with all final treatments. Removing a residual solvent leads to significant reinforcing fibers up to level of technical threads, i.e., novel PAN precursors for carbon fibers.

# PROSPECTS OF COMPOSITES WITH METAL- AND INTERMETALLIC MATRICES

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Successful applications of carbon fibre reinforced polymers (CFRP) during the last decades have left metal- and intermetallic matrix composites (MMC and IMMC, respectively) in a shadow. On the same time, analyzing (i) the present design of machines, in which the usage of composites is critical; (ii) the future challenges of high tech industries; (iii) an existing scientific and technological base for the future usage of composites, - leads to a conclusion on an inevitable wide usage of new generations of metal- and intermetallic matrices composites. This will be an example of the development along the spiral: the first classical work by A. Kelly,<sup>1,2</sup> which gave a start to the modern science of composites analyzed mechanical behavior of metal matrix composites.

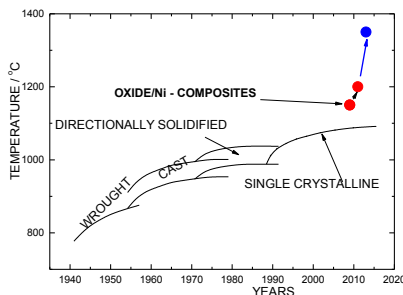
The usage of CFRP in modern aircraft structures<sup>3</sup> has reached about 50% by mass and is certainly approaching a limit for the present design of the aircraft. The modern space technique is also impossible without the wide usage of CFRP (see, e. g.<sup>4</sup>).

Unlike the usage of fibre reinforced plastics (FRP) in large structures, their usage in small structural elements, like e.g. frame elements, does not yield an essential weight saving since heavy joining elements make the whole structure weight comparable with the weight of metallic structure. Moreover, special requirements to material properties in some applications, such as resistance to elevated temperatures, low anisotropy, high thermal and electric conductivity etc., restrict the usage of FRP. In such cases MMC and IMMC become the best solutions. Together with ceramic matrix composites (CMC) they are the base for prospective heat resistant composites, which are absolutely necessary for future generations of gas turbines of any kinds, high temperature nuclear reactors, supersonic aircrafts etc.

The previous experience of a number research groups all over the world forms a solid scientific and technological basis to meet the challenge. In the full-text paper, the experience of the author's team

in developing light structural elements made of MMC and composites for elevated, up to about 900°C, and high temperatures, up to about 1300°C, is described.

Within the frameworks of the abstract it is possible to show just one example of a recent development that is the development of heat resistant MMC based on oxide fibres obtained by using the internal crystallization method<sup>5</sup> invented by the author and his PhD student V. Kazmin.



The figure presents the history of nickel-based superalloys, density of which is now approaching 9 g/cm<sup>3</sup>, as a growth of the use temperature with time to meet requirements to high temperature material for turbine blades of jet engines.

It is shown that present composites can yield a jump in the use temperature to provide an essential enhancement of characteristics of the engines.

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# **ELABORATION OF PP/EPDM BLENDS USING AN ELONGATIONAL FLOW MIXER : DISPERSIVE EFFICIENCY AND IMPACT ON THE (CO)-CONTINUITY DEVELOPMENT**

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This work presents the effect of a recently developed elongational flow mixer (RMX®), on a plasticized thermoplastic elastomer blend based on polypropylene (PP) and ethylene-propylene-diene terpolymer (EPDM). After an optimization of the processing conditions, the dispersive efficiency of this mixer was evaluated on a PP/EPDM 80/20 (wt/wt%) system : the matrix-droplet morphology was characterized through selective solvent extraction of the EPDM phase and scanning electron microscopy. To assess the distribution/dispersion state of the EPDM phase, image analysis was performed in order to calculate the number ( $Dn$ ) and volume ( $Dv$ ) average diameters, as well as the polydispersity index ( $PDI$ ). These results were compared to those obtained with an internal batch mixer (Haake Rheomix 600) at equivalent specific mixing energies: better dispersive efficiency was obtained with the RMX® at lower energy input, especially for high viscosity ratio blends.

Then, a study of the whole composition range of this blend was made in order to identify the composition window where co-continuous morphologies exist. Solvent extraction experiments were performed to measure the EPDM continuity index in combination with morphological characterization. It was observed that PP/EPDM blends elaborated in the RMX® showed a shift of the co-continuity interval towards the high EPDM content side of the composition diagram. Low frequency rheological measurements based on the evolution of the elastic modulus  $G'$  as well as a gel approach were successfully carried out to assess the existence of this co-continuity interval.

Finally, a PP/EPDM 30/70 (wt/wt%) blend exhibiting a co-continuous morphology was dynamically crosslinked in the RMX® using a bromo-activated phenolic resin as a curing system. 98% of EPDM insoluble fraction was obtained by solvent swelling experiments, showing good curing efficiency and phase inversion was observed by TEM. Rheological and mechanical properties were also consistent with those of a TPV.

# EFFECTS OF DOUBLE-WALLED CARBON NANOTUBES UPON SOME MECHANICAL PROPERTIES OF T700 CARBON FIBRES / RTM6 EPOXY COMPOSITES

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Carbon nanotubes (CNT) have been extensively used to modify of improve the properties of polymeric matrices since their discovery in 1979 by A. Oberlin et Al. [1] who considered them as ‘hollow carbon fibres’ and the confirmation of their structure by Iijima in 1991 [2]. More than 2200 papers were published between 2000 and 2010 on CNT in polymeric matrices [3]. When focusing on long fibres (glass or carbon) reinforced composites with a polymeric matrix filled with CNT, the number of publications seriously decreases: around 210 papers for the same period [3]. And when considering only carbon fibres only 21 publications are available. The work summarized here was to: (i) manufacture by a LCM process [ $0^{\circ}_8$ ] and [ $0^{\circ}_{16}$ ] composites laminates made of RTM6 epoxy matrix filled with double-walled carbon nanotubes (DWCNT) and also reinforced with T700 carbon fibres; (ii) measure the mechanical performances of such hybrid composites and compare these performances to those exhibited by the same laminates but without DWCNT. In fact, filling RTM6 epoxy matrix with DWCNT was motivated only by the creation of a quasi-isotropic composite from an electrical point of view. This was achieved by filling the RTM6 matrix with only 0.7wt% DWCNT (i.e. electrical percolation threshold of RTM6 matrix + DWCNT). The dispersion of DWCNT into the RTM6 matrix was facilitated by the use of non-covalent functionalization (i.e. with an amphiphilic molecule). The mechanical and physical properties of these hybrid composite laminates were determined according various mechanical tests performed according European standards. Among these tests, strain energy release rates in mode I ( $G_{IC}$ ) for a  $0^{\circ}/0^{\circ}$  interface were determined. Figure 1 shows



the delaminated surface with carbon fibres and also with DWCNT. The presence of only 0.7wt% DWCNT inside the RTM6 matrix enables  $G_{IC}$  to be increased by +30%.

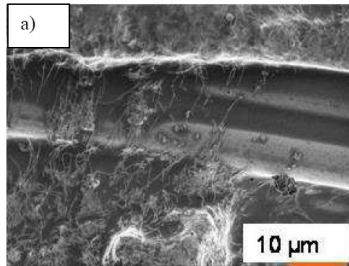


Fig.1:  $[0^\circ_{16}]$  delaminated surface showing the DWCNT in the matrix and around the carbon fibres.

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# STRUCTURAL FEATURES OF ARAMID FIBERS AND OUTLOOK OF THEIR APPLICATION WITH THE NEWEST BINDERS

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Application of up-to-date polymer composite materials (PCM) has become the most considerable potential in efficient improvement of load-bearing shell structures.

In the process of PCM's actual development there is emerged the new conception of designing and commissioning the cocoon-type shell structures notable for their high mass perfection (fig.1). As is generally known, PCM's application efficiency is estimated by the  $W=PV/G$  criterion, where P is pressure, V – net volume, G – mass of structure. The value of W with

$V = \text{const.}$  is determined by P and G parameters which depend on strength and density of reinforcing agent (RA).

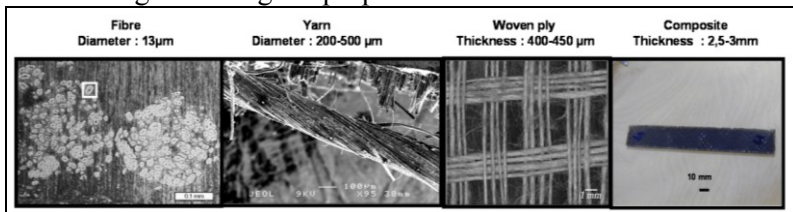
For the first time in manufacturing process of PCM's cases there has been applied the new reinforcing fiberfill with amorphous-crystal structure from the Rusar-S aramid fiber. There are gained results of studying polymer matrices with alternative epoxy binders which curing agents are considerably different in aggregate state, branching of chemical structure and ecological compatibility.

# STATIC AND FATIGUE DAMAGE MECHANISMS IN WOVEN HEMP/EPOXY COMPOSITES

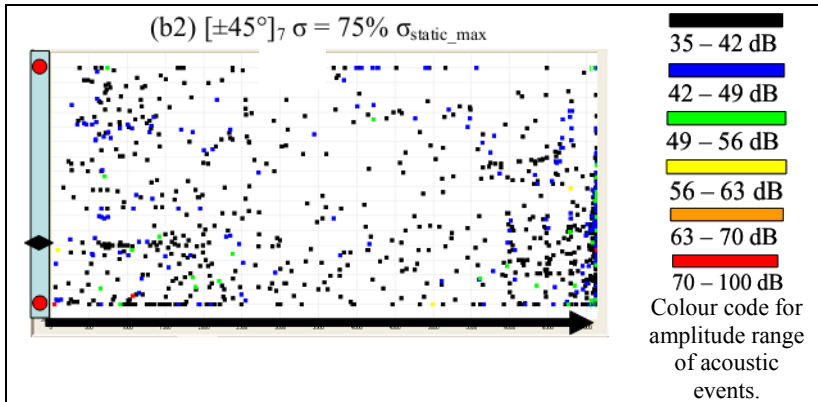
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The worldwide emphasis on environmental awareness triggers scientific researches on the development of recyclable and sustainable composite materials. Recent studies have pointed out hemp fibre composites as a promising option for applications that are currently attended by glass fibres composites and other materials with similar mechanical properties [1,2]. The use of hemp (*Cannabis sativa* L.) phloem fibres as reinforcement in composite materials offers various advantages compared with glass fibres such as low density and low energetic consumption [3]. However, a better understanding of mechanical properties of these eco-composites is still necessary. In this work, damage mechanisms are analysed in woven hemp/epoxy composites. Tensile static and cyclic fatigue tests have been carried out on samples made of seven plies of balanced 2x2 hemp fabric impregnated with epoxy resin. Different techniques have been applied: Acoustic Emission (AE), Scanning Electron Microscopy (SEM), X-ray microtomography and infrared (IR) measurements. The several types of damage that occur in these composites submitted to mechanical loading such as matrix cracking, interfacial debonding and fibre breaking have been characterized. Scenarios of damage development in hemp/epoxy composites due to static or fatigue loading are proposed.



**Figure 1.** Different scales in the microstructure of hemp-fibre woven fabric/epoxy composite.



**Figure 2.** Acoustic events during fatigue lifetime (horizontal axis), plotted against its location in the specimen (blue rectangle), between the AE captors (red points) for a  $[\pm 45^\circ]_7$  woven hemp/epoxy composite. Failure zone is represented by a black diamond in the specimen.

### Acknowledgements

The authors are grateful to the partners of the “Compochanvre” project and thank the Region Poitou-Charentes for its financial support.

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# ORAL PRESENTATIONS

# NEW HEAT-PROOF COATINGS FOR CARBON-CARBONIC COMPOSITE MATERIALS PROTECTION FROM HIGH-TEMPERATURE GAS CORROSION AND EROSION

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Heat-proof carbon-based composite materials (C–C, C–SiC, SiC–SiC) having high strength-to-weight ratios are widely used in high-temperature machinery, especially in heat-loaded structure elements of hypersonic flight vehicles and propulsion systems. However carbon composites subjected to oxygen-containing high-temperature gas flow impact have low corrosion and erosion strength and can be modified by siliconizing only up to 1300-1400<sup>0</sup>C, so that the protection problem is now actual and cannot be solved completely, primary in space vehicles design. An aero capturing hypersonic flight vehicle is subjected simultaneously to aggressive plasma flow, limit heat and mechanic loads. An ambient air in the wave front is almost completely dissociated and the vehicle is by chemically active oxygen and nitrogen atoms, ions and excited particles mixture streamlined. Flow and surface temperatures during capturing are extremely high and reduce to the intensive gas corrosion and erosion, thus it is quite essential to use both volume protections by siliconizing and surface heat- and erosion-proof protection. Some multifunction protective coatings designed in Moscow Aviation Institute (State University of Aerospace Technologies) using the original conception of self-healing hetero-phase coatings [1].

Coatings' forming was made by the method of slip fusing of suspense with micro-, submicro- and nanoscale powders from the preliminary melted alloy of optimum system Si-TiSi<sub>2</sub>-MoSi<sub>2</sub>-B-Y [2] and alloyed supplementary by fine-dispersed SiC to reinforce dendritic cell structures generating the refractory Ti<sub>0.2-0.95</sub>Mo<sub>0.05-0.8</sub>Si<sub>2</sub> and TiSi<sub>2</sub>-skeleton of main layer of coating.

The effect of the proposed carbon-carbonic material protection from oxidation was proved by mass losses estimation due to erosion of the

surficial layer subjected to hypersonic non-steady and high-enthalpy dissociated and ionized air flows for temperatures up to 1900<sup>0</sup>C (and for short-time peaks up to 2100<sup>0</sup>C). Eutectic refills defects in coatings' structures and recuperates ultra-thin protective silica layer consuming during operation. Coating's skeleton reinforcement due to erosion's reduction increases its protective effect under high-temperature influence. The effectiveness of coatings under  $T_w = 1800^0\text{C}$  was increased twice up to 400 s. The proposed coatings secures low catalytic activity of surfaces (Nitrogen and Oxygen atoms heterogeneous recombination's velocity  $K_w = 3\text{-}5$  m/s) and satisfactory emittance ( $\varepsilon \approx 0,7$ ).

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# THE INFLUENCE OF ULTRASMALL ADDITIVES OF SINGLE-WALL CARBON NANOTUBES ON THE PROPERTIES OF POLYMER BINDERS AND OF COMPOSITE MATERIALS

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Carbon nanotubes are capable to change properties of polymers, such as mechanical strength, the Young modulus, the tensile strain, optical properties etc. However, the insufficient attention is given to studying of influence of micro (ultrasmall) additives of single-wall carbon nanotubes (SWCNT) on the polymers structure.

In our work it is shown for the first time that the addition of ultrasmall amounts of single-wall carbon nanotubes leads to a significant increase in the main mechanical characteristics of the crosslinked poly(urethaneurea) elastomer. The elastic modulus and the tensile strength pass through maxima as the nanotube concentration is increased from 0 to 0.018 wt %; at a nanotube concentration of 0.002 wt %, the maximum values of the modulus and strength are higher by factors of 2.5 and 1.5, respectively, than the corresponding values for the unfilled polymer. The thermomechanical, spectral, and structural characteristics of nanomodified elastomers are investigated. Recent studies have been shown that the extremum experimental dependence of Young's modulus on the volume fraction of the filler may be theoretically described only in terms of the interfacial-layer gradient model without resorting to the particular mechanism of gradient structure formation.

Adding of SWCNT (0.002 – 0.008 wt. %) in polyurethane block copolymers (PUBCP) also leads to various changes of mechanical properties and structural parameters. Changes of supramolecular structure of polymer under the influence of SWCNT consist in increase in the Young modulus and tensile elongation by 20-30 %. At the same time, tensile strength of the filled and unfilled samples does not change practically. The SWCNT additives influence



noticeably on relaxation behavior of polymer. Thus, recovery of the initial sizes of the samples, containing up to 0.008 wt. % of SWCNT, after deformation requires more high temperatures and prolonged time in comparison with unfilled samples. Data of DSC and analysis of X-ray diffraction patterns of PUBCP, containing SCNT, testify considerable structural changes in comparison with unfilled polymer. The results of investigation of the influence of SWCNT ultrasmall additives on the epoxy polymers properties are presented also in this study. Nanomodified binders with improved tensile strength and tensile elongation at the concentration of approximately 0.002 wt % are obtained. The simultaneous increase of these parameters leads, as a rule, to an increase in the impact characteristics, which is very important in the plan of the creation of construction materials. The composites on the basis of epoxy binders, modified by SWCNT ultrasmall quantities, and of carbon and glass fibre fabric were prepared and their mechanical properties were investigated. In the report, possible causes of the influence of SWCNT on structure and, therefore, properties of both nanomodified binders and polymer composite materials are discussed.

*Financial support by the Russian Foundation for Basic Research (the grant № 12-03-00919-a) is gratefully acknowledged.*

# **EFFECT OF RECYCLING ON POLYPROPYLENE / ETHYLENE OCTENE RUBBER BLENDS AND POLYPROPYLENE / TALC COMPOSITES USED IN AUTOMOTIVE APPLICATIONS**

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The utilization of thermoplastic olefins (TPOs) is currently growing in the automotive industry and particularly for both exterior and interior parts of automobiles. This is due to the fact that TPOs are selected to replace others materials such as polycarbonate, ABS and PVC compounds because of their lower weight, higher resistance to aging and lower price. However, the post-consumer TPOs wastes from end-of-life vehicles represent a threat for our environment. In this context, the European directive 2000/53/EC imposes to increase their rate of recovery. Among the different recycling methods, the most acceptable and more ecological one is the mechanical recycling. To date, little quantitative information is known about the impact of recycling TPOs on their properties.

The objective of our study is to quantify the influence of recycling on the rheological, chemical, thermal, and mechanical properties of polypropylene / ethylene octane rubber (PP/EOR) blends and polypropylene / talc (PP/talc) composites used for car bumpers. It is important to note that in this work recycling was simulated by multiple re-extrusion procedures (up to 6 recycling) for simplification, and hence, we did not worked on real recycled materials from wastes. The properties of the materials were assessed by melt flow index measurement (MFI), differential scanning

calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), tensile testing and scanning electron microscopy (SEM). We found a significant increase of MFI with recycling number for PP/EOR blends, while for PP/Talc composites the increase of MFI is less marked than for PP/EOR. This result is explained by chain scission mechanisms. The lower molecular weight of recycled materials leads to a higher crystallization degree, as measured by DSC. Although PP-based materials underwent multiple extrusions, there is no significant change in chemical structure as shown by FTIR. By means of tensile testing, we found that elastic modulus, and yield stress decrease with recycling number in the case of PP/EOR systems, while in the same time the strain at break remains constant. In the case of PP/Talc systems, there is no effect of recycling on elastic modulus and yield stress, while the strain at break slightly decreases. The evolution of mechanical behavior of PP-based materials with recycling is explained by competition between mechanisms of modification of inclusions size and dispersion state (studied by SEM), and mechanisms of chain scission of the polymer matrix. The high-rate impact behavior of the PP-based systems is currently under investigation to verify either the recycled materials would be suitable or not for car bumpers applications.

# INTERFACES IN BIOCOMPOSITES REINFORCED BY FLAX FIBRES

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In a composite material the quality of the fibre-matrix interface is critical. When the reinforcement is flax fibres however, there are additional parameters to consider. In the plant the individual fibres, assembled in bundles with shared walls, make up the skeleton which reinforces the stem. This is therefore already a composite material. Retting, a biological treatment generally performed on the ground in the field, damages the liaisons between the fibres and facilitates the extraction of fibres during subsequent mechanical operations (scutching, hackling). After these steps the fibres are more or less separated and have irregular surfaces. Additional treatments are also possible before introduction into the polymer. The individual flax fibre can also be considered to be a composite material, it is made up of a stack of layers (a primary wall and a secondary wall itself made up of three layers, S1, S2 and S3) reinforced by cellulose oriented at different scales (micella, micro-fibrils, macro-fibrils). The main constituents of the walls each provide a particular function, such as reinforcement (cellulose), matrix (pectins) and interface between cellulose and pectins (hemicellulose).

There is also a percentage of water absorbed in the walls at room temperature which acts as a plasticiser. Manufacturing of composites with organic matrix polymers (thermoplastic and thermoset) is often performed at temperatures above 100°C, resulting in modification to the amount of water present and changes to the properties of the different constituents and their interactions.

In order to study the interfaces in polymers reinforced by flax fibres (biocomposites) a multi-scale approach is required (liaisons between fibre and polymer, between fibres in a bundle, and within the walls between the cellulose micro- and macro-fibrils), which must also take account of the thermo-mechanical forming cycle.

This contribution will describe, with a multi-scale approach, the different interfaces in a bio composite. The quality of interfaces with flax fibres (epoxy and PLA) will be studied using a micro-droplet debonding technique, in order to estimate interfacial shear strengths and show the different damage mechanisms.

# ON THE MICROMECHANICAL MODELING OF THE THERMOMECHANICAL BEHAVIOR OF SEMI-CRYSTALLINE POLYMERS AND POLYMER NANOCOMPOSITES

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In this work, we will address some of the new developments in the micromechanical modeling and simulation of the thermomechanical properties of semi-crystalline polymers and polymer nanocomposites. For this, different polymer matrices filled with different nanofillers such as clay nanoparticles are considered. We will also address different homogenization techniques used to compute the effective elastic properties and yield behavior.

The obtained results will be discussed as function of the microstructure such as the crystallinity of the matrix, the distribution of the nanofillers in the polymer matrix and the shape effects of these fillers. We will also confront the predicted results to our experimentally measured ones.

We will particularly address the effect of temperature and strain rate on the elastic and yield behavior. For this, quasi-static and dynamic loadings are considered along with test temperatures ranging from well below to above the glass transition.

# OXIDATION EFFECT ON FATIGUE BEHAVIOUR OF A PA66/GLASS FIBERS COMPOSITE MATERIAL

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In automotive industry, the long term behaviour of composite materials used in the processing of under hood parts is a crucial problem due to the increasing temperatures and pressures in motors. These under hood parts made of Polyamide 66/glass fibers composite material are submitted to the coupling effect of oxygen and temperature which induce a surface oxidation. The concentration of oxidation products is high in the skin layer and decreases quickly towards the core of parts. The oxidized layer (about 200 $\mu$ m thick) of polymeric parts has not the same mechanical properties as the core [1] and in particular is more brittle [2]. The first question is: does this oxidized layer decrease the fatigue life time? The Fig 1 displays the fatigue lifetime of oxidized samples versus the thermal ageing time. The number of cycles at break decreases effectively with the increasing ageing time.

A recent work [3] showed that polysequential tests induce a fatigue lifetime higher than non-stopped tests. The rest times allow the relaxation of macromolecular chains in the region of micro-defects, which increase the number of cycles before fracture. Our study shows that the microdefects build-up by thermal oxidation is not reversible. The aim of this work is to establish a possible relationship between the concentration profile of oxidation products and the fatigue life time of oxidized specimens.

The PA66/glass fiber compound is provided by Rhodia Co. Dogbone samples were injected in our laboratory by using an injection machine DK Codim 175 tons press. Specimens are oxidized at 120°C in a ventilated oven. The concentration profile of oxidation products is determined by micro-infrared spectrometry and an attenuated total reflectance accessory. The fatigue test [4] is performed in a flexural

alternative bending device, at a frequency of 10 Hz with a  $R = \frac{\epsilon_{\min}}{\epsilon_{\max}}$

value equal to -1, an applied amplitude strain  $\epsilon_0$  of 0.019, at 23°C and 50% RH.

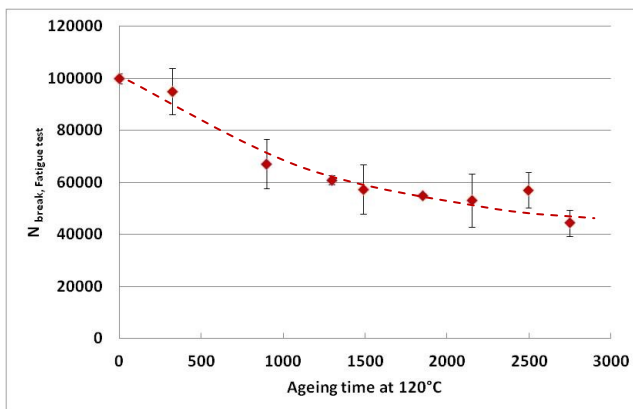


Fig1: Fatigue lifetime of oxidized specimens versus thermo-oxidative ageing time at 120°C.

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# INORGANIC-ORGANIC BLENDS. NEW METHOD FOR PREPARATION OF POLYMER COMPOSITES

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Materials based on organic and inorganic polymer blends prepared from their melts presents a new line in the polymer materials science, which will extend the range of materials with new performance.

Let us note the principal distinction of the proposed method from the filling of organic polymers by disperse inorganic fillers.

As the effective mechanical blending of polymers in melts is only possible, when the softening and flow temperatures as well as polymer viscosities under the blending conditions have similar values, “low-melting” inorganic polymers corresponding to high-molecular hydrocarbon polymers must be synthesized.

By analyzing the properties of inorganic polymers on the base of the energy theory, which relates the polymer properties to the energy of chemical bond between the chain units, allowed one to choose “low-melting” inorganic polymers like boron and phosphorus polyoxides, to develop the methods of the “mild” synthesis and to study their rheological, thermal and thermomechanical properties.

Polyoxides have some advantages compared to organic polymers: extremely high thermal and radiation stability, the absence of volatiles under thermal action, very low vapor pressures at high temperatures, oxidation stability, inflammability, high elastic characteristics, ecological purity, with their nature resources being practically inexhaustible.

Polyoxides are characteristic of other features, such as the possibility of their synthesis under mild conditions and chemical activity, which makes it possible to use synthetic procedures of organic chemistry for their modification.

The main disadvantage of polyoxides is a low deformability, which is related to the high energy of internal chemical and physical interactions and is responsible for the mechanical stresses and material brittleness.

The synthesis of low-melting polyoxides under mild conditions, namely, oligomer boron oxides, borates and phosphates of different



elements allowed one to obtain polymer–polymer composites in the Brabender mixers, a Scamex RMX elongational flow mixer, and an extruder.

The rheological properties of blends of oligomers of boron oxides, aluminum borate and phosphates with PE, PP, ethylene–vinyl acetate copolymers were measured as well as thermal, thermomechanical and mechanical characteristics of the related composites.

Both filled composites using a “softening filler” and hybrid materials characteristic of the component mixing at the molecular level were prepared.

In compositions of boron polyoxides with organic polymers, a tribomechanical effect pronounced as a drop of stress needed for the melt flow under extrusion conditions was found. It was shown that the effect of a planar macromolecular structure of boron polyoxides on the rheology of blend melt is observed when polyoxide is in the rubberlike state.

# PROCESSING PARAMETER OPTIMISATION OF C/PEEK COMPOSITES USING FAST THERMO-COMPRESSION TECHNOLOGY

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Novadays, pushed by environmental and energetic constrains, there is a general trend in aeronautical industry, to move from thermoset towards thermoplastic composites and to develop new processing technologies aiming to reduce production times and energies.

The results reported in this paper were obtained in the frame of a French research program managed by Airbus, and were concentrated on C/PEEK materials processing parameter optimisation using fast thermo-compression technology, involving induction heated die technology.

The use of rapid die heating technologies (up to 100°C/mn in heating or cooling) aims on one hand to reduce manufacturing time and environmental product costs and on the other hand to allow complex shape part manufacturing based on non pre-consolidated semi-products.

Nevertheless process parameter optimisation has to face with several physical constrains in order to obtain composite materials with high quality and properties. Amongst them the two major parameters investigated and reported in this paper are: PEEK degradation at high temperature in air environment and PEEK crystallisation mastering during rapid cooling steps. High temperature rheological studies and DSC fast crystallization experiments have permitted to define interesting processing windows, and for the later to propose also a crystallization kinetic models taking into account the presence of carbon fibers.

These results were applied to the processing of two C/PEEK materials using powdered fabrics and NCF-commingled semi-products. As a result, an optimum processing cycle was proposed permitting the reduction of C/PEEK manufacturing down to 55mn when the today standard autoclave is not lower than 250 mn.

# THERMOSTABLE POLYCYANURATE-POSS HYBRID NANOCOMPOSITES: SYNTHESIS, STRUCTURE, DYNAMICS, AND PROPERTIES

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V.A. Ryzhov<sup>1</sup>, A.B. Sinani<sup>1</sup>, B. Youssef<sup>3</sup>, M.-R. Garda<sup>4</sup>,  
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Last years the large attention has been paid to hybrid polymer-inorganic nanocomposites containing 3D polyhedral oligomeric silsesquioxane (POSS) particles of cage structure and ~1 nm in size, with functional surface groups reacting with a matrix monomer or polymer [1]. The ability of POSS as “silica clusters” to be dispersed at the molecular level and covalently incorporated into a matrix is the key to impact POSS on polymer dynamics and properties.

Densely cross-linked polycyanurates (PCN) have attracted much interest because of their good thermal and mechanical properties, which commend them for use in high performance technology, e.g., as matrices in composites for high-speed electronic circuitry [2]. In the present study, a series of PCN nanocomposites based on dicyanate ester of bisphenol E (DCBE) and epoxy cyclohexyl-functionalized POSS (ECH-POSS) nanoparticles, with ECH-POSS content  $c$  varying from 0.025 to 10 wt. %, were synthesized [3, 4]. The DCBE/ECH-POSS mixtures were stirred for 3h at 1700C for pre-polymerization, and the filled prepolymer was cured at 170-3000C. The structure, dynamics, thermal and elastic properties of the nanocomposites were characterized by FTIR and far-IR spectroscopy, gel fraction analysis, TGA, densitometry as well as by WAXS, DSC, DMA, and laser-interferometric creep rate spectroscopy (CRS [5]).

FTIR monitoring of the curing process confirmed that cyanate-epoxy co-reaction (matrix-filler hybridization) took place along with the

main reaction of DCBE polycyclotrimerization. The main result was revealing the large changes in matrix dynamics after introducing as low as 0.025 wt. % nanofillers. This relates to network dynamics including vibrations of cycles and skeletal vibrations (far-IR spectra, absorption bands at  $\sim 80$  and  $200\text{-}250\text{ cm}^{-1}$ ) and PCN glass transition dynamics. Thus, the strong shift of the glass transition onset to higher temperatures, from 209 to 2600C, and manifesting the second glass transition at 360-3900C (unfreezing of interfacial dynamics) were observed by DSC. The enhanced thermal stability at the earlier stages of degradation was registered for the nanocomposites with  $c \leq 1$  wt. % compared to that for neat PCN. Thus, after heating to 4000C in nitrogen atmosphere, the glass transition started from 1870 for neat PCN but from 2500C for the nanocomposite with  $c = 0.025$  wt.%. CRS/DMA measurements indicated the pronounced dynamic heterogeneity within glass transition, constrained dynamics effects, possible increase in dynamic modulus at 20-2000C by 30-40%, and enhanced creep resistance at high temperatures for the nanocomposites with low POSS contents. This was treated in the frameworks of extraordinarily high interfacial area, covalent bonding at interfaces, and long-range impact of POSS clusters to the densely cross-linked PCN.

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# NATURAL FIBRE REINFORCED COMPOSITES: MECHANISMS OF FIBRE BREAKAGE UNDER PROCESSING AND FINAL PROPERTIES

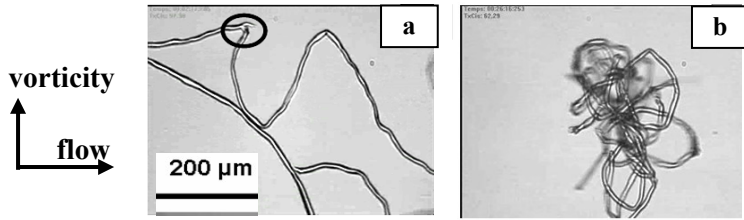
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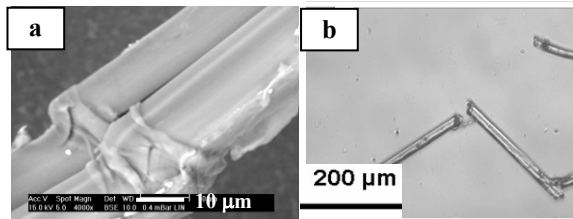
Polymer-fibre composite properties depend on the quality of fibres dispersion, on fibres final length and aspect ratio. During the compounding step, fibres are broken and partially lose their reinforcing action. It is thus important to understand the breakage mechanisms in order to control and to minimize their rupture. In this work, we are interested in composites made of polypropylene reinforced with natural cellulosic fibres.

The behaviour of two types of fibres, flax (cellulose I) and Tencel<sup>®</sup> (cellulose II,) is studied and compared. The first part of the work is devoted to the analysis of the behaviour of a single fibre under shear using counter-rotating rheo-optical set-up (A. Le Duc, B. Vergnes, T. Budtova, *Composites Part A*, **42**, 1727–1737, 2011). Under shear, the fibre is progressively submitted to successive bending and then it tears and breaks (Figures 1a, 2b). The rupture of natural fibres occurs after an accumulation of fatigue in time (strain and specific mechanical energy). At the rupture point, both Tencel<sup>®</sup> and flax fibres are fibrillating. Tencel<sup>®</sup> fibres are initially elementary fibres and are breaking at the points where the fibre bends. Long Tencel<sup>®</sup> fibres tend to form agglomerates (Figure 1b). Flax fibres are initially in bundles that may, or may not, dissociate. Flax has numerous defects all along the length (Figure 2a); it is these defects that are the points where the fibre breaks (Figures 2b).

Fibres length and aspect ratio distributions after compounding and composite mechanical properties will be then discussed and correlated with the rheo-optical observations.



**Figure 1.** Tencel<sup>®</sup> fibre under shear



**Figure 2.** Flax fibre: SEM image of defects (a) and single fibre breaking under shear (b)

### **Acknowledgements**

The work is performed in the frame of the Industrial Chair in Bioplastics supported by Arkema, L'Oreal, Nestlé, PSA and Schneider Electric.

# NUMERICAL MODELING OF PROCESSES INVOLVED IN DAMAGE ACCUMULATION AND FAILURE OF MULTIAXIAL FIBERGLASS COMPOSITE MATERIALS

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The paper discusses the results obtained in numerical modeling of the damage accumulation in composite materials under static loads. The materials under consideration have a matrix of vinyl ether binder reinforced by multiaxial fiberglass fabrics consisting of stitched roving layers. Each layer may have its own orientation angle so that one fabric layer may have up to four reinforcement directions.

The paper considers various types of damage in the monolayer having a unidirectional structure and a fabric made by knitting of warp and weft lines. Based on the analysis of experimental studies a number of main scenarios are considered for damage development related to adhesive and cohesive matrix failure under tangential and normal stresses acting in transverse direction to the reinforcement as well as separation of monolayers. The results of this analysis are used to generate a mathematical model for damage and failure of a multilayer composite material incorporating the damage level parameters taking into account changes in the elastic properties of monolayers due to damage development.

The paper discusses the methodology for experimental evaluation of unidirectional and fabric monolayer parameters required for this model. These parameters determine the inception of fine cracks in the layer and in the matrix at the fiber/matrix interface as well as plastic transition of the layer.

The results of numerical modeling of damage and failure processes for two types of fiber-reinforced plastics are given, namely the material based on the quadri-axial fabric ( $0^\circ/+45^\circ/90^\circ/-45^\circ$ ) and the material based on two types of fabrics – plain weave roving fabric ( $0^\circ/90^\circ$ ) and bi-axial diagonal fabric ( $+45^\circ/-45^\circ$ ) with uniform alternate pattern over thickness. The differences in the mechanism of damage inception and propagation for these two materials are

indicated, which is proven by the results of their mechanical tests. Also the paper discusses the results of numerical modeling for a hybrid composite material consisting of plain weave roving carbon-fiber fabric layers ( $0^{\circ}/90^{\circ}$ ) and bi-axial diagonal fiber-glass fabric ( $+45^{\circ}/-45^{\circ}$ ) with different number of layers. Advantages of introducing diagonal fiber-glass fabric layers in carbon fiber plastic are demonstrated.

The obtained results of numerical modelling make it possible to refine the requirements which the composite materials have to meet for application in ship hull structures.



# A COUPLED THERMAL AND DAMAGE MODEL FOR HIGH PRESSURE HYDROGEN STORAGE VESSEL

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The purpose of this work is to study the thermomechanical behavior of a type IV hydrogen storage tank: a wound carbon/epoxy composite wrapped over a polyurethane liner and 316L steel bases. Each part have a significant role in the structure: the composite part ensures the strength, the polyurethane part acts as hydrogen barrier and thermal insulator and the steel bases allow the connection process. This study principally focuses on the thermomechanical behavior of the composite part. In fact, during the fast filling of such a tank, there is simultaneously a significant increase in the pressure and in the temperature of hydrogen [1], causing biaxial stresses and gradual heating of the structure and thermal gradients. The aim of this study is to characterize the behavior of such a structure submitted to this complex thermomechanical loading.

An axisymmetric numerical model is developed to simulate the filling of a 2L tank. The model takes into account wind angle and ply thickness variation in the dome of the tank. Moreover, mechanical and thermal behavior laws are determined from mechanical tests carried out at different temperatures (- 40°C, 25°C, 85°C) and from DSC tests (from -50°C to 150°C) which covers the entire temperature range of use of the tank. These tests show a significant influence of temperature on the behavior laws, highlighting the importance of thermo-mechanical modeling to simulate the tank behavior. Polyurethane and steel parts present a plastic behavior. An orthotropic and thermo-dependant behavior is used for the composite part which takes into account matrix cracking by the degradation of transverse modulus  $E_{22}$ . The evolution of this transverse cracking is governed by the transverse deformation  $\epsilon_{22}$ .

Several simulations are performed to analyze the influence of transverse cracking and temperature on longitudinal stress  $\sigma_{11}$ . An example of this stress field is presented in figure 1. Results show a significant influence of this parameter on longitudinal stress. Failure

of tank is governed by fiber breakage and therefore by the longitudinal stress  $\sigma_{11}$ . Finally, a simulation with simultaneous and progressive increase of internal pressure and internal temperature [2] is performed to better understand phenomena occurring during filling.

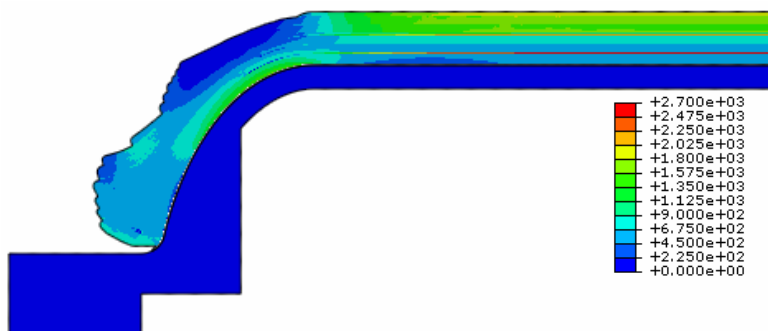


Figure 1: Longitudinal stress field in 2L tank for an internal pressure of 1600 bars and temperature of 25°C (axisymmetric model).

**Acknowledgements:** We express our thanks to the partners of H2E OSEO innovation project.

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# **MATHEMATICAL METHODS OF THE NUMERICAL ANALYSIS AND OPTIMUM SYNTHESIS INHOMOGENEOUS COMPOSITE STRUCTURES WITH THE REQUIRED COMPLEX OF THE PROPERTIES AT THE WAVE INFLUENCES**

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On the base of a mathematical and computer modeling of the problems of the numerical analysis and optimum synthesis of a structure of the inhomogeneous composite systems with a required complex of the properties, both with a flat, and curvilinear symmetry are investigated.

In a variational statement of the one of the most efficient methods of building of decisions with a required complex of the properties are the methods, founded on principle of the maximum L.S. Pontryagin [1-2]. However the methods of the optimum synthesis, founded on the necessary conditions of a optimality, base on a principle of the maximum L.S. Pontryagin, allow to build the local-optimum decisions.

In accordance with this, appear the necessity of the development of a new efficient methods numerical analysis and optimum syntheses composite structures with a required complex of the properties ,that were free from this defects.

One of the most efficient approaches to decision given problem is an development approach, founded on installed characteristic internal symmetry in structure of optimum decisions and theory of multiciphered images [3-7]. On base a theory of multiciphered images [8, 9] is designed strategy of continuation of decision on the parameter, allowing realize the efficient continuation an ensemble global-optimum decisions supporting problem of a synthesis on the parameter.

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# DISPLACEMENT AND STRAIN FIELD MEASUREMENT BY DIGITAL STEREO- CORRELATION

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The stereo-correlation measurement gives the opportunity to measure the shape, the displacements of an object and to calculate the strain under constrains.

CORRELI<sup>STC</sup> was developed in collaboration between Holo3<sup>(1)</sup>, LMT<sup>(2)</sup> and EADS IW<sup>(3)</sup>. This development was a part of a project dedicated to the study of the vulnerability of composite materials subjected to shock loading (project Vulcomp). This software is already used for different measurements : in aeronautics, cars, boat, motor, composite material, wood, plastic, cartons...

CORRELI<sup>STC</sup> uses a finite element description of the displacements. As the measurement has the same base than the FE simulations, and it's easy to compare directly the results, without any interpolation. We will show you some results between the experiment and simulation.

In the post-treatment, it's possible to add virtual gauges (or profiles) to compare the measure between CORRELI<sup>STC</sup> and the real gauges, taken like a reference. We will show some results on different types of material.

A metrology study has been carried out, considering CORRELI<sup>STC</sup> as a displacement sensor and as a strain sensor. The uncertainties depends strongly on the quality of the random pattern (needed for the image correlation), the light, the CCD size, object size, .. For the displacement, the uncertainty is around the 1/10 pixel size, for example with a 4 millions pixels camera, and an object's size around 500 x 500 mm, the uncertainty is 25  $\mu\text{m}$ . For the strain, the most important difference between the virtual and the real gauge, is around 300  $\mu\text{def}$  (ie 0.03%).

# **SIMULATION OF SHELLS OF REVOLUTION FROM SPIRAL REINFORCED CARBON-CARBON MATERIAL**

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Shells of revolution from carbon-carbon materials made by spiral lay out method "Rozetta", are used in manufacturing of rocket cones. Method "Rozetta" is found on filling of hollow symmetrical structure in the form of a preselected body of revolution by packet of predetermine number of identically shaped and sized exact involute surface plies which are successively disposed and joined circumferentially in a contacting, stack-like layered and overlapping relationship. Reinforcing woven ply lays on the linear developable surface, from top to bottom and from inside to outside shell's boundaries [1,2].

Material's reinforcing scheme is determined by the shape of linear developable surface. It is variable on length and thickness of shell. Material properties of ply in warp and weft directions are determined by woven material properties and manufacturing process.

The stress analysis model of shells of revolution with spiral reinforcing is based on two hypothesizes:

1. The shape of reinforcing ply in structure is described by surface of tangent lines to spiral line on a cylinder.
2. Carbon-carbon ply material properties are invariable in the structure.

The simulation process of shells from spiral reinforced carbon-carbon material includes the following steps:

1. Calculation vector field of woven warp direction

The hypothesis 1 allows describing analytical transformation of woven ply on the plane to spiral surface ply. The direction of woven warp is known on plane, so this direction at reinforcing surface ply can be calculate by differential geometry's methods. Three angles define the direction of warp: angle of reinforcing is the angle between the warp and the shell meridian, angle of spiral and angle of

cone are angles between ply surface and coordinate plates. Angle of reinforcing depends from initial orientation ply to warp, two other angles depend from shell geometry.

## 2. Calculation of material properties distribution

Material matrix of elasticity in structure points are calculated using the layer matrix of elasticity by transformation in according to reinforcing angles, which are defined in step 1. In coordinate system which connected with shell geometry (meridian, tangent and normal directions) the material is anisotropic and material properties depend of length and thickness of structure.

## 3. Creation of finite element model

3D finite element which allowed modeling variable on volume anisotropic material, was developed and added to finite element system "Composit-NK"[3,4]. A script was written using input language system "Composite-NK" for finite element model creation. Input data for the script are: shell geometry, parameters of spiral surface, carbon-carbon layer material properties and standard loads. Carbon-carbon layer material properties and strength parameters should be measure by specimen-witness tests. Six components of stress tension in warp and weft directions are calculated at the end of the procedure.

# THE EFFECT OF SURFACE MODIFIER ON THE INTERPHASE STRUCTURE OF POLYIMIDE/SIO<sub>2</sub> COMPOSITES: ATOMISTIC SIMULATION

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The modification of nanoparticles with surface-grafted polymers is a promising method that makes it possible to manage the properties of polymer nanocomposites. The need to change filler properties is caused by the fact that the physical mixtures of polymers and nanoparticles do not always produce nanocomposites. In immiscible heterogeneous systems, the features of intermolecular interaction (polymer–polymer, polymer–nanoparticles, and nanoparticles–nanoparticles) may cause phase separation, which inevitably results in the deterioration of the properties of the composite as a whole.

When a surface modifier is used, the thickness of the transition layer can be several orders of magnitude larger than that for unmodified nanoparticles depending on the surface density of the modifier, its molecular weight, and its compatibility with the matrix. In general, the issues associated with the formation of an interface between the polymer matrix and the modified nanoparticles have been less investigated.

Theoretical studies of the properties of the interface between the polymer matrix and surface-modified nanoparticles encounter a lot of problems which are caused by the need to take into account many parameters simultaneously. Nevertheless, the large body of facts accumulated recently makes it possible to consider the problem of studying ultrathin polymer films in a direct connection with the research of nanocomposite materials. This analogy is explained by the large contribution of the matrix located in the range of surface forces in the case of both ultrathin films and filled polymers.

In this work, we studied the effect of the surface density and molecular weight of a modifier on the properties of a polymer–nanoparticle interface in the frame of atomistic simulation. The model of polyimide–SiO<sub>2</sub> nanocomposite was constructed as



alternate layers of polymer matrix and inorganic substrate, which may be considered on account of the above analogy. As a matrix we used a polyimide obtained from two monomers: 3,3',4,4'-biphenyltetracarboxylic dianhydride and 1,3-bis(4-aminophenoxy) benzene. For the sake of simplicity, the model of the substrate was built assuming a unit cell of silicon dioxide (in the crystalline form of  $\beta$ -cristobalite) as an infinite layer. Alkylsilyl molecules and hydroxyl groups were used as surface modifiers.

The main parameters of our model were i) the molecular weight of alkylsilyl; and ii) the surface grafting density. All simulations were performed by the method of atomistic molecular dynamics using the DL POLY package. The obtained results show that the interface between the polymer matrix and the modified SiO<sub>2</sub> surface forms due to the mutual diffusion of the polymer matrix and molecules grafted onto the nanoparticle surface. Upon an increase in the surface density and the weight of the modifier molecules, they can form a separate phase on the surface of the nanoparticles. This indirectly evidences that the aggregation of nanoparticles can occur during the melting–solidification of the material if the molecules of the modifier and polymer matrix are incompatible.

This work was supported by the Russian Foundation for Basic Research (projects nos. 11-03-12142-ofi-m-2011). We also thank the Supercomputing Center of the Lomonosov Moscow State University for providing computer power of the cluster «Chebyshev».

# MATRIX-FREE ARAMID PLASTICS AND MOLECULAR COMPOSITES

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Strong and rigid aramid plastics were prepared by solid-state consolidation of polymeric fibers from rigid-chain poly(p-phenylenebenzimidazoltereththalamide) (PABI), and copolymer (CPA) with poly(p-phenylenetherephtalamide) without using any additional binder. Structure and mechanical properties of matrix-free plastics from PABI, CPA and composite fibers were studied.

Industrial fibers (SVM and Armos) spun from PABI and CPA solutions in DMAA were used in as-spun (AS) and heat-treated (HT) form. Fibers from molecular composites were spun from blends of PABI and CPA with thermoplastic polysulfone in DMAA solutions.

PABI and CPA have  $T_g$  in the region 270 – 300 °C. Under compression at the temperature above the glass transition of the polymer the cylindrical fibers transforms into polygonal rods and their consolidation results in formation of anisotropic plastics..

Modulus and particularly strength of plastics from AS- fibers are connected with disorientation angle of rigid chain macromolecules in the material which is very dependent on consolidation pressure.

Composite fibers were spun from solutions of PABI and CPABI mixed with polysulfone, soluble in DMAA.

By changing ratio of components in the blend and spinning conditions, it is possible to govern structure and properties of fibers and composites on their base in wide range - from high performance heat-resistant materials to fusible reinforced thermoplastics.

# PRODUCTION AND APPLICATION OF SINGLE-WALLED CARBON NANOTUBES (SWCNTS) AS NANOMODIFIERS FOR POLYMERIC BINDERS

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Initially, the idea of applying carbon nanotubes (CNTs) as enhancing fillers in polymers consisted in transferring the results obtained in traditional technology of polymeric composites using long carbon glass and organic microfilaments to the nanoscale level. Moreover, additional advantage, namely, several times higher material isotropic strength it was assumed to be attained. Nevertheless, the data published now are rather disappointing. The following key questions have not been answered so far: (i) what requirements should dispersion of discrete aligned filling elements in polymeric matrix meet to achieve the maximal strength? (ii) How do strength and Yang modulus depend on concentration of filling elements? (iii) What is the upper limit of isotropic strength? As a result, three requirements were formulated for successful application of CNTs: (i) nanotube walls should be wetted well by polymer, (ii) agglomerates of nanotubes should be absent in polymer to avoid stress concentration on them, (iii) nanotubes should be aligned in polymer similarly to microfilaments in traditional polymeric composites.

It was found that isotropic strengthening up to 50-70% can be attained by the addition of SWCNT at mass concentration of  $10^{-5}$  -  $10^{-4}$ . The effect was essentially higher than simple theoretical estimation based on the rule of addition. We found that such low concentration of nanotubes increased mass density of the polymeric matrix by 5% - 9% that clearly indicates structural rearrangement of polymer matrix. We also found that the effect of reinforcement can be translated to carbon-polymeric composites. This opens possibility of improving strength parameters of polymeric composites by 30%-70% in directions where polymeric matrix resists to stress.

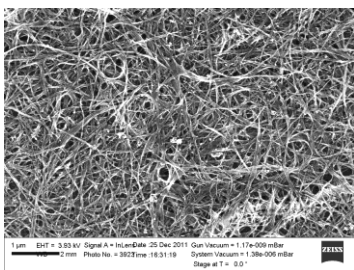


Fig. 1. Acid-treated *f*-SWCNTs. Scanning electron microscopy (SEM).

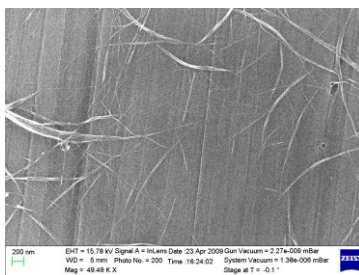


Fig. 2. Image of individual nanotube ropes and bundles in the *f*-SWCNT product (SEM).

Carbon Chg Ltd. has developed technology regulations and equipment and starts producing some SWCNT products tailored for different technical applications [1]. The arc discharge process of SWCNT synthesis was chosen to be scaled up. Measurement techniques for SWCNT product certification were developed. The product properties important in technical application of SWCNTs were chosen as standard parameters of the product in technology regulations. Figs. 1-2 show one of the products, namely, acid-treated SWCNTs (*f*-SWCNT-90A) tailored for production of nanostructural modifiers.

## References

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# WHY LCA IS AN IMPORTANT TOOL FOR BIOCOMPOSITES DEVELOPPMENT?

A. Le Duigou, C. Baley

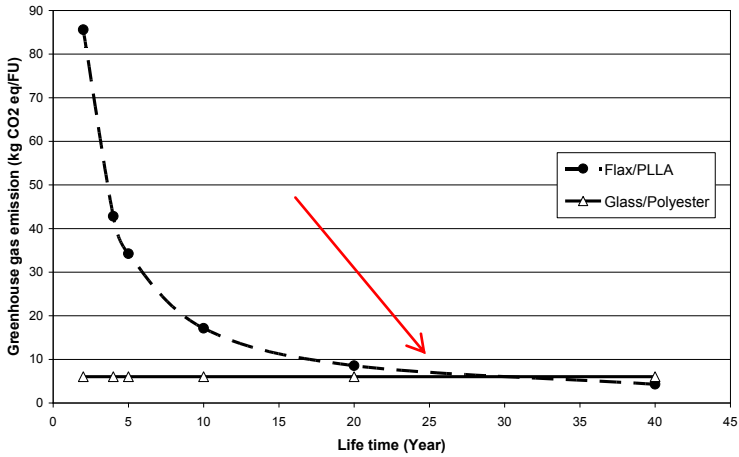
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Extensive works on biocomposites are already available in the literature. However the simple fact that they come from renewable resources does not necessarily mean that their environmental impact is lower. The aim of this paper is to quantify the environmental impacts of flax/PLLA biocomposites using a standard life cycle analysis (LCA) in order to evaluate their use as a replacement for glass/ unsaturated polyester composites. To fulfil the same mechanical functions under tensile loading and over the life cycle flax/PLLA biocomposites require significantly less non-renewable energy than glass/ unsaturated polyester.

However the lifetimes of biocomposites in severe environments are still not well known, Moreover they are composed of biopolymers such as PLLA which is biodegradable during composting when the temperature, humidity and bacterial activity are controlled, so one might expect the long term durability of biocomposites to be limited. Therefore the whole life cycle is difficult to assess and parametric analysis become very useful. In this study an internal glass/polyester bulkhead application was considered (not directly exposed to the environment) with lifetime fixed at 40 years.

Figure 1 presents the evolution of greenhouse gas emission indicators with respect to the lifetime. End-of-life by incineration is considered.



**Figure 1** Relation between the lifetime of biocomposites and greenhouse gas emissions

If the biocomposite lifetime is less than 40 years, the amount of biocomposite needed to fulfil the function will increase, which will be a disadvantage from an environmental point of view. Hence a lifetime of at least 25 years is necessary (Figure 1), in order not to exceed the values for the glass/polyester composite.

# DEVELOPMENT OF BINARY PREPREG TECHNIQUE FOR FORMING HIGH-TENACITY COMPOSITE MATERIALS

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In manufacturing the products from polymer composite materials (PCM) semi-finished materials are often used. These are so-called prepregs, i.e. reinforcing materials previously impregnated by binding substance: textile, ribbon – roving, fibers. The main process requirement to binding substance in prepreg is its vitality at a temperature of storing. Conventional approaches for chemical control of vitality of mixed binding substances in prepreg has sufficient weakness – along with increase of storage time the conditions of processing become more complicated – time and temperature do increase.

In the Institute of Problems of Chemical Physics of RAS together with NPO Stekloplastik the new physical approach is developed for regulation of prepreg vitality by means of separate application of resinous and curative binding substances on separate reinforcing elements. This seemingly unexpected method of attaching binding substance to armature is named a method of separate application of components (SAC method). Technique that uses its method called binary. Semi-finished products received with this technique, SAC prepregs, can be stored and transported in separate rolls in form of resinous and curative parts. The products manufacturing is conducted either by laminated laying out from alternating prepregs of different type with the following moulding or vacuum forming or by joint build from two giving devices.

The major issue in using binary prepreg technique is the attainment of full mixing of binding substance components during products manufacturing. It is found that mixing takes place due to two physical effects. The first, predominant in the early stages of formation of PCM, is the mechanical mixing of components of the

binding substance. It occurs because of filtration microflow of components in vertical and horizontal directions since reinforcing fabrics are physically a large set of drawholes where shear loads appear that can increase an intensity of mixing different-type components. The second process, predominant at later stages of forming, is mutual diffusion of binding substance components along with the process of chemical structuring. It is evident that relative intensity of mentioned processes of mixing and chemical structuring does depend on many factors: origin and structure of reinforcing materials, chemical structure and viscosity of binding substance components, products forming conditions etc.

An impact of these factors has been studied by integrated structure-kinetic analysis of the composite forming process. Combined approach is developed that allowed to select optimal regimes of PCM forming on the basis of SAC prepregs.

An integrated comparative study of relaxation properties of glass and carbon-fibers on the basis of SAC prepregs and prepregs of mixed type has been carried in order to understand the structural changes during PCM forming process. The methods of NMR spectroscopy, bending resonance oscillations and thermo-mechanical dilatometry have been used. The results obtained points out that the full mixing is not achieved in the process of solidification of composites on the basis of binary prepregs. Consequently, full conversion of functional groups of binding substance is not achieved too. But it is found that varying some factors this major drawback of binary prepreg technique can be minimized or mitigated.

It is shown that during SAC prepreg forming micro-non-homogeneous mosaic structure is formed within polymeric matrix, where thickly cross-linked micro-regions alternate thinly cross-linked ones, especially in the zones directly adjacent to surface of reinforcing fibers. These defective micro-regions, having higher molecular mobility and shorter relaxation times, stipulate significant reduction in residual internal stresses of shrinkable and thermal nature usually localized at the boundary of polymeric matrix and surface reinforcing fiber. With optimal selection of ratio of magnitudes of micro-volumes and relaxation time thickly- and thinly- cross-linked micro-regions the strength properties of composites are increased.

During forming of hybrid carbonglass- and organic-glass-fibers the importance of residual heat stress in composites increases even



further. This strengthens the relaxation effect of specific micro-non-homogeneous structure of polymeric matrix. It has been found that in many hybrid combinations the application of binary technique results in higher strength properties of composites compared to mixing technique.

It has to be mentioned that an application of SAG prepregs brings an improvement of important operating factors (especially in the case of large-products manufacturing) such as consolidation, shock resistance, crack resistance.

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# COMPUTER SIMULATION OF POLYIMIDES AND HEAT-RESISTANT NANOCOMPOSITES

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Polyimides (PI) are considered as a perspective polymer matrix for heat-resistant nanocomposites. Correct estimation of equilibration times ( $t_{eq}$ ) in atomistic computer simulations of melts of heat-resistant polymers represents serious problem. Typical  $t_{eq}$  is usually in the range 1-10 ns and in most cases no longer than 100ns;  $t_{eq}$  is determined by the. A definition of  $t_{eq}$  through the calculation of relaxation time of the squared radius of gyration  $R_g^2$  of a single chain can be inexact and can lead to incorrect calculation of glass transition temperature  $T_g$ .

In present study we considered three types of plastic PI matrices, synthesized which were synthesized in the Institute of Macromolecular Compounds on the base of dianhydride R: 1,3-bis-(3',4'-dicarboxyphenoxy)-benzene and one of three diamines: 4,4'-bis-(4''-aminephenoxy)-diphenyl sulfone (BAPS), 4,4'-bis-(4''-aminephenoxy)-diphenyl (BAPB), and 4,4'-bis-(aminephenoxy)-diphenyl oxide (BAPO). Computer simulations were carried with the help of the GROMACS package (parameter set Gromos53a6). Partial charges were calculated by different methods with the use of semi-empiric and *ab initio* quantum-mechanic simulations (DFT, Restricted Hartree-Fock, and AM1). For all calculated types of partial charges we observed that typical times of the single chain diffusion at 600K on a distance comparable with  $R_g$  are around 100  $\mu$ s. To decrease  $t_{eq}$  of PI melts we simulated equilibration of neutral PI melt. Typical times associated with diffusion of a single polymer chain on a distance  $R_g$  in a neutral melt was decreased to  $\sim$  500ns, i.e.  $t_{eq}$  was considerably reduced. After turning on partial charges in polyimide melts all local reorganizations of a structure were characterized by the times as short as  $\sim$ 10 ns. For the R-BAPB matrix we observed excellent agreement of the calculated thermal volume expansion coefficient with experimental data.

The 1  $\mu$ s-long simulations performed showed that the degree of equilibration of neutral samples of the studied PIs influenced considerably the corresponding values of  $T_g$ . After adding a short single-walled carbon nanotube (SWCNT) in the neutral melt of the investigated PIs we observed an increase of  $t_{eq}$ . We also witnessed re-orientation of benzene rings of the PI along the SWCNT surface which agrees well with known experimental data.

This work was carried out under financial support of RFBR grant № 11-03-00944-a and in the framework of the state contract № 16.523.12.3001 with Ministry of Science and Education of Russian Federation. Computer simulations were carried out on the computer cluster of IMS RAS and supercomputers “SKIF-Chebyshev” and “Lomonosov” of Moscow State University.

# MODEL OF TEMPERATURE-NONEQUILIBRIUM ELEMENTARY CELL FOR HETEROGENEOUS MATERIALS WITH A DISPERSE MICRO-SPHERICAL FILLER

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Methods for calculating equations of state (EOS) of heterogeneous materials (GM) using the EOS of their components are of considerable practical interest and developing intensively [1, 2]. It is known [3], for GM, which absorbs the radiation, there is no EOS in the usual sense (as a means of describing the sequence of quasi-statically changing the equilibrium states). Finding relationships to describe the GM behavior has to be used in conjunction with the calculation of the energy characteristics. This is necessary because the stresses setting to the material depend on the energy doles absorbed in the filler and binder. Thermal nonequilibrium of GM components is the result of transient radiation absorption. It has a fundamental and decisive importance. To emphasize this fact we shall not call EOS when we have the relations describing the behavior of GM, non-equilibrium absorbing radiation. We'll call them the defining equations (DEQ).

In this paper we propose a method for constructing DEQ of heterogeneous material by known EOS of its components and the energy doles absorbed in the filler and binder. Wide-range non-equilibrium model of the elementary cell having dispersed microspherical fillers is offered. It is assumed that the cell is generally in a uniaxial strain state. Calculation of the stresses within the elementary cell is based on the numerical solution of two-dimensional equations of equilibrium of an elastic medium in a cylindrical coordinate system. This system of equations is complemented by wide-range EOS of GM components.

The system of equations with appropriate boundary conditions is solved by the iterative method of elastic solutions proposed by A.A. Ilyushin for materials whose behavior is described by a shift in the theory of small elastoplastic deformations. We set the slip condition

at the boundaries between the filler and binder (the cases of continuity of displacements and stresses at the sites corresponding to the orientation were also considered).

Wide-range model of the cell allows to calculate the behavior of GM in the whole range of densities of energy having practical interest (as low energy deposition, when influenced by shear stress and significantly during the elastoplastic and large, in which there are phase transitions in the GM components).

Much attention in the model of the elementary cell of GM is given a detailed description of the structural features of multilayer microspherical fillers used in heterogeneous coatings for protection against ionizing radiation. Loss of stability, the destruction and irreversible collapse of the microspheres are taken into account in the process of absorption of radiation energy in the GM components.

The results of calculations of stress profiles taking place in heterogeneous coatings with dispersed fillers of glass and carbon-coated microspheres with heavy metals (tungsten and nickel) are given for the proposed model of the GM cell.

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# ORGANIC-REINFORCED PLASTICS BASED ON ARAMID FIBROUS MATERIALS

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Some physical-mechanical properties of organic-reinforced plastics based on Armos and Rusar-S aramid fibers, produced by a wet winding method using epoxy binders, are considered.

Filament characteristics, such as twist value, filament and tow wettability with a binder and tension of reinforcing material in winding, as well as a content of polymer matrix in the organic-reinforced plastic were estimated in terms of their influence on physical-mechanical properties of organic-reinforced plastics.

The influence of twist on strength characteristics is retraced both on dry filaments and tows and microplastics on their basis. Twisted filaments and tows have higher breaking load, while microplastics based on them are less strong than ones based on untwisted filaments and tows.

Strength of a tow-based microplastic is reduced when increasing a diversity in length of filaments in a tow that is defined by the size of their sag in the tow.

The increase in tow tension in winding causes the increase in a reinforcing coefficient of the composite and effects on its strength. Elastic modulus of unidirectional organic-reinforced plastics based on Armos and Rusar-S tows rises with increasing the reinforcing coefficient.

The state of Rusar-S and Armos surfaces was evaluated using the scanning electron microscopy. Rusar-S fibers have the plane and smooth surface, while the surface of Armos fibers has some quantity of defects and adhesive joints.

The capillary-rise height of an epoxy binder along the Rusar-S filament is less than in the case of the Armos filament because of the less developed surface of Rusar-S fibers.

It leads to the lesser content of a binder in the organic-reinforced plastic based on Rusar-S fibers in comparison with one on the basis of Armos fibers.

Reinforcing materials under consideration have high indices of tensile strength and elastic modulus. A dynamic elastic modulus of the Rusar-S complex filament exceeds 165 GPa and its strength in the microplastic is more than 6.5 GPa that is higher by 15% than the corresponding characteristics of Armos fiber based materials.

# CALCULATION OF COMPOSITE THREE-LAYER SHELLS WITH CUTOUTS

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Composite three-layer shells are widely used in modern aviation and space technology. Often these structural elements have features of different nature (cuts, overlays, rigid inclusions, etc.). Stress-strain state near the hub of the above is characterized by rapidly changing fields of displacements and stresses. The calculation of such structures is a rather complex task and requires constant improvement of methods of calculation of such structures.

Currently, one of the most effective methods for solving problems of determining the parameters of the stress-strain state of composite irregular layered and the three-layer shells is the finite element method. The accuracy of the results depends on the density of the finite element partition. In this regard, it becomes necessary to determine the optimum density of the partition of the structure. In [1] to determine the density of the grid, which provides sufficient accuracy of the calculation, the algorithm of sequential treatment with multiple choices of the growing density of the partition. In this paper, the proposed algorithm is applied to determine the optimal partitioning of the density in the problems of calculating the composite three-layer shell structures weakened by cutouts. To simulate a number of three-layer shells using finite element (FE) of three-layer and multilayer composite shells having a sufficiently effective approximation with a minimal number of degrees of freedom [2,3]. In these papers, the construction of approximating functions for the displacements of the filler used FE approximation of the effective movement of CE bearing layers, which ensures compatibility of displacements at the interfaces of carrier layers and the filler. Also in the approximating function CE movements bearing layers are clearly expressions that describe the movement of these layers as a rigid body, which leads to a significant increase in the rate of convergence of the numerical results of the modeling of shells.

The above-described algorithms and models used in the problems of determining the parameters of the stress-strained state of composite



three-layer shells, weakened by rectangular cutouts. The object of investigation chosen composite three-layered cylindrical, conical and ogival compartments with two diametrically opposed rectangular cutouts loaded with uniformly distributed internal pressure. The bearing shells are made of layers of fiberglass and filler - foam. It is assumed that the pressure acts only on the membrane. It is believed that the boundary conditions at the ends of the shell correspond to the case of rigid fixing. The values obtained for the optimal partition of the density of the proposed EC in comparison with traditional demonstrated high efficacy of the proposed finite element models in problems of statics of composite three-layer shells.

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# PROTEIN FUNCTIONALIZED CARBON NANOTUBE-POLYMER COMPOSITES

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We have developed fully integrated nanotube composite materials through the functionalization of carbon nanotubes by covalently attaching protein molecules onto their surface. Functionalization of multi-wall carbon nanotubes by ferritin produces a dramatic enhancement in the mechanical properties of PVA. Samples containing functionalized nanotubes show a stronger influence on glass transition temperature than those containing the same amount of non-functionalized nanotubes. Functionalization of single-wall carbon nanotubes with denatured collagen increases the PVA matrix crystallinity, resulting in a dramatic enhancement of the Young's modulus, tensile strength and toughness. A supramolecular organization at the interface is associated with the increased crystallinity.

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# MODIFICATION OF POLY(METHYL METHACRYLATE) AND POLYCAPROAMIDE BY POLYIMIDES AND NANOPARTICLES

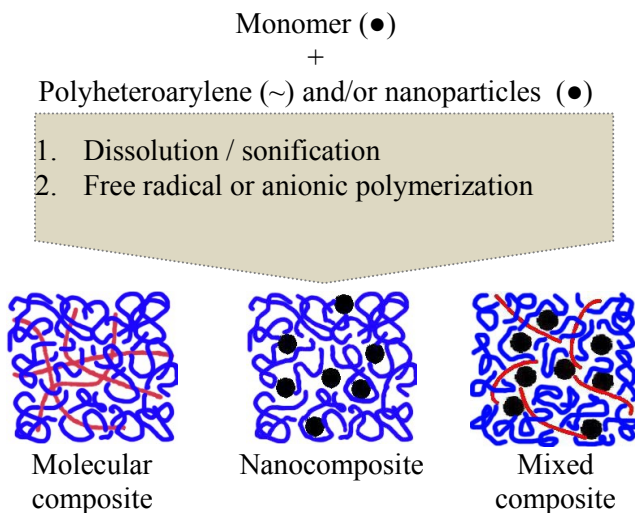
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The technology of *in situ* block polymerization of methyl methacrylate (MMA) or  $\epsilon$ -caprolactam (CL) in the presence of different compounds has been applied for the synthesis of new materials with improved properties. The basic principle consists in adding of the modifier to the initial monomer and its further polymerization.



Different polyimides soluble in above cited monomers (in CL at elevated temperatures higher than its m.p.) have been tested as

additives. Interaction react imides cycles with free radicals or anions of the reaction system leads to the formation of covalent bonds between PMMA or PCL matrixes and polyimides macromolecules. It has been approved by kinetic studies (isothermal or differential scanning photocalorimetry, real time FTIR spectroscopy), ESR-spectroscopy, etc. As a rule it results to the improvement of obtained composites properties.

It is necessary to note that an introduction of a small amount of various additives allows reaching outstanding characteristics of polymer materials: Izod impact strength of modified PCL grows up to 12 times and a wear decreases in 8 times, thermal stability of PMMA grows up to 80°, etc. It was established that increasing of polyimide's aliphatic fragments length leads to the decrease in the transparency of obtained PMMA blocks. This observation may be due coil-globule transition of polyimide's macromolecules.

Different nanoparticles such as carbon nanotubes (CNT), SiO<sub>2</sub> etc. have been used as additives into initial monomer as well. The structure and properties of obtained composites are investigated using SEM, AFM, TGA, TMA methods, etc.

The silica fumed containing *tert*-butyl peroxide groups have demonstrated high ability to initiate radical polymerization of MMA at 80 – 90 °C. It has been stated the influence of silica quantity and functionalization degree onto yield, MM, thermal and mechanical properties of obtained polymer composites. The addition of silica into polymer favours in the significantly reduction of the composite wear and thermal properties improvement.

The addition of 0.1-3.0 wt. % of CNT into PCL allows reaching outstanding characteristics of materials: thermal stability of filled PCL grows up to 95°, water uptake is reduced to 5 times, composite wear – 2-4 times, friction factor – up to 5 times.

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# **PERSPECTIVE FUEL TANK DESIGN DEVELOPMENT. EXPERIMENTAL RESEARCH OF MODIFIED CARBON COMPOSITES**

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One of the main problems of space rocketry development is to ensure the minimum specific weight, to reduce costs and increase mass-energy characteristics.

Due to the high cost of payload orbiting per kilogram and certain limitations of design development, operation and payload mass associated with the heavy weight of launch vehicles, intensive works are being performed to decrease the weight of launch vehicles.

Rocketry development and enhancement are closely connected with the area of materials science and with extensive use of new structural materials, of which Polymer Composite Materials (PCM) are the most important.

At present attempts are being made to obtain PCM with improved properties by means of introducing nanoscale additives into the matrix.

The paper presents experimental investigations of mechanical properties of the modified carbon composites for a three-layer load-bearing cylindrical fuel tank shell. The paper also presents the results of the tests of carbon composite coupons with the modified matrix and dependence of their properties on the concentration of nanomodifiers.

# A TWO-LEVEL PHENOMENOLOGICAL MODEL OF RUBBER COMPOUNDS

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A new two-level phenomenological model for rubber materials was developed. This model takes into account several physical characteristics of the elastomers like length of polymer chains, chemical cross-linking density, density of entanglement, and, additionally, the volume fraction of fillers. Structural features of the filler network and of the interactions between polymer and filler particles are taken into account by two additional constants. Furthermore, specific phenomenological equations are introduced to simulate the relationship between the macroscopic large scale mechanical rubber properties and the effective local mechanical behavior of polymers which are trapped within the gaps between neighbouring filler aggregates.

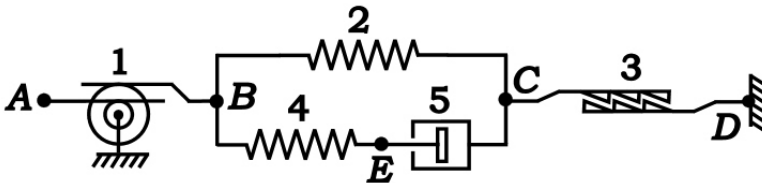


Figure 1: Mathematical model. Each element in the diagram corresponds to tensor equations which are formulated for finite deformations. Element number 1 is used for modelling the relationship between stress/strain at macroscopic level and the effective stresses/strains within the gaps between filler aggregates.

Experiments were carried out with different rubber compounds that were produced by the same mixing and vulcanization technology. Solution-polymerized styrene-butadiene rubber (S-SBR) was applied

as a matrix rubber. Aerosil R974, Aerosil 200, Ultrasil VN3, Carbon Black N330, Coupsil 8113 were used as fillers. The mass filler content was 30 phr (parts per hundred parts of rubber), 40 phr and 50 phr. Experimental studies of mechanical properties were carried out with a Zwick universal testing machine and with EPLEXOR testing machine machine for dynamic mechanic thermal analysis. Good coincidence of theoretical values with experimental data was obtained. Common relationships for all materials were obtained between the constants that describe peculiarities of the mechanical behavior of reinforced elastomers. We believe that these relationships are a reflection of the following fact: Between the energy of activation of polymer-filler interaction, rate of damage accumulation of filler network and structural deformations of elastomer should exist dependences. These dependences are reflected in relations between the macroscopic constants in our model.

The work was supported by the Fundamental Research Program of RAS 12-C-1-1015, Grants for State Support of Leading Scientific Schools 5389.2012.1 and grant RFBR 12-08-00740-a.

# CHANGES IN THERMOMECHANICAL PROPERTIES DURING THE THERMAL AGEING OF A THERMOSTABLE EPOXY MATRIX

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There is a lack of organic matrix composite materials for civil aeronautical applications above 200°C in Europe. Highly aromatic epoxy matrices are candidate for such applications because of their high thermomechanical performances. However, these thermostable matrices could be used only if their long-term durability in current use conditions is clearly demonstrated.

A general kinetic model of thermal oxidation of epoxy matrices has been proposed in a series of previous publications [1-2]. This model gives access to the distribution (in the sample thickness) of structural changes at the molecular scale as a function of exposure time. The objective of the present communication is to complete this model in order to predict the resulting changes in thermomechanical properties. The incremental approach used to reach this goal is schematized in Figure 1.



**Fig.1: Incremental approach used for kinetic modeling.**

1) The first step of this approach consists in calculating the concentration of macromolecular events responsible for the progressive embrittlement of the epoxy network, i.e. the concentration of chain scissions. Considering that the main source of chain scissions is the  $\beta$  scission of alkoxy radicals in the initiation reaction, thus one can write:

$$\frac{dS}{dt} = \gamma_1 k_1 [POOH]^\delta$$

(1)

where  $\gamma_1$  the yield of chain scissions,  $k_1$  the initiation rate constant, and  $\delta$  is the molecularity of the POOH decomposition.



2) The second step consists in establishing non empirical relationships between the macromolecular structure and the thermomechanical relationships.

a) For the glass transition temperature  $T_g$ , the point of departure is the Di Marzio's theory [3]:

$$T_g = \frac{T_{gl}}{1 - K_{DM} F x} \quad (2)$$

where  $x$  is the concentration of crosslinks,  $K_{DM}$  a universal constant,  $F$  the flex parameter, and  $T_{gl}$  the glass transition temperature of a hypothetical linear polymer containing all the structural units of the epoxy network under study except crosslinks.

As an example, in the case of an ideal TACTIX epoxy network:  $x = 3.4 \text{ mol.kg}^{-1}$ ,  $K_{DM} = 2.91$ ,  $F = 31.8 \text{ g.mol}^{-1}$  and  $T_{gl} = 370.1 \text{ K}$ . These values lead to a theoretical  $T_g$  value of  $267^\circ\text{C}$ , i.e. very close to the experimental one of  $263^\circ\text{C}$ .

In the case of trifunctional crosslinks, the concentration of elastically active chains is:  $\nu = 3/2 x$ . Since one chain scission eliminates three elastically active chains and two crosslinks, it comes:

$$\nu = \nu_0 - 3S \quad \text{and} \quad x = x_0 - 2S \quad (3)$$

where  $\nu_0$ ,  $\nu$ ,  $x_0$  and  $x$  are the concentrations in elastically active chain and crosslinks before and after thermal ageing respectively.

The derivation of Equ. 2 against  $\nu$  and the introduction of Equ. 3 leads to:

$$\frac{dT_g}{d\nu} = -\frac{1}{3} \frac{dT_g}{dS} = \frac{2}{3} K_{DM} F \frac{T_g^2}{T_{gl}} \quad (4)$$

$$\text{i.e.} \quad \frac{dT_g}{T_g^2} = -2 \frac{K_{DM} F}{T_{gl}} dS \quad (5)$$

The integration of Equ. 5 leads finally to:

$$\frac{1}{T_g} - \frac{1}{T_{g0}} = \frac{2K_{DM} F}{T_{gl}} S \quad (6)$$

b) For the elastic modulus in rubbery state, the point of departure is the classical rubber theory [4]:

$$E_C = 3\nu\rho RT \quad (7)$$

where  $\rho$  is the volumetric mass in  $\text{kg.m}^{-3}$ ,  $R$  is the constant for perfect gas ( $8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ ) and  $T$  is the absolute temperature in K. The derivation of Equ. 7 against  $v$  and the introduction of Equ. 3 leads to:

$$\frac{dE_C}{dv} = -\frac{1}{3} \frac{dE_C}{dS} = 3\rho RT \quad (8)$$

The integration of Equ. 8 leads finally to:

$$E_C - E_{C0} = -9\rho RT S \quad (9)$$

3) The last step consists in checking the validity of Eqs 1, 6 and 9 from accelerated ageing experiments. In this communication, the material under study is an ideal TACTIX epoxy network. Epoxy plates of 1 mm thick have been exposed at 200°C under high  $\text{O}_2$  partial pressure (typically 10 MPa) in order to have a homogenous oxidation within the whole sample thickness. After thermal ageing, the samples have been characterized by conventional laboratory techniques. The concentration of by-products generated by the chain scission has been determined by high resolution mass spectrometry (for volatile compounds) and IR spectrometry in ATR mode (for carbonyl groups) and gravimetry (for evaluating the competition between mass losses due to release of volatile compounds and mass gain due to oxygen grafting to polymer). The glass transition temperature and the elastic modulus in rubbery state have been determined by mechanical spectrometry (DMTA) in a tensile mode. All these experimental results will be presented and discussed.

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# THE CVI AND PIP METHODS TO OBTAIN CERAMIC COMPOSITE MATRICES

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The chemical vapor infiltration (CVI) and polymer infiltration and pyrolysis (PIP), as well as combinations thereof are the most promising methods to obtain ceramic composite matrices.

The results have been presented of the joint work of Kompozit JSC and FSUE GNIKHTEOS to obtain ceramic matrices of the update precursor-base composites. Amongst the ceramic-matrix composites, the silicon nitride-, carbide- and carbonitride-matrix materials are of the thorough interest. The interest in them is due to the combination of high specific strength and oxidation resistance within the operating temperatures of 1400 -1900°C. Silicon carbonitride is a comparatively new material in this family, but, perhaps, the most promising one since it combines properties both of the silicon nitride and silicon carbide. Besides, it is known this is the silicon nitride that offers the most resistance to thermal-cycle loads.

For chemical silicon-carbide vapor infiltration monomethylsilane (MMS) is used being decomposed into silicon carbide SiC and hydrogen with pyrolysis. A chemical aspect of the process is expressed by the MMS pyrolysis equation:  $\text{CH}_3\text{SiH}_3 = \text{SiC} + 3\text{H}_2$ . The use of this reagent allows the silicon-carbide infiltration in the range of rather low temperatures (600-800°C). Today this technology provides the pilot production of the silicon-carbide matrix-composites and articles thereof. A UT-900 carbon fabric-base carbon-silicon-carbide composite of KMK-MC-type has been developed.

The equipment developed allows for manufacturing articles of various shapes using a reactor of 1100 mm in diameter and 1300 mm in height such as plates, shells, and pipes etc.

The opportunity has been considered of producing refractory metal compound-modified matrices using the PIP method.

It is shown the way of considerable promise for producing high-density ceramic-matrix composites is the combination of the PIP and CVI (CVD) methods.

## COMPOSITES BASED ON HOLLOW GLASS MICROSPHERES

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Composites (Syntactic) based on hollow glass microspheres (HGM) possess a unique complex of properties. It predetermined their wide application not only in shipbuilding industry but in aerospace industry as well. Application of the hollow glass microspheres, when making moulding materials SMC and BMC type, allows to decrease their density from  $1.8 \text{ g/cm}^3$  down to  $1.3 \text{ gc/cm}^3$  without noticeable reduction of elastic and strength properties of the composites. New generation of these polyester low density moulding materials opens wide perspectives for implementation of HGM in automotive industry. One more field for application of the HGM, which is of big practical interest, is creation of heat protection for ablation materials. NPO Stekloplastic has developed a volumetric-reinforced syntactic material for fabricating a space return vehicle frontal heat protecting shield. Application of the new heat protection of low density will allow to considerably increase weight efficiency of the whole article.

One of the most challenging fields or application of low density composites based on HGM is origination of multilayer thin wall structures (sandwiches) with high specific mechanical characteristics. Application of the syntactic allows to many times, in comparison with the traditional types of cores (foam plastics and honeycombs), increases both absolute and specific elastic and strength characteristics of sandwich structures. Application of the syntactic based on HGM in the capacity of the core increases considerably not only cyclic and longstanding strength of the multilayer structures but it also solves the problem of low resistance of the traditional (based on honeycomb and foam plastics) sandwich-composites towards local static and impact loads. High bearing strain strength of syntactic composites makes it possible to use not only glued but, in some cases, even bolted connections of these materials. One more essential advantage of the sandwich-

composites with syntactic core is low level of water sorption and high heat and chemical resistance.

Low adaptability to manufacture of the composites based on polymer binders and HGM for a long time restricted use of the syntactic when manufacturing multilayer high load structures. But thanks to the development of plate semifinished items based on HGM, there were opened fundamentally new possibilities for designers and industrial engineers when designing complicated multilayer composites. One of these semifinished items developed at NPO Stekloplastic has got name SYNLAY.

In essence, SYNLAY is an analogue of the plate moulding material type SMC and tissue prepreps. SYNLAY plate semifinished item, thanks to specially developed recipe for polymer binder, remains elastic even at 70% filling with HGM. It allows to mould on its basis multilayer items the most complicated shapes with use of many well known technological approaches (moulding, vacuum and autoclave molding, blowing etc.) Plate semifinished product based on HGM allows to make very thin (up to 1 mm) sandwich composites and multilayer complicated structures with many layers. In such articles every power layer has its own thickness and precalculated scheme of reinforcement. Joint work of power layers and the core layers are calculated in such a way in order to secure the highest weight efficiency of a structure operating under complex loads. It is evident that when creating such structures there is no equal alternative to HGM. When using epoxy resins, shelf life of SYNLAY may be 3 months at +20 oC and up to 2 years at – 5oC.

# COMPOSITES BASED ON POLYMER-MONOMER SYSTEMS

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Monomer-polymer systems based on styrene, its derivatives, and acrylates in combination with rubbers and thermoplastics have found wide use for preparation of high-impact polystyrenes ABS plastics, graft copolymers, and other polymeric composite materials.

The authors of this paper are used this paradigm to create a new hybrid composites and present the results of these studies.

The free-radical polymerization of styrene and methyl methacrylate initiated by the peroxide-tertiary aromatic amine system in the presence of dissolved aromatic polyethers, fluoroelastomers polyurethane and epichlorhydrin rubbers has been studied with the use of differential scanning calorimetry, ultraviolet and infrared spectroscopy, thermometric, and gravimetric analyses. It has shown that the rate of polymerization of monomer-polymer solutions is higher than that of pure monomers. The influence of the content of dissolved polymers on the conversion of monomers corresponding to the onset of the gel effect has been estimated. In the presence of the polymer being added, this phenomenon manifests itself at a lower fractional conversion of the monomer. The greater the content of the polymer and the higher the viscosity of the reaction system, the sooner the rise in the rate of polymerization. The experimental evidence of this study makes it possible to control the synthesis of composite materials from monomer-polymer systems.

In addition the formation of homopolymers, graft copolymers, and the gel fraction in the course of polymerization of monomer-polymer systems has been studied. It has been demonstrated that the graft copolymers form at monomer conversions up to 30-40% and the intense accumulation of homopolymers corresponds to the degree of conversion at which autoacceleration begins. Structural features of the polymer composites have been revealed by electron microscopy measurements. The use of comonomers containing two double bonds has been shown to provide a way of controlling the properties of final polymeric materials.

Discusses the practical application of the monomer-polymer systems as binders for prepregs, optical adhesives, formulations for additive technology and other applications.

# MAGNETIC SHIELDS TECHNOLOGY OF NANOCRYSTALLINE SOFT MAGNETIC ALLOYS BASED ON FE AND CO

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In order to create the effective safeguard system against the electromagnetic irradiation the new construction of magnetic shield has been developed and patented in FSUE CSRISM "Prometey" (Federal state unitary enterprise Central Scientific Research Institute of Structural Materials «Prometey») [1].

For this was developed the method of controlled crystallization from amorphous state. The essence of the method consists in the fact that by the thermal treatment of the initial alloy in the certain temperature range and certain soaking time the nanocrystalline dropping in the amorphous tape take place; controlling these two parameters we could produce material with specified combination of magnetic and mechanical properties. Thus there is no need in universal material "for all cases" and we obtain the ability to produce material optimally working in defined operating conditions.

This paper shows the effect of various types of heat treatment on magnetic properties and structure of alloys AMAG200 and AMAG172. Based on these data are governed by the optimal mode for the subsequent production of shields. For the manufacture of shields made of heat treated alloy AMAG172 performed in through-type furnace in the chamber on the mandrels of different diameters to study the effect of mechanical stress.

It is shown that the mechanical stresses arising from bending and inflection heat-treated tapes, substantially reduce the permeability and screening capabilities of a magnetic shield. To maximize the shielding factor, heat-treated tapes to produce the same mechanical state in which they will be in the shield.

# STUDYING THE KINETICS OF FORMATION THE PAN GEL-FIBER BY MEASURING THE ELECTROCHEMICAL POTENTIALS

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It is known that PAN fibers obtained from solution have a large number of pores and microcracks. They are formed because of the boundary layer between the surface of the spray solution and the precipitant, deposited fiber and hardener. These layers prevent the exchange between the molecules of the solvent, precipitant and hardener, which leads to an increase in shrinkage stresses and the formation of pores and cracks.

Kinetics of the permeability of the boundary layer is given the rate of diffusion of the molecules of the solution, precipitating agent and hardener. Simultaneously, the diffusion leads to a change in the electrochemical potential of the jet - setting bath or deposited fiber - hardened bath.

In the present paper the kinetics of the permeability of the boundary layers by analyzing the time dependences of the electrochemical potentials. The optimum composition of precipitants, providing high permeability of the boundary layer of precipitant and solvent molecules was found. Their use allowed us to obtain, defect-free fibers of PAN.



# STUDY OF THE DAMAGE TO COMPOSITE STRUCTURES BY LOW-VELOCITY PERFORATION

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In passive safety structures, the use of composite materials has significantly increased recently because of their low specific mass and high energy absorption capacities. Specifically, a helmet must pass the perforation test standard, which is performed with a conical impactor that creates damages on the composite shell structure of the helmet. The purpose of this paper was to study the damage created by a low-velocity impact test on a helmet and to reproduce similar damage on representative structures. After designing the experimental test, candidate materials to improve the helmet shell were tested. Tests were performed with a drop weight tower on square plates clamped to a circular fixture. The cross-sections of the impacted plates were observed and revealed similar damage as matrix cracking, matrix shearing and failure in the bi-axial tension. The only damage not reproduced was the flexional damage; however, this damage can be determined separately by a dynamic 3-point flexion test.

# INTERNAL FRICTION IN COMPOSITE STRUCTURES

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The paper discusses the results obtained in a series of studies undertaken to develop the methods for evaluating the elastic damping characteristics of polymer composites and predicting the dynamic response of composite structures.

A mathematical model for decaying bending-twisting vibration of anisotropic rod is given, and the algorithm for solving the equation of motion is elaborated. Vibration modes of a free-free composite beam and a clamped composite beam are investigated. It is shown that the bending-twisting coupling should be taken into account when the elastic damping characteristics of anisotropic polymer composites are determined by the resonance method on rod specimens with arbitrary orientation with respect to the material axes of symmetry.

The paper describes the algorithm of experimental and analytical iteration method for determining the elastic damping characteristics of polymer composites based on the processing of natural frequencies and loss factors in bending, twisting and coupled bending-twisting vibrations obtained experimentally on rod specimens of rectangular cross-section. It is estimated how manufacturing tolerances of rod specimens affect the accuracy of elastic damping characteristics. The elastic damping characteristics of some polymer composites are given and the reliability of these data is analysed.

The mathematical models of decaying vibrations in layered anisotropic composite structures are developed using the Hamilton variational principle, updated neoclassical theories of rods and plates as well as the principle of elastic and viscoelastic correspondence in the linear viscoelastic theory. A two-step method is proposed for solving the complex eigenvalue problem making it possible to calculate eigenfrequencies and mechanical loss factors in layered anisotropic composite structures. The convergence and reliability of the proposed numerical solution are assessed. The effect of reinforcement composition and pattern on eigenfrequencies and mechanical loss factors for various vibration modes of layered

anisotropic composite structures is discussed. It is demonstrated that the natural frequencies and mechanical loss factors can be managed by varying the anisotropy rate of layer materials, orientation of layers with respect to the main axes of structures and through-thickness non-uniformity of layers.

The paper studies the general complex differential matrix equation of mechanical system oscillations taking into account energy dissipation. It is shown that the so-called the method of natural mode potential energy gives significant error in estimation of loss factors for layered composite rods and plates. The applicability range for the approximate method of natural mode potential energy is defined by comparing it with the results obtained by a generalized problem of complex eigenvalues.

Based on decomposition of potential strain energy and system's kinetic energy the coefficients of elastic and inertial coupling are introduced which can be used for quantitative estimation of couplings between the modes of layered anisotropic composite structures.

Examples are given illustrating the practical application of the method in the development of vibration damping composite structures.

# VISCOELASTICITY AND FRACTURE TOUGHNESS OF FIBERS REINFORCED COMPOSITES BASED ON THERMALLY STABLE POLYMER MATRICES

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The fibers reinforced composites based on high-strength fibers and polymer matrices are widely used in various fields of engineering. The extension of the temperature range in which they operate is an important problem. Polymer fiber composites that can operate for a long time not only under standard conditions but also at temperatures above 200°C are of special interest for the design of units and parts of the so-called high-speed transport.

It was established that an increase in the loss modulus of a polymer matrix decreases the probability of forming a brittle crack in the matrix at the fiber break and increases the time interval between breakages of adjacent fibers. This leads to retardation of the correlated breakage of fibers in fiber composites under loading, i.e., to an increase in their strength and fracture toughness. The matrix of high-strength heat-resistant fiber composites with high fracture toughness should possess not only a high elasticity (this has been long known) but also good dissipative properties over the entire temperature range of operation. It seems likely that the most promising way to design new heat-resistant composites with large values of the strength and interlaminar fracture toughness is to develop structured polymers as semicrystalline polymers or matrices with a structure similar to semi interpenetrating polymer networks.

The other way s to develop new types of polymer matrices with special viscoelastic properties is design of hybrid organic-inorganic nanocomposites. The polyimide nanocomposites are remarkably different from traditional polymer composites because they can be designed to contain prescribed structural organization not only within the polymer matrix volume, but also at the filler/matrix interface. Introduction of a second component – filler or reinforcement – into semi-crystalline polymer can change its crystalline structure, relative amount of amorphous and crystalline portions, crystal modification, size and perfection of crystallites and dimensions of spherulites.

Among others, fillers increase stiffness and heat deflection temperature, improve or regulate electrical characteristics, modify rheological properties, decrease shrinkage and have significant influence on polymer properties. This facilitates formation of new polymer nanocomposites with unique physical and chemical properties including high heat and thermal resistance, strength, fracture toughness, and gas/liquid barrier properties, which can be used as new generation of polymer matrices for fibers reinforced composites.

# INSIGHT OF CARBON NANOTUBES LOADING IN POLYMER MATRIX FOR ADVANCED COMPOSITE

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Carbon nanotubes dispersed in polymer matrix has been studied extensively in the last two decade as they represent the ideal candidate as matrix for a new class of advanced systems: the multifunctional polymer composites. The continuous demand for new high performance polymers to use as matrix for composite systems with peculiar and specific property has lead many researchers to investigate the potential use of the carbon nanotubes (CNTs) as tailoring nanofillers of polymer matrix to manufacture of traditional laminate composite. The “tailored multifunctional” matrix may represent the break-through of the new concept of laminate composites in which not only fibre arrangement and constituent coupling play a rule for the final performance of the manufactured composite but also the matrix could contribute significantly to add further peculiar features.

Final composite properties such as elastic modulus, fracture toughness, electrical, damping and rheology could be significantly “tuned” and “altered” by adding nanotube to the bulk polymer with important effect on the overall behaviour of the final composite materials. A number of issue arise which need to be faced and analysed.

Experimental measurements of both mechanical moduli and electrical conductivity of nanocomposites [1-2] have highlighted the relevance of nanotubes networking in determining the effective macroscopic behavior of such nanocomposite systems. In particular, the reinforcement capability of carbon nanotubes in a polymeric matrix certainly depends by both their length and amount but, undoubtedly, their arrangement and contacting [3-4] within the hosting medium plays a fundamental role in the load transfer mechanism. In addition, experimental findings support the evidence that the clustering of the nanotubes implies a sensible decrease of the

effective mechanical efficiency of the carbon nanotubes in the polymer matrices reinforcement.

In literature the enhancing reinforcement of CNT loading for the Young's modulus is commonly reported [5-6]. However, at the same time, discrepancies among the different data are highlighted thus the overall "ratio" on using carbon nanotube filler is still to assess and a reliable database for this property is still missing. Characterization and structure-properties of nano-mechanics modelling research have shown that enhancement in mechanical properties of nanocomposites are strongly dependent upon the level of dispersion and the final morphology of the nano-fillers. Dispersion and homogenization stands as a very complex phenomenon due to the natural tendency of CNTs to bundle and to aggregate mainly due to Van der Waals interactions among nanotubes thus CNTs dispersion still represents a critical issue for the widely usage of these nano-structures as reinforcements. A mechanical property model can be build up to explicitly accounts for the reduction of the stress transfer efficiency between reinforcing nanotubes and hosting matrix via a reduction of the effective filler length with the increasing nanotubes content. This modeling approach which takes origin by the Philipse's Random Contact model [5] and it relates the excluded volume of a particle to the average number of contacts between an ensemble of such shaped particles, is hereafter described and tested with literature data and new experimental data, reporting a very good agreement.

As recently demonstrated, electrical property could be suitably modified not only by changing the CNTs concentration, but also and, for some features, primarily to the ability of tuning the formed network morphology to provide the optimization of the final nanocomposite properties [6]. Experimental results showed the existence of a multiscale dispersion state, where nanotubes form a hierarchical structured networks of micro aggregates and nanoelements which indeed play effect on the electrical performance of the system.

The combination of extremely large interfacial contact area and low mass density of nanofiller materials implies that frictional sliding of nanoscale particles within the matrix has the potential to cause significant dissipation of energy with minimal weight penalty. Damping property of polymer matrix change suitably enhancing the final composite dissipative behaviour. The addition of multi-walled carbon nanotube provide some improvement of damping

performance and experiments confirm the existence of an optimum nanofiller content related to the dispersion state.

Rheology behaviour of polymer matrix which represents a key factor for optimal manufacturing conditions is drastically effected by the presence of nanotube contents. In fact, pristine nanotube network increases the unreacted resin viscosity, as expected, and it gives arise to an elastic contribution of the dynamic mechanical modulus; whereas upon reaction, the same effect is switched depending on the nanotube content. In the case of functionalised nanofiller, depending on the reactive group, the nanotube content at which the viscosity arise is significantly “amplified” allow the dispersion of an higher nanfiller content thus increasing the reinforcement effect of the nanoloads.

Different approaches to build an appropriate theory for predicting reinforcement efficiency of CNTs within an hosting matrix have been presented in the literature however a complete understanding of the overall effects of nanotube addition on different properties is still missing.

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# POSTER PRESENTATIONS

# GRAPHITIZED CARBON FIBER PREPARATION FROM OILSTOCK

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Oilstock based pitch usage is a most promising method of carbon fiber fabrication. Such carbon fiber is characterized by good enough stress-strain properties, and thermal conductivity factor of petroleum pitch-based carbon fiber has a unique value among other kinds of carbon fibers and amounts to 600 W/mK.

The researchers of SSC RF GNIChTEOS are currently engaged in the development of isotropic fiber-forming petroleum pitch produced from refinery waste, syntheses realized through polycondensation reaction under an inert atmosphere resulted in petroleum pitches different in terms of composition and properties and having fiber-forming capability. Discrete pitch fibers were prepared from the fiber-forming pitch by means of melt extruding in a manual mode. The pitch fibers were subject to thermal oxidation and carbonification. The resulting carbon fiber of isotropic structure had the following parameters: diameter – 30-80  $\mu\text{m}$ , strength – 300-900 MPa, elasticity modulus – 20-70 GPa, thermal-oxidative stability – up to 530 °C. At the temperatures of 2100 °C and 2200 °C in an inert atmosphere carbonized carbon fiber was graphitized with the purpose of heat conductivity increase. Insignificant strength decrease of the isotropic carbon fiber, its electrical resistance drop, heat conductivity increase were observed; elasticity modulus of the prepared graphite fiber did not virtually changed.

The conducted experiments results demonstrated the possibility to increase the heat conductivity of isotropic carbon fiber based on oilstock by means of carbonized fiber graphitization at high temperatures and in an inert atmosphere.

# APPLYING OF POLYMERIC COMPOSITE MATERIALS AND MODERN TECHNOLOGIES OF IT'S PROCESSING IN CONSTRUCTIONS OF VERTICAL-AXIAL WIND POWER PLANTS OF LOW AND MIDDLE POWER

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Vertical-axial schemes of rotors of wind power plants (WPP) has a row of advantages in comparison with traditional – which are lack of orientation machinery by wind and lower speed of rotor while operating, what provides cardinal decrease of aerodynamic noise during operation. The shortcomings of vertical-axel WPP are traditionally considered the lower coefficient of using the wind power and complexity of rotor construction. The main feature of vertical-axel rotor is the action to rotating blade of diametrical centrifugal force, considerably exceeding aerodynamic one, which causes very high level of diametrical overload (on the small diameter rotors the overload is up to 1000).

Applying of materials with high specific durability and strength together with optimization of rotor geometry and scheme of reinforcement of fibrous polymeric composite material (PCM) allows to make elements of rotor with operational overload in diametrical direction providing necessary frequency of rotor rotation in wide range of wind speeds without limitations on overload. Modern technologies based of direct steeping of reinforcing material (perform) in individual form-set technological gear and selection of optimal regimes of forming allows to considerably increase the stability of material structure and geometrical sizes of constructions from PCM.

As a conclusion it should be said that applying of modern pcm in wpp constructions of low and middle power together with selection of optimal structure of material allows to implement maximal coefficient of using wind power for vertical-axial schemes (up to 0,43). Manufacturing of plants applying vacuum and injection

steeping of reinforcing material by connecting in closed technological gear with individual stabilization system of regimes of thermo-treatment allows not only to minimize the influence of hazardous factors of manufacturing but also to considerably decrease man-hours and duty of manufacturing processes of wpp elements from pcm.

# REDUCING THE TOTAL MATERIAL PROCESSING TIME USING THE CONCEPT OF DUMMY MACHINES IN CDS HEURISTICS

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Processing the materials in different centers in minimum possible time is an important task for a shop floor supervisor. Finding an optimal sequence in terms of total completion time for processing 'n' jobs in 'm' processing centers is NP hard as the total number of sequences is (n!) for a permutation flow shop scheduling problem. This has been an interesting topic for more than six decades for the researchers. Starting from Johnson's Algorithm, classical Heuristics like Palmer Slope index Algorithm, RA method, CDS method, Gupta's Algorithm were proposed in earlier days. After the invention of evolutionary algorithms and Meta Heuristics, finding an optimal sequence becomes comparatively easier. However, in the shop floor, still the Classical heuristics are popular because of their simplicity. For smaller problems, these Heuristics give reasonably accurate results.

However, in most of the cases, we get only one sequence except in CDS algorithm where the best sequence is selected from (m-1) alternatives. Among the classical Heuristics - Palmer Slope Index Method, Gupta's Algorithm, RA Algorithm, CDS Algorithm - generally it has been agreed that CDS Algorithm gives better results for most of the problems. This paper deals with further improving the make span (total processing time) in a Permutation Flow Shop Scheduling problem of materials processing using the concept of Dummy Machine in the popular CDS Method. In such cases, we can get more sequences (maximum m+1) for every alternative that will be computed in CDS Algorithm. That is, a total of  $(m+1)(m-1)=m^2-1$  options will be evaluated and many new sequences are obtained having make spans equal to or less than the one obtained from parent algorithm.

The dummy machines have processing time of zeros for all jobs. This machine is introduced initially before the first machine and a sequence & corresponding make span will be determined. Then, the

dummy machine will be introduced between the first and second machine and another sequence & make span will be determined and the procedure continues. Altogether,  $(m+1)$  sequences will be computed and they will be evaluated for the optimality in terms of make span requirement.

The effect of dummy machine is analyzed using the well known Taillard bench mark problems. For smaller problems, 5 m/c, 20 jobs; 10 m/c, 20 jobs; 20 m/c, 20 jobs are considered from the Taillard paper, considering the seeds, lower bounds, number of machines and jobs without any change. For larger problems (above 100 machines and 100 jobs), the seeds are taken from last three Tables and lower bounds are calculated using an algorithm. The codes are generated in MATLAB R2008a for computing the lower bounds, Make Span using the original CDS Algorithm and Make Span after applying the Dummy Machines concept in CDS Algorithm.

In smaller problems, that is with 20 jobs, the movement of total processing time towards the lower bound is up to 9%. For larger problems, the improvement is reduced when compared to smaller problems. However, in about 60% of the problems, we get additional sequences with the same make span that of original algorithm or less than that. It can be seen that by using the concept of Dummy Machines in CDS Algorithm, the make span can still be reduced in many problems with many more sequences and alternatives in hand to decide with, in case of any constraints. The concept is so simple that a shop floor supervisor can easily compute the results manually with nil error for smaller problems. The interesting part is that this concept can be applied in other Classical Heuristics also effectively for obtaining many new sequences having optimal/ near optimal make spans.

# EFFECT OF MWCNTS ON PAN THERMAL STABILIZATION: FTIR STUDIES

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Addition of carbon nanotubes (CNTs) to polyacrylonitrile (PAN) precursors is known to improve the mechanical properties of the carbon fibers resulting from PAN thermal stabilization. The interaction of PAN with single wall carbon nanotubes (SWCNTs), and the effect of the latter on the mechanism of PAN thermal stabilization and its product properties have been widely studied. On the other hand, multi wall carbon nanotubes (MWNTs) are cheaper and easier to be produced than SWCNTs, but little information is available on details of the thermally induced stabilization of PAN/MWCNTs composites.

The ultimate appeal of this work is to demonstrate the peculiarities of thermal stabilization of PAN/MWCNTs composite films as compared with PAN. Our studies have revealed that under the same conditions of thermal processing, pure PAN and MWCNTs-containing material result in different stabilization products.

In particular, the composition of low-molecular weight volatile products of thermal treatment of the studied materials has been examined. In case of PAN/MWCNT, considerable amounts of carbon dioxide, water, ammonia are released. Pure PAN releases ammonia and hydrogen cyanide (most probably, due to aromatization and elimination of acyclic nitrile groups) at 550-1000°C. Addition of MWCNTs shifts these processes to significant lower temperature range. This finding is important in designing energy-saving technologies of carbon fiber production.

After the thermal stabilization of PAN/MWCNT composites show no nitrile absorption bands in FTIR spectrum, while pure PAN still have nitrile group stretching absorption band shifted to lower wavenumbers ( $2223\text{ cm}^{-1}$ ), supporting formation of fragments containing nitrile groups conjugated with acyclic C=C bonds.

Detailed FTIR studies of pure PAN thermal stabilization product revealed a wide absorption band at  $1700\text{-}1400\text{ cm}^{-1}$ , in the range

characteristic of aliphatic ketones C=O stretching ( $1715\text{ cm}^{-1}$ ) and stretching of C=C conjugated with C $\equiv$ N ( $1667\text{-}1640\text{ cm}^{-1}$ ). In the FTIR spectrum of PAN/MWCNTs stabilization product narrower absorption peaks at  $1610\text{ cm}^{-1}$  and  $1575\text{ cm}^{-1}$  are found, assigned to (C=O stretching + C=C stretching) and (C=C stretching + N-H deformation) combination bands, correspondingly.

To conclude, oppositely to PAN thermal stabilization product, in case of PAN/MWCNTs bands assigned to aliphatic fragments or nitrile groups are absent in the FTIR spectrum. As compared to pure PAN case, the composite stabilization product reveals less of non-cyclic moieties. Thus, addition of MWCNTs to PAN is proved to increase conversion of the stabilization reactions, leading to more perfect structure of the product. Moreover, spectral studies of the intermediate materials during the linear heating demonstrated that in case of PAN a set of reactions run at the same temperature range (simultaneously), whereas during thermal stabilization of PAN/MWCNTs gradual increase of temperature induces first preferably cyclization reactions, and dehydration along with nitrile elimination from acyclic fragments occur at higher temperatures.



# POLY(VINYL ALCOHOL) NANOCOMPOSITE FILMS FOR BIOMEDICAL APPLICATIONS: DYNAMICS, THERMAL BEHAVIOUR, AND ELASTIC PROPERTIES

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Poly(vinyl alcohol) (PVA) possessing excellent biocompatibility and water solubility has been widely employed in a variety of biomedical applications including hydrogels, bone tissue engineering, drug delivery and artificial articular cartilage. To improve mechanical and thermal properties of this polymer, PVA based nanocomposites with 1D, 2D or 3D nanofillers have recently been studied (see refs. in [1]). However, very scant information can be found in the literature concerning PVA dynamic behaviour in nanocomposites.

In this work [1], a combined DSC, DMA, and laser-interferometric creep rate spectroscopy (CRS [2]) approach has been applied to analyse the dynamics, thermal behaviour, creep resistance and elastic properties of PVA and PVA-based nanocomposite films with 0.05-0.1 mm thickness at temperatures from 20 to 220<sup>0</sup>C. 3D amorphous fumed silica (SiO<sub>2</sub>) nano-particles of ~ 9 nm in average diameter (specific surface area  $S_{\text{BET}} = 330 \text{ m}^2\text{g}^{-1}$ , bulk density  $\rho_b = 0.045 \text{ g cm}^{-3}$ ), initial and compacted by mechanochemical activation to  $\rho_b = 0.32 \text{ g cm}^{-3}$  (dense SiO<sub>2</sub>, with a small change in  $S_{\text{BET}}$ ), and exfoliated graphite (EG, oxidised at 900-1000<sup>0</sup>C,  $\rho_b = 0.01 \text{ g cm}^{-3}$ ,  $S_{\text{BET}} = 21 \text{ m}^2\text{g}^{-1}$ ) as 2D sheets packed in stacks with the overall thickness of ~200 nm were used as nanofillers at contents of 1, 10 or 20 wt. %. Nanofillers were characterized by low-temperature nitrogen adsorption, AFM, SEM and Raman spectroscopy techniques. The presence of -OH and other polar groups at nanofiller surfaces

controlled enhanced interaction with PVA via H-bonding and Coulomb forces. Insertion of PVA chains into EG could result in formation of both exfoliated and intercalated structures.

The effects observed depended on the filler type and content. The most pronounced effects of modifying structure, relaxation spectrum and characteristics of thin PVA films were found for the nanocomposite with 10 wt. % EG. These included up to a 14<sup>0</sup>C rise of  $T_g$ , the pronounced dynamic heterogeneity within glass transition range, and reducing the ability of PVA to physical ageing (DSC); a dramatic rise of creep resistance at different temperatures up to 140<sup>0</sup>C with 2-7-fold increase in static (CRS) and dynamic (DMA) moduli over the temperature range between 20 and 180<sup>0</sup>C compared with neat PVA. This is due to a large 2D size of the thin EG sheet stacks resulting in strongly anisotropic local behaviour.

### **Acknowledgments**

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## CARBON-CARBON COMPOSITE MODIFIERS

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Experts of GNIChTEOS developed impregnating compositions based on carbosilane oligomers and organometallic compounds of zirconium, hafnium and tantalum that may be used for the production of high-temperature oxidation resistant matrices and protective coatings. Liquid-phase matrix material processes offer more control over composite functional capabilities due to comparatively (in regard of CVD methods) easier control over impregnating compositions structuring and formulation. Peculiarity of carbon-carbon material modifying by means of impregnating compositions based on carbosilanes and organometallic compounds of refractory metals consists in the possibility to introduce silicon carbide and refractory metal precursors (Zr, Hf, Ta) in the carboniferous frame. This allows creation of uninterrupted extra strong ceramic structures in the bulk of the material. With the use of the impregnating compositions GNIChTEOS in collaboration with N.E. Bauman MSTU and on the processing base of Komposit JSC fabricated test samples of the composite materials. The compaction modes results of the 4D and 2.5D carbon framing structures proved high adaptability of the impregnating compositions: desired phase composition ceramic yield – 60-90%; pyrolysis completion temperature - no more than 900 °C. The resulting carbon-ceramic composite materials ( $C_f/SiC_m$ ,  $C_f/(SiC+ZrC)_m$ ,  $C_f/(C+HfC)_m$ ) demonstrated a satisfactory level of mechanical-and-physical, thermal characteristics in combination with high stability in gas-dynamic flow at a temperature of 1600 °C and higher.

# STRUCTURE AND PROPERTIES OF POLYACRYLONITRILE/MULTI WALL CARBON NANOTUBE COMPOSITES

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A number of studies have been reported in processing PAN films and fibers reinforced by SWNT. The improved tensile properties of the stabilized PAN/SWNT fibers were observed, which suggests the carbonized composite fiber would also have superior properties. It was reported that PAN/SWNT composite films have been processed with unique combination of tensile properties, electrical conductivity, dimensional stability, low density, solvent resistance, and thermal stability. All these results reveal that PAN has strong interaction with CNT, resulting in enhanced physical and mechanical properties of composite films and fibers.

However, multi wall carbon nanotubes (MWNT) are easier to produce at low cost than SWNT. Therefore PAN/MWNT composites are of great interest.

The aim of this work was to make a comparative analysis of the structure and properties of PAN/MWNT composite films and to investigate the role of MWNTs as a reinforcing phase which can trigger stabilization of PAN.

Composite films containing different amount of MWNT were prepared by solvent cast technique from dimethyl sulphoxide solution.

To investigate the effect of the amount of MWNTs on the structure, thermal properties and stabilization process wide-angle X-ray diffraction and scanning electron microscopy studies, simultaneous thermogravimetric analysis and infrared spectroscopy were employed.

It was found out that addition of low amount of MWCNTs significantly effects on degree of crystallinity and structure of composites. These changes result in stabilization process leading to low-temperature and more complete stabilization with higher product yield.

# MACROKINETIC MODEL OF HEAT AND HUMIDITY AGING OF ARA-MIDE ORGANOPLASTS

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Aramide organoplasts based on Ruser and Armos fibers currently attract attention of investigators as challenging materials for use in various branches of industry and construction. Technology of these materials, their mechanical and physicochemical properties and, primarily, resistance to aging under various operation conditions are the subject of intensive study.

This work was aimed at determination and comparison of kinetic regularities and parameters of heat and humidity aging (moisture transfer and decrease of the shear strength) of wound epoxy organoplasts based on high-strength and high-modulus aramide Ruser S 600 and Armos 600 ANK fibers.

The study of moisture transfer kinetics for the studied composites show that under boosted heat and humidity tests (95°C, saturated water steam) water steam diffusion into organoplast Ruser S 600 + EDT-10 obeys the Fick law. For the organoplast Armos + EDT-10, diffusion is anomalous, and Fick's regularities are not strictly met. A decrease in the shear strength happened monotonously with aging to a level of about 65% of the original.

Ruser and Armos fibers are nearly identical by chemical composition and only differ by their production technology (molding conditions). Noted differences are therefore associated with distinct surface layers of the fibers and different organization of adhesive interaction in these materials, respectively. The anomalous type of sorption in case of Armos + EDT-10 organoplast indicates greater degree of microstructural heterogeneity of this composite material.

Regularities of the shear strength, moisture transfer parameters and the macrokinetic model developed on their basis can be used for the heat-and-humidity aging of organoplasts under various conditions of boosted tests.

# STUDY OF MORPHOLOGY AND PIEZOELECTRIC PROPERTIES OF COMPOSITE MATERIALS BASED ON MATRIX FROM POLYVINYLIDENE FLUORIDE AND POLYAMIDEBENZIMIDAZOLE

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Creation of novel composite materials with necessary properties is an urgent problem. Composites based on polymeric blends with inorganic fillers are related to such materials. It is known that particles characteristics – particle concentration, average particle size, particle size distribution – have the great influence on the properties of the composite materials.

A novel film composite material based on mixture of polyvinylidene fluoride (PVDF) and polyamidebenzimidazole (PABI) is prepared. Piezoceramics niobate-zirconate-titanate lead (NZTL-1) is used as filler. Composition of the films is changed a wide range due to different ratio of the matrix polymers (PVDF and PABI) and various content of the filler. The composite films were obtained by casting from solution in dimethylacetamid (DMAA).

Averaged filler particle size and their distribution in the polymeric composite matrix are evaluated by a special FTIR spectroscopic approach developed by authors\* and by means of FTIR imaging performed on “Hyperion 3000” microscope. To confirm the spectroscopic estimations optical microscopy (“Neophot 30”) is used. Data on the size of particles in the composite films determined by various techniques are in good agreement. It is found that averaged particle size is about 3  $\mu\text{m}$ , that is nearly coincides with the size of individual filler grains. It means that particles of piezoceramics are weakly aggregated and uniformly distributed over the volume of the polymeric matrix.

Investigation of piezoelectric properties of PVDF–PABI–NZTL-1 composite films performed by different techniques showed the presence of the dielectric hysteresis loops in pure polymeric matrix as well as in the composite in fields up to 1 kV/mm. In a constant

electric field the composite materials have constant capacity and  $\text{tg}\delta$ . It is established that the dielectric properties of the composite films essentially depend on temperature. Heating of the polymeric matrix samples leads to an increase of loss tangent, in contrast this characteristic for the composite materials are lower than that of for the pure polymeric matrix. This is a positive feature of the composite materials.

Thermogravimetric analysis of the composites based on PVDF – PABI matrix showed higher thermal stability (up to 400 °C) in comparison to thermal properties of the individual polymer: PVDF (300 °C) and PABI (350 °C).

Thus, a novel composite materials on the bases of PVDF/PABI blends and piezoceramics NZTL-1 with improved piezoelectric properties and thermal stability are obtained.

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# MATHEMATICAL FORMALISM FOR PREDICTION OF ELECTROMAGNETIC AND MECHANICAL PROPERTIES OF EPOXYAMINE POLYMERS FOR COMPOSITE MATERIALS

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Current approaches to predict the properties of composite materials greatly simplify the complexity of the process of preparation of polymeric composite materials with desired properties. However, despite the apparent simplicity of the, in predicting the properties of polymeric composite materials main difficulty is to predict the properties of the polymer matrix.

Depending on the establishment of the "structure - property" of the polymer is an urgent task and the main problem is the difficulty of establishing the topological structure of the polymer, especially cross-linked. Computer simulation techniques are often complex and not always they can be used when the reactivity of the components of the reaction system.

In this paper, based on the concept of block relations, combining the kinetic and statistical approaches have been developed relatively simple mathematical description of the formation of spatial topological structure epoxyamine polymers and establish the structural transitions.

In connection with the idealization of the topological structure of the polymer in the prediction of its properties has been developed methodology for determining the time-temperature conditions of the synthesis step epoxyamine polymers, allowing guaranteed to receive the same mesh structure, the average bulk density of elastically effective nodes and a small number of topological defects. The method of broadband dielectric spectroscopy have been established characteristic relaxation times for structural and relaxation transitions. The possibility of using the method to «in



situ» control of formation process of the topological structure of the polymer mesh are showed.

The above studies have developed mathematical formalism and the prediction of the viscoelastic and deformation electromagnetic properties of cross-linked epoxyamine polymers.

It was designed and cross-linked epoxyamine polymers experimentally confirmed mathematical description of linear operators associated relaxation of shear yielding and deformation electromagnetic susceptibility, generalizing the qualitative understanding of the mechanisms of conformational mobility of dense polymer networks. It is shown that the mathematical formalism may be possible to quantify the viscoelastic properties and deformational electromagnetic anisotropy of cross-linked polymers. A fundamentally new feature is that the operators introduced by the relaxation of shear yielding and deformation of the electromagnetic susceptibility describe the mechanical and electromagnetic response at all characteristic of the physical states cross-linked polymers: glass, highly elastic, and the transition zone between them.

Proposed and experimentally verified analytical temperature function that relates the relaxation times as a topological structural characteristics of the mobility of the polymer's chains with a share of the fluctuation free volume in cross-linked polymers.

# TRIBOELASTIC MODELING OF TIME-DEPENDENCE OF NANO-STRUCTURAL ELASTOMERIC COMPOSITES

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The time-dependent behavior of particulate composites arises from the action of several independent structural mechanisms, such as proper matrix viscoelasticity, matrix debonding from filler particles, plastisizer migration within nonuniformly stressed matrix microvolumes. Using nanoparticles as a filler of rubber composites introduces one more time-dependent process that also needs to be taken into consideration.

In nanocomposite systems, the size of filler particles is so small that the mean space between the neighboring particles becomes much shorter than the contour length of rubber molecules.

Under this condition, one macromolecule comes in touch with many adsorbed adjacent particles, forming links between them. The extension of this model includes the interaction between the elasticity of rubber and the friction force between the particle and rubber.

Such system can be regarded as a model of triboelastic process occurring in triboelastic composites.

This work presents a variant of the triboelastic structural model which involves the relaxation mechanism showing the interaction of two governing mechanisms: elasticity and surface friction. The model can also be used to describe the peculiarities of the cyclic behavior of elastomeric nanocomposites observed experimentally. Triboelasticity means that the friction force of rubber molecules (spring) over the surface of filler particles (substrates) is dependent on the sliding velocity of molecules (in the absence of detachment of molecules from the particle surface).

The proposed model includes two substrates (filler particles) separated by a space simulating filler concentration and an elastic spring simulating a rubber molecule absorbed on the particle surface and placed on the substrates. The spring is deformed due to

separating and approaching the substrates. During extension, the spring in the space between the substrates becomes engaged into the elastic resistance, which forces the part of the spring to slip into the space between the substrates. The slip is impeded by the adsorption bonds of the spring with the substrate surface, which can be overcome by applying an additional force.

Hysteresis curves are plotted for different cyclic loading conditions. The unusual effect of the reverse motion of the cyclic process has been observed experimentally.

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# ASSESSMENT OF EFFICIENCY OF TECHNOLOGICAL ADDITIVES IN THE WOOD FLOUR–PLASTIC COMPOSITES

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Wood flour–plastic poliolefinovy compositions (DPK) find more and more wide application in construction. They possess a number of advantages: are harmless, resistant to atmospheric influences, allow to utilize a waste of wood-processing productions, easily are exposed to machining. However, despite advantages, in production of DPK there is a number of the problems connected with their manufacturing and application. As a rule, compoundings and technologies of receiving DPK with a high complex of operational and prochnostny properties the know-how of firms of producers is. In this regard, development of DPK on the basis of the polyolefins made in the Republic of Tatarstan, is an actual task. This work is devoted to research influence of a compounding and technology factors on DPK properties on the basis of polyolefins.

As technological additives additives were estimated at DPK of several leading global manufacturers – the Du Pont companies (Fusabond M603), the company 3M (Dyneon FX-59 H) and Baerlocher (Bauerlab W 93125). Their dosage varied in a range of 0,5-5 %.

For an assessment of efficiency of introduction of fillers and additives physicomachanical tests of compositions (durability were carried out at a gap, relative lengthening at a gap, the elasticity module). Also tests by a TMA, DSC method were carried out.

For comparison distribution of fillers in a polymeric matrix the x-ray microtomography was used. This method allowed to estimate influence of technological additives on efficiency of mixture DPK. The received results speak about efficiency of use this method for an express assessment of change of morphology of DPK when using various modifiers.

# **THERMALLY DRAINED COMPOSITE PANELS FOR THE MORE ELECTRIC AIRCRAFT**

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At present, aboard conventional aircraft systems and equipment are powered by different means: pneumatic (cabin pressurization, air conditioning, and icing protection), hydraulic (flight control surface actuation, braking, doors, landing gear extension/retraction and steering) or mechanical (fuel and oil pumps local to engine). These devices contribute significantly to the aircraft's weight, raise the fuel consumption and induce high operating and servicing costs (10 to 13%). The more electrical aircraft concept aims at reducing these drawbacks and rationalizing power sources and networks by using electrical or electromechanical actuators fed by power electronics (with "classical" electronics, electrical currents and voltage are used to carry information, whereas with power electronics, they carry power). Thus, heat losses ensue, which appear by high temperatures likely to damage the equipment. Hence, new solutions for heat transfer and draining off must be studied so as to insure an optimum cooling of the power electronics devices by acting for the best with the local cold sources. Within this scope, a solution for cooling devices is promoted, which consists in a composite thermally drained panel associated with a cooling loop and allowing heat transfer from the electric equipment to the panel.

At first, a literature survey was implemented to list all the conceivable solutions for the raw materials (nature of the fiber and the matrix). Then the consideration of different imperatives (availability and cost of the raw materials, density, compatibility with aeronautic standards, etc.) led to the selection of organic matrix composites. These composites are different from one another by the type of matrix and the possible presence of nanocharges, the reinforcement being made totally with high resistance carbon fiber or partially substituted with metalized carbon fiber, metallic fiber or a metallic mesh.

In order to verify the quality of the layout, the materials' health was evaluated by physiochemical and thermal measurements (curvature,

porosity, glass transition temperature, effective volume fractions of the constituents). The most discriminating mechanical parameters relatively to the conditions of use of these composite panels, the interlaminar shear strength and compression strength, were measured on dry and hydrothermally treated samples (70°C at 80% RH for 1000 hours). In-plane and transverse thermal conductivity were assessed basing on specific heat and diffusivity measurements in the temperature range 23-100°C. The results reveal a weak dependence of the thermal behavior on the presence of the carbon nanocharges or the metallic mesh. Moreover, the woven composite with the mesh shows the best interlayer adhesion and an orthotropic mechanical behavior. After hydrothermal treatment, the interlaminar shear resistance is noticeably sensitive to the testing temperature (23 to 55% reduction in the mechanical properties for testing temperature of 80°C well below T<sub>g</sub> value). A numerical simulation of the thermal behavior was implemented with the aim to identify the structural parameters to master for the elaboration of materials with the highest performances. It was first put to the test by comparing the predicted results with the experimentally measures on the materials elaborated with this end. Then, the numerical simulation was used to define the composite materials capable of showing the highest conductivity values; the used parameters for the simulation were the nature and volume fraction of the matrix and the different fibers, anisotropic thermal characteristics of the fibers, layout influence of interplay contact resistances...

## MODERN BASALT FIBERS AND BASALT FIBROUS POLYMERIC COMPOSITES

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Continuous basalt fibers and polymeric basalt fibrous composites are advanced materials which mechanical and operational properties are currently intensively studied, and ways of their modernization and the fields of effective application are being sought for.

The work objective is the comparative analysis of properties of modern basalt and glass rovings, basalt and glass fibers, respectively, and determination of the ways for the most effective use and disclosure of potential of basalt composite properties.

The investigation presents comparative analysis results for mechanical and physicochemical properties of various basalt fibers, as well as epoxy basalt and glass fibers produced by roving winding, press molding and pultrusion. It is shown that modern continuous basalt fibers represent a new independent type of silicate fibers approaching E-fibers by strength and S-glass fibers by modulus of elasticity, respectively. Chemical resistance of the basalt fibers exceeds that of E- and S-fibers but is lower than that of special zirconium glass fibers.

It is shown that mechanical properties of modern basalt fibers exceed these of the glass fiber based on alkali-free E-type fibers and approach properties of high-strength and high-modulus S-type glass fibers. Hence, the strength of basalt fibers subject to severe temperature and humidity impacts and aggressive alkaline medium exceeds that of similar (by structure) glass fibers.

The increased level of mechanical properties and operation durability of basalt fibers has defined their technical and economic attractiveness for application of basalt-based composite structures in the fields, where mechanical loads are combined with a long-term

impact active media, and the previous experience of structure creation is based on the application of HM and HDMP glass fibers. The work considers some examples of structures, which production from basalt-based composites is most desirable due to technical and economic reasons, namely, conduit pipes for road embankments (including thermally insulated ones), microtunnel lining pipes, and blast-proof containers.



# INFLUENCE HYDROXYETHYL REPLACED UREA ON PROPERTIES OF POLYURETHANE COMPOSITIONS

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Now researches in the field of chemistry of polyurethane composite materials are carried out in two directions: the first - is synthesis of new monomers and oligomers applied at receiving polyurethanes; the second - is modification of polyurethanes received from initial components widespread in the industry. The second way is less labor-consuming and economically more favorable. According to it we synthesized and investigated polyurethanes compositions (PUC) on the basis of difficult oligoether adipin acid (oligoether P6-BA), 4,4-difenilmetandiisocyanate, toluenediisocyanates the brands T-100 and T-80, an amine hardener 4,4'-metilenbis(o-hloraniline) (MOCA) and hydroxylethyl replaced urea (HEU). HEU were synthesized by interaction diethanolamine with diisocyanates the various nature.

Synthesis the PUC carried out in the two-stage way. At the first stage interaction oligoether P6-BA with corresponding diisocyanate at ratio  $\text{NCO:OH}=2:1$  and temperatures  $60-70^{\circ}\text{C}$  duration 3 hours received oligourethandiisocyanates - urethane forpolimers (FP). The second stage - solidification FP carried out by dissolution in them of hinge plates of MOCA and HEU at  $105-110^{\circ}\text{C}$ . Researches on studying of influence structure and the contents of tetrafunktsionalny HEU on PUC properties were carried out. For this purpose the part of hardener MOCA was replaced with HEU. Synthesized the PUC was represented by firm polymers with glossy shine of light yellow color. Their main physicomechanical properties were investigated: strength at a gap, the high-elasticity module, relative and residual lengthenings, hardness according to Shor and the contents gel fraction. During researches it is established that the most expedient is replacement of only small part hardener MOCA by HEU. It is caused by that introduction of a large number of urea groups considerably lowers elasticity the PUC. Besides at this method of synthesis introduction of large numbers of HEU is impossible because of their small solubility in FP.

Thus we synthesized PUC by solidification of the received urethane forpolymer by MOCA and HEU. Influence of structure and contents of HUM on physicomechanical properties of PUC with establishment of change of these properties in depending on the nature diisocyanates is studied. Results of researches expand the range of PUC which can be mastered on the basis of available productions on the basis of industrially available raw materials.

# CALCULATION OF COMPOSITE MATERIALS CONSTRUCTIONS BY FINITE ELEMENTS METHOD

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In aerospace structures are widely used shells, and to ensure the highest weight, size and strength parameters, the composite materials are used. To ensure a high bending stiffness of thin-walled structures, bearing composite layers are often made in a three-layer construction with a light elastic filler. At a low stress gradient the filler bears insignificant load, and it's minimum density can be used. But for the placement and securing of cargo, as well as for reasons of ease of operation and maintenance in the shell there appears sites of stress concentration: zones of application of local stress and cuts. In such cases, when calculating the filler layer within the shell it is necessary to use three-dimensional problem of elasticity theory. The problem of calculating the stress-strain state of such structures from composite materials currently is essentially solved using the finite element method (FEM), implemented in different software packages. Zones of concentration of stress are characterized by locality and high stress gradient. If for the slowly varying stress field in the whole construction it is enough to have a rough partition of finite element net (FEN) - that is, FEN of low density, so in a neighborhood of hubs it is necessary to increase the density of the FEN. Using of FEN of equally high density throughout the whole structure is unjustified because of a significant increase in the order of a system of linear algebraic equations, which leads to the risk of accumulation of computational error.

Assuming the density of the FEN  $t$  as an argument for the approximation of the selected function (stress, displacement, etc.), there are offered calibration functions in the form of the exponent in two versions:

$$\text{deadbeat - } f_1(t) = f_1(\infty)(1 - e^{-\gamma t}) \quad (1)$$

$$\text{vibrational - } f_2(t) = f_2(\infty)[1 - \cos(\delta t)e^{-\gamma t}],$$

(2)

where the ...  $f_1(\infty)$ ,  $f_2(\infty)$  - Appropriate limits

$\delta$ ,  $\gamma$  - the convergence of some parameters.

If to understand the exact solution as a limit value, then based on (1), (2) it is clear that it can be approached using a sufficiently large values of the local density of the grid. As the parameter  $t$  can be used the local density: linear in the radial direction and the meridional membrane, as well as the density on its thickness.

Applying the interpolation of discrete values of the calculated and based on the properties of exponent, can be estimated the degree of proximity of current value to the limit [1]. As an example, the results of the calculation of three-layer cylindrical shell from composite material under the action of local loads are presented.

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# APPLICATION OF GALERKIN'S METHOD FOR DESCRIPTION OF MICROPHASE SEPARATION OF COMPRESSIBLE POLYDISPERSE MARKOVIAN COPOLYMERS

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As it is wellknown, the validness of Landau's theory of phase transitions is restricted by vicinity of the critical point. We consider the molecules of heteropolymers with the Markovian links distribution. The expression for free energy of such systems has been derived in refs. [1,2], that allows to find the parametric dependence of the temperature corresponding to formation of the stable nucleus (binodal) and its morphology independently on the closeness to critical point. The problem is reduced to non-trivial solutions finding of the system of nonlinear elliptic equations under periodic boundary conditions.. Numerical study of these equations with involving the bifurcation analysis to find a starting approximation was presented in the papers [3,4]. Corresponding calculations are very lengthy that restricts strongly their wide application.. Therefore we have elaborated an alternative techniques based on the Galerkin's method in which the solution is presented as Fourier sum consisting of the eigenfunctions of the Laplace operator of given symmetry. Similar procedure was successfully applied earlier to monodisperse copolymers in refs. [5.6]. We have derived the equations for Fourier coefficients and the equation for binodal. The initial approximation of iteration procedure for finding the non-trivial solution of derived nonlinear algebraic equations was obtained with using the bifurcation analysis.. We present the results of calculations for several Markovian copolymers, and compare them with numerical integration results. The restrictions on the applicability of the method are also discussed.

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# **A NEW GENERATION OF FIRE PROTECTION ON THE BASIS OF DISPERSED AND FIBROUS MATERIALS**

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Fires in the modern buildings and facilities bring great environmental injury, considerable economic damages and human victims, as the enormous flows of non-controlled heat energy during a fire have the huge destructive force. The quantity of fires is increased every year almost proportionally with the rise of funds being expended on the capital construction. The value of annual injury for industrially advanced countries is about 2 per cent of their national income. The huge detriment from fires is estimated not only by the cost of burnt material values. Besides the property being in buildings and facilities, the fire destroys building constructions, technological and engineering equipment, elements of service lines, even if they are made of noncombustible materials. This is stipulated by the fact that the heat absorbed by the structures during the fire causes the loss of their strength on which they were designed for the operation under normal conditions.

In order to avoid the damage caused by fires, it is required to increase the fire-resistance of structures, i.e. their capability to preserve their intact, stiffness and strength under fire conditions. This is reached with the aid of the fire protection which blocks the heat flow going from the flame to the structure being protected.

On the basis of an experience obtained during long-term researches in the field of the rocket and space engineering, at the TSNIISM the mathematical model of behavior of structure with fire protection has been developed that takes into account the complicated physical and chemical processes taking place in heating: decrease of rigidity and strength of materials under the action of high temperature, internal evolution of vapor, complex-stressed state and structure failure. On the basis of the model, the algorithms and programs for designing the fire protection of structures and parameters of their optimal

protection have been developed which form the basis of the methodology of flexible designing the fire protection for various-purpose objects.

Our investigations have shown that the effective solution of the problem of fire protection for modern buildings and facilities is possible on the basis of a principle of compositionally, i.e. by using light-weight heat-resistant fibrous materials in combination with substances that while acting the fire produce the steam blocking the heat flux. When using that type of fire protection, the temperature of protected structure does not exceed 100°C during the 3-hour fire action, while the temperature of unprotected structures reaches 1,000°C.

That structure of fire protection has not world analogues in its high fire-protective characteristics with comparatively low cost and mass. Its advantages are also reliability and durability of attaching to structure being protected, vibration resistance as well as easy mounting and dismounting the structure to be protected during the repair.

Technical decisions obtained with the aid of this methodology are successfully used in Russia at the unique objects.

The developed progressive methodology for designing the fire protection may be efficiently used to increase the fire safety of the following objects:

- enterprises of oil-gas producing industry (sea oil-gas producing platforms);
- ships of commercial fleet;
- storehouses and means for transportation of the combustible, explosive and toxic substances;
- atomic power stations;
- transport facilities.

Results obtained on the basis of the methodology should be also used in organization and carrying out of international cooperation in the field of fire safety and ecological safety at any level.



## **OBTAINING OF ANTI-FRICTION CR<sub>3</sub>C<sub>2</sub>-TI HARD ALLOYS USING EXPLOSIVE STRESSING**

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The experimental research of the materials received by explosive compacting of Cr<sub>3</sub>C<sub>2</sub> with Ti powders mixes in a wide range stressing parameters has shown that under certain conditions similar powder mixes are condensed to practically pore-free conditions and their hardness reaches 1100 HV.

The researches held with FIB/SEM Quanta 3D FEG system have shown that phase composition of hard alloys doesn't change after explosive stressing, and redistribution of elements doesn't occur between phases in appreciable volumes.

It is experimentally established that the bottom temperature's border of hard alloys's formation at the consolidation stage is 500-600 °C. Alloys's break character changes with intergranular on transgranular with excess of these temperatures that show about formation of strong interface.

Transmission electronic microscopy (Tecnai G2 20F) has shown that strong interphases look like layers with thickness about 50 nanometers different by structure both from carbide and from metal alloy's phases that allows to identify them as a «boundary phase» which formation provides consolidation of powder alloy's components.

Correlation between the most important anti-friction characteristics in hard alloys and parameters of their structure and hardness are established. Observed dependences which are based on analysis of contact interaction features in friction pair is explained.

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# MODELING OF PAIR INTERACTION BETWEEN RIGID INCLUSIONS SURROUNDED BY AN INTERFACIAL LAYER IN A POLYMER MATRIX SUBJECTED TO HIGH UNIAXIAL LOADING

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Modern studies of the properties of interfacial layers in an elastomeric carbon black filled composite have introduced novelty into the application of the known structural-phenomenological approach that is based on the physical discretization method and gives a satisfactory description of the behavior of materials. The proposed method consists in replacing links in a real composite formed in the space between particles by elastic rods with a similar functional relation between load and elongation.

The physical discretization method was based on the results obtained in the solution of the problem of interaction between pairs of rigid inclusions of a filled elastomer. In order to extend the applicability of this method, the problem on pair interaction of inclusions must be solved again, but along with the consideration of the influence of special properties of interfacial layers. In a new formulation of this problem, the Gent hyperelastic material model is used to predict the behavior of layers and the neo-Hookean model – the behavior of the matrix. For the pair interaction differing in particle sizes and in values of the gaps between inclusions, 16 variants of the problem have been solved. The thickness of the interfacial layer is assumed to be the same for all options. The analysis of the results yields a general approximate relationship between the applied tensile and compressive strength and the elongation of the gap. It should be noted that the values of the coefficients and the applicability limits of the approximate relation are the functions of particle sizes and values of the gaps between particles.

The work is supported by the RFBR under the project N 12-08-00740-a and Fundamental research program of RAS N 12-T-1-1004.

# **SIMULATION OF THE BEHAVIOR OF RIGID PARTICLE-FILLED ELASTOMER UNDER HIGH UNIAXIAL LOADING IN THE FRAMEWORK OF THE PAIR INTERACTION PROBLEM TAKING INTO ACCOUNT THE INTERPHASE LAYER**

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The results of experiments carried out using modern devices lead us to conclude that the properties of interfacial layers in an elastomeric carbon black filled composite differ significantly from the properties of an elastomeric matrix. These studies have introduced novelty into the application of the known structural-phenomenological approach that is based on the physical discretization method and gives a satisfactory description of the behavior of materials. The proposed method consists in replacing links in a real composite formed in the space between particles by elastic rods with a similar functional relation between load and elongation. Such simplification is a reasonable one, because the area of the material in the gap between inclusions exhibits the greatest resistance to deformation. This technique has been used by us earlier, but in its simplest form, namely, the influence of interfacial layers whose properties are mainly responsible for the macroscopic characteristics of composites has been ignored.

At this stage of research, the obtained relationships are adequate for describing the behavior of a model that represents a chain of inclusions. They can also be applied to modeling the behavior of a sample with a random distribution of filler particles. It has been found that the more material in the gap, the higher the deformation properties of the chain. On the other hand, the greater the inclusions, the higher resistance of the chain to loading, and the deformation properties of the chain decrease.

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# THE EFFECT OF FILLER AND SOLVENT ON THE INTERNAL STRUCTURE AND PHYSICAL PROPERTIES OF PAN BASED NANOCOMPOSITES

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Polyacrylonitrile (PAN) is the main type of raw materials which is used for the preparation of precursor fibers for the production of the high-tensile carbon fibers. Up to now a large amount of research articles have been appeared which deal with the insertion of different fillers into PAN solutions for improvement of the mechanical properties of the precursors. The carbon nanotubes, graphene and their modifications seem to be the most suitable fillers for PAN. They can provide high interphase adhesion which, in case of the uniform distribution of the filler in the volume of the matrix, may cause an increase in the structural integrity and the effective redistribution of the load between the matrix and the filler in the nanocomposite.

The main goal of this work is the experimental and theoretical study of the influence of different parameters (DMSO/water composition, temperature) at the stage of the preparation of fiber precursor solution (gel) and at the stage of film casting on the internal structure and the physical properties of materials for carbon fiber production based on PAN with several fillers – multiwall carbon nanotubes (MWCNT), graphene (G) and graphene oxide (GO).

To understand better the system behavior at the molecular level, we used the dissipative particle dynamics (DPD) computer simulations. This method is a highly effective coarse-grained tool for simulating soft materials. The basic idea of DPD is that it should be possible to replace many “atomic groups” or even “droplets” of a fluid with individual “DPD-particles or beads” which interact in such a way that the Newtonian hydrodynamics of the fluid as a whole is reproduced. The resulting coarse-grained beads interact with each other via a pair-wise potential related to the Flory-Huggins interaction parameters.

We have performed mapping of all atomistic structures (PAN, DMSO, water, MWCNT, graphene) on the corresponding coarse-grained models (linear bead-spring chains, set of beads connected by bonds of high rigidity and spherical particles). All coarse-grained force field parameters have been obtained from the atomistic Monte Carlo simulations. Using the DPD-model, we have studied the effect of the temperature and DMSO/water composition on the properties of precursor solution and the effect of the amount of the filler (graphene and graphene oxide) on the structural properties of the composite films.

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# CORRELATION ANALYZING OF STRENGTH AND DEFECTS OF CARBON FIBERS USING STABLE DISTRIBUTIONS

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The strength of carbon fibers is determined by their structure and structure defects. The presence of defects in the fiber affects the strength characteristics of fibers and increases their spread. The presence of significant variations in the strength properties of fibers, a change of variations during the strength tests, the dependence of variations from the base of the tests suggest that the "dangerous" defects effect crucially on mechanical properties of fibers. The concentration of dangerous defects may be small, but they define not only the average values of strength characteristics, but also lead to their significant variations. Statistically, the effect of rare dangerous defects on parameters of fibers can not be taken into account in the standard statistical data processing, built on Gaussian statistics. To identify dangerous defects and describe their influence on the parameters of fibers it is necessary to process statistical data using the stable distributions.

The purpose of this work is to apply modern statistical methods to determine correlations between the defectness and the strength of carbon fibers.

The UKN brand carbon fibers produced by LLC "Argon" were investigated. Data on the strength of the fibers was obtained in the laboratory of "Argon", using FAVIMAT type tearing machine.

The study of defects was performed using a scanning electron microscope DSM-960 Opton. The shots of five fragments of single fiber 5 mm length were made. As a result, the defects data was obtained from the length of 25 mm. All the observed surface imperfections were divided into five classes: growth – the surface object that has the size in three dimensions more than 1 mkm; rough surface – area of the fiber, which have featuring character of the

surface roughness from the rest fiber surface; dot – microdefects on the surface of the fiber smaller than 0.5 mkm, thread-like defect – very elongated three-dimensional surface imperfection; hole – defect in the form of hollow larger than 1 mkm.

Pair correlation functions showing the effect of various defects on the strength of carbon fiber before sizing were obtained with using of stable distributions.

From the analysis of correlation functions it follows that defects such as growth and hole influence on the strength of carbon fiber, so that an increasing concentration of this type defects on carbon fiber surface reduces its strength. The concentration of other types of defects (thread-like defect, rough surface, dot) is not correlated with the strength of carbon fiber.

The developed method allows to carry out not only the correlation analysis between strength and defect, but also between other mechanical properties of carbon fiber, as well as analysis of correlations between the mechanical characteristics of fibers at different stages of production. For example it is possible to find out the correlation between the strength of PAN precursor and carbon fiber strength.

# ECOLOGICALLY CLEAR HIGH-DENSITY THERMOPLASTIC COMPOSITES FOR PROTECTION AGAINST RADIATION

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Thermoplastic polyurethanes are perspective polymeric binders for composite materials with non-organic fillers due to the unique combination of high tensile strength, wear resistance and elasticity. They can be used also for compositions filled with micro dispersed metals of high density for materials protecting various objects against radiation. But increase in content of filler in compositions on the base of traditional thermoplastic polyurethanes leads to increase in effective viscosity, and power costs of technological process. Plasticization of thermoplastic polyurethanes by low-molecular-mass liquids leads to significant downgrade in mechanical properties.

The task of investigations is developing of ecological clear materials manufactured using low-power intensive processes. These materials should be used in natural environment conditions to protect various objects and people against radiation.

One knows that grade of decrease in radiation intensity during transfer through various materials is proportional to their density. The substitution of toxic lead by ecological friendly elastic polyurethane composite of density 9500-10500 kg/m<sup>3</sup> is proposed. This value is close to the density of lead (11000 kg/m<sup>3</sup>).

Using of new low-melted plasticizers synthesized by authors has led to develop structure of thermoplastic polyurethane binder allowing processing of composites on their base lower than usual thermoplastics processing temperatures in 50-70°C. Decrease in binder processing temperature in the first allows to obtain polyurethane thermoplastics containing up to 95% tungsten that is a metal of high density. Preliminary estimation of physical-mechanical properties has provided in the wide diapason of relative air humidity.

Articles of various shapes and sizes can be made from new materials including ones for protection of equipment, devices, and people against radiation. Sphere of application: medicine, aerospace technique, communication equipment etc.

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# THE STUDY OF MICROWAVE ABSORBING COVERS BASED ON HYDROGENATED CARBON THIN FILMS WITH FERROMAGNETIC NANOPARTICLES

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In this work the results of the study of technology and properties of microwave absorbing materials base on amorphous hydrogenated carbon (a-C:H) films with nanoparticles of 3d – metals such as nickel (Ni), cobalt (Co) and iron (Fe) are presented. The films were deposited on high modulus textile substrate by ion-plasma method with simultaneous sputtering of graphite and metallic targets in argon and hydrogen atmosphere on ZV-1200 Leybold-Heraeus inline type vacuum system used for experiment and production, the thickness of the films varied from 50 nm to 4  $\mu\text{m}$ .

The value of complex permittivity ( $\epsilon^*$ ) varied from hundreds to several thousand depends of ferromagnetic nanoparticles concentration in hydrogenated carbon film. Broadband microwave absorbing covers (MAC) on the base of such thin films are made according to principle of the gradient of film thickness and ferromagnetic nanoparticles concentration. Absorbing covers were 500x500 mm size and its surface density varies from 0.18g/cm<sup>2</sup> to 0.4 g/cm<sup>2</sup>. Samples of microwave absorbing covers based on nanostructured films demonstrated high absorption of electromagnetic radiation with modulus of reflection coefficient as high as (-12) dB in ultra wide frequency band from 1 GHz to 750.000 GHz ( $\lambda$  varied from 30 cm to 400 nm). The electromagnetic wave reflection spectrum for the samples of MAC in the ultrahigh frequency region (1 – 100 GHz) is shown on Fig. 1.

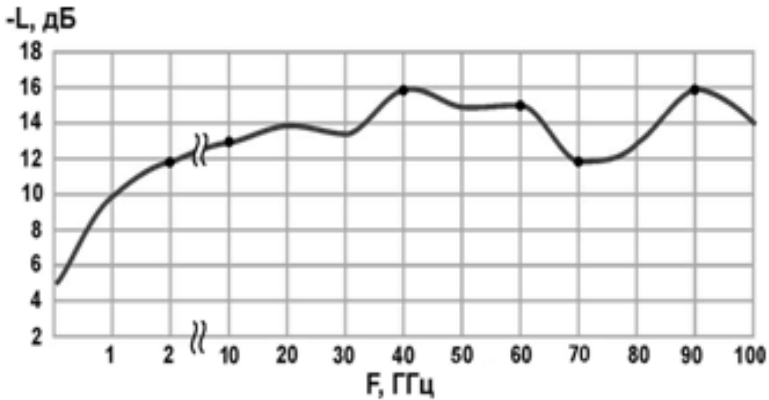


Fig. 1. The frequency dependence of electromagnetic waves reflection coefficient for MAC in microwave region.

Developed new microwave absorbing materials can be used for the solution of problem of electromagnetic compatibility in electronic devices, for the protection of computer data processing systems from unauthorized access, for the decreasing of radar visibility of weapons and special technique, and for the protection of biological objects from electromagnetic radiation.

# STRUCTURAL COMPOSITES BASED ON METHYL METHACRYLATE

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Modern construction and transfer industries require materials with improved technical and technological properties, as well as high-efficiency technologies of building and repair. Such materials should be characterized by a high rate of cure and physico-mechanical properties, resistance to changing temperature and weather conditions, and preservation of a complex of properties during all term of operation, as well as minimal shrinkage and good adhesion to other structural materials (the "old" concrete, metal). Currently used on the Russian market, domestic and imported construction materials like cement-based and organic binder does not meet these requirements.

Composites based on methyl methacrylate (MMA) have significant advantages: it is a system with a high cure rate over a wide temperature range (from -30 to +30°C), high level of physical and mechanical properties, corrosion and frost resistance and durability [1]. Positive properties define prospects of use of composites on the basis of MMA (reduction of terms of construction and commissioning, increase of an operational resource by the expense of durability, anticorrosive and frost resistance), and in some cases (such as high-speed repair, operative restoration of bearing ability, work in extreme weather conditions, etc.) their application is the only way for technical solution. The purpose of our research work was to develop composition and application technology of high-strength quick-setting composites based on MMA with adjustable speed of curing for carrying out year-round building, planning and emergency repair work in different climatic regions of Russia.

We study the full strength (expressed by the magnitude of the damaging stress in compression  $\delta_{\text{comp.}} = 40\text{-}110$  MPa), and process of it's growing for composites based on a set of MMA at curing temperatures from -25 to +25°C, set the extreme nature of the dependence of the strength of components under different conditions

hardening. The influence of composition and temperature of the curing composite for strength and speed of its set with the object of regulation and prediction of these parameters, set the relationship between the responses studied and developed appropriate mathematical model. For each temperature, the optimal formulation of composites for rapid curing. It is shown that the optimization of components makes it possible not only to increase the strength of the composites, but also considerably speed up the curing process.

According to tests at the Research Institute of Concrete and Reinforced Concrete (Moscow) composites based on MMA match strength brand M800. The test for frost hardiness within 500 cycles, the strength of the fall was not observed, and the frost limit set in the ongoing investigations.

The industrial technology of use of composites on the basis of MMA for year-round construction and repair work in the conditions of limited time of their carrying out is finished and works on repair of coverings on various objects of Moscow are carried out.

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# OLIGOELEMENTORGANOSILAZANES – PRECURSORS FOR SILICON NITRIDE NANOCERAMICS, SELF REINFORCED BY NANOTUBES

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In service ceramic coatings and composite material (CM) matrices, obtained at 550-900°C from organoelement compounds, the formation of crystalline phases take place in the amorphous ceramic phase at temperatures  $\geq 1400^\circ\text{C}$ , leading to the emergence of large-sized cracks and, consequently, to decreasing the stability of physical and mechanical properties and oxidation resistance of the CM. The introduction of nanostructures such as 2D (carbon nanotubes), or the formation of nanostructures type 1D (whiskers) in the process of crystallization provide stabilization and improvement of physical and mechanical characteristics of CM. Therefore, this paper discusses the approaches to obtaining at elevated temperatures of the amorphous ceramics that is self reinforced by nanotubes.

Have been synthesized and investigated organoelement compounds and amorphous ceramics obtained by pyrolysis of them. Three ceramic types that are self reinforced by nanotubes of various compositions, depending on the nature organoelement compounds and on different temperatures have been obtained: multi-layer carbon nanotubes in the form of beams coated with silicon oxide, coaxial nanotubes from silicon nitride and carbon nanotubes in the form of a network structure. Ceramic surface microstructure was analyzed by x-ray microanalysis, SEM, X-ray diffraction technique, X-ray phase analysis.

Nanoceramics that is self reinforced by multilayer carbon nanotubes (MWNTs) in the form of beams was produced by pyrolysis of  $\text{>Si-O-B<}$  fragments modified by organosiloxysilazanes at the temperature of  $850^\circ\text{C}$ . Compared to the ceramic-reinforced coating of MWNTs without the molecular layer  $\text{SiO}_x$  nanoceramics received

is characterized by high adsorption capacity and high thermal-oxidative stability up to 1250 ° C. The ratio of length to diameter of nanotubes (~ 50 nm) was more than 10/1.

Nanoceramics were produced through the pyrolysis of polyorganoelementsilazanes modified by Si-N-B (OMHS-B) fragments. Study of ceramic surface microstructure with various B/Si ratios demonstrated that on the background of lamellar microstructure both on the surface and in the bulk, cellular nanostructure formation was observed (1000°C). Nanotubes (or fibers) diameter amounted to 50-200 nm.

Zirconiumoligomethylhydride silazanes (OMHS-Zr) pyrolysis resulted in ceramics that was self reinforced by hollow flawless coaxial nanotubes of 15 до 200 nm diameters. The nanotubes are formed with the participation of spherical ceramic particles of  $\text{SiC}_a\text{N}_b\text{O}_c\text{Zr}_d$  formulation, acting as a catalyst. Spherical ceramic particles determine nanotube diameter. The nanotube length and diameter ratio is from 600/1 to 8000/1. The crystalline structure study of ceramic samples surface and space have been testified to the fact that the nanotubes consisted of micro crystals whose phase composition was close to that of  $\alpha\text{-Si}_3\text{N}_4$  bulk phase.

# OPTIMIZATION OF ALKYL BENZENE MODIFIED PHENOLIC RESIN MATRIX% IN A SEMI METALLIC BRAKE PAD FORMULATION – EFFECT ON FRICTION AND WEAR PERFORMANCE

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The formulation of a brake pad requires the optimization of multiple performance criteria. To achieve a stable and adequate friction ( $\mu$ ), the brake pad materials should have low fade and higher recovery characteristics coupled with less wear and noise. Of this resistance to fade is very difficult to achieve. The type and amount of resin in the friction material is very critical for structural integrity of the composites. The thermal stability of friction materials and its capacity to bind its ingredients collectively under diverse conditions depend upon the quality and proportion of resin. Hence in our earlier work a series of three thermo set resins with variation in the molecular weight was synthesized in a laboratory having desired features. Their potential for application in friction materials was explored by developing three Non Asbestos semi metallic brake pads. The tribo performance was carried out in a Friction Test rig following SAE j661 a standards and found that the medium molecular weight resin has good fade and recovery properties. The current work addresses the issue related to the variation in the amount of resin selected based on our previous work . The variation in amount of resin ( 10.11,11.11,12.11.wt%) was achieved by compensating with inert filler namely Barites in the parent composition. Rest of the ingredients was in equal amount in all the three composites. In this paper, the evaluation was carried out on more rigorous conditions to determine the optimum weight % of the polymer matrix. Testing was carried out in a Brake Inertia Dynamometer as per test schedule JASO C-406. The focus was mainly on the braking effectiveness, fade and recovery as it would be

reflected by the stability of  $\mu$  under ascending austerility. It was observed that composites with 10.11% resin proved remarkably better performer in our formulation especially when operating in severe conditions. Wear resistance, in general, improved with increase in percentage of resin. Scanning electron microscopy was used to help understand the wear mechanisms.



# OPTIMIZATION OF ORGANIC FIBERS % (KEVLAR / AROBOCEL / ACRYLIC FIBERS) IN A FRICTION COMPOSITE – ITS EFFECT ON THERMAL STABILITY AND FRICTION CHARACTERISTICS

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Non-Asbestos Organic Composite friction materials are increasingly used in automotive brake disc pad applications. Loss in braking effectiveness at elevated temperatures ( 300 to 400<sup>0</sup>C) because of reduction in friction coefficient  $\mu$  and the revival of the same at lower temperatures is referred to as fade and recovery respectively. One of the main reasons for the phenomenon of fade is due to the degradation of the organic ingredients in the formulation. In Non asbestos Organic friction composites, resin, friction dust and some organic fibers that are most vulnerable to thermal degradation undergo charring, which results in glazing and deterioration in friction performance. Hence it becomes necessary to optimize these organic fibers in the formulation. The present paper deals with the role of various organic fibers namely Kevlar, Acrylic fibers and the Abrocel fibers on the fade and recovery behavior of friction composites. Also, Thermal Degradation (weight Loss %) is very important to determine the Thermal stability of the product considering the Brake application. The optimization of organic fibers percentage for thermal behavior is considered using Thermo Gravimetric Analysis. The temperature raise during brake application will be between 150-400<sup>0</sup> C and this zone of temperature is very critical to determine the fade characteristics during friction testing. Less weight loss between 150 – 400<sup>0</sup>C during TGA testing is a better thermally stable product. Hence, three different friction composites were developed with same formulation varying only the percentage of Kevlar, Arbocel and Acrylic fibers within the formulation.. The formulations containing 16% of these fibers were developed as brake

pads and designated as NA01, NA02 and NA03 respectively. It was observed that with increasing organic fiber contents, mechanical properties decreased. The TGA test reveals that the composite NA02 had minimum weight loss during the temperature zone of 150 - 400<sup>0</sup> C. The composites were then tested for the tribo-performance using Friction Coefficient Test rig following SAE J 661a standards. The fade  $\mu$  and recovery  $\mu$  % were significantly influenced by the amount and type of fiber combinations. It was observed that increase in organic fiber content increased the Shear strength. Also increase in fiber content lead to increase in  $\mu$  value as found in the composite NA03 when evaluated under SAE J661 schedule conducive to precipitate the fade and recovery behavior of the materials. Also the results proved that the brake pad with minimum weight loss during TGA had good friction stability Thus we could able to correlate the thermal stability with the stability of friction. Wear properties however, did not show any significant change with the amount of fibers. Overall, composite NA03 proved to be the best performer. Worn surface analysis by SEM has proved to be useful in understanding the wear behavior of the composites.

# PHENYL SUBSTITUTED MQ-RESINS AS BINDER FOR POLYMER COMPOSITE MATERIALS

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MQ-co-polymers are hybrid organosilicon siloxane-silicate polymers consisting of mono- and tetra-functional units. The studies have shown that MQ systems with a high content of inorganic units are promising for hybrid composite materials production. But their use is limited due to low compatibility with the organic polymeric matrixes.

Comprehensive study of methylsiloxane MQ-systems properties makes it possible to reveal a molecular structure organization of such objects. This research was aimed to development of molecular parameter adjustment methods as well as to investigation of composition homogeneity of copolymer samples, obtained under different conditions. As a result, a model which regards MQ-co-polymers as composite material (MQ-composite) was suggested. And the individual fractions act as nano-dimensional filling agent, polymeric matrix and softener.

The analysis of the suggested model enabled us to pick out the main direction of MQ-composite materials performance enhancement. Practically, it means the modification of their composition by the introduction of linear polymers having high physical-mechanical characteristics. In particular, it is suggested to introduce polyimides into MQ-composite material. However, the conducted experiments showed the poor compatibility of the components in such a composition in the presence of the classical MQ-systems.

To solve this problem it is necessary to increase the compatibility of the main components of the MQ-composite with high-modular organic matrixes built from aromatic structural units. For this purpose, the new MQ-system were synthesized in which a few methyl groups in the mono-functional unit were replaced with phenyl groups during polymer synthesis. In this report the synthesis and investigation of the properties of phenyl-containing MQ-copolymers with different contents of organic and inorganic parts will be represented.

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# TEMPERATURE DEPENDENCES OF THE TENSILE STRENGTHS OF A CARBON FIBER AND A THREE-DIMENSIONAL REINFORCED CARBON–CARBON COMPOSITE

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It was studied temperature dependences the strengths of a carbon fiber and three-dimensional reinforced carbon–carbon composite in temperature range 293 – 3000 at loading rate  $\approx 0.5$  GPa/s. It was found that tensile strength of a carbon fiber decreases nonlinearly with increasing temperature  $T$ . This nonlinearity is caused by a change in the statistics of atomic vibrations from quantum (at  $T < 2250$  K) to classical (at  $T > 2250$  K) statistics. To take into account the quantum statistics, quantum function  $F q$  is introduced into Zhurkov's equation instead of temperature. The value of this function is calculated from the temperature dependence of the specific heat of carbon. We found that the new quantum mechanical modified Zhurkov's equation describe temperature dependences the strengths of a carbon very well. This equation gives the values of the fracture activation energy ( $\approx 16$  eV) and parameter  $\gamma$  ( $\approx 0.15$  nm<sup>3</sup>). The tensile strength of the three-dimensional reinforced carbon–carbon composite decreases up to  $\approx 1800$  K and increases as the temperature grows further. The decrease in the strength is explained by an increase in the rate of fiber and matrix fracture with increasing temperature. Increasing the strength above 1800 K is explained by a decrease in the strength of the fiber–matrix adhesion bonds at high temperatures. As a result of this decrease, fibers begin to move with respect to each other under load, and the stresses applied to them level off. Although the fiber strength continues to decrease with increasing temperature, this effect increases the composite strength.

# STUDY OF THE MECHANICAL BEHAVIOUR OF MULTI-SCALE OPEN-CELL FOAMS

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The cellular materials are used as core in composite sandwich. The mechanical properties of these materials are still subject to numerous theoretical and experimental investigations. In particular, the impact of cell size on the foam elastic response has not been studied systematically mainly due to the lack of experimental techniques allowing to produce materials for which cell size and relative density can be varied independently. This paper presents the results of a study on the mechanical behaviour of open-cell foams as a function of relative density and size of the spherical interconnected pores. First, an original chemical procedure used to produce polystyrene open-cell foams of different relative densities with several average cell diameters is exposed. Then, the results of compression tests performed on these foams are shown revealing an unexpected influence of the cell diameter on the mechanical response. Analysis of the microstructure foam revealed that a complex nanostructure in the edge of open cells was created during the chemical procedure to obtain calibrated diameter cells. The results of the mechanical tests and microstructure observations are interpreted to propose an analytical model (an extension of the Gibson-Ashby model).

# HIGH-STRENGTH LOW-TEMPERATURE QUICKLY CURING POLYURETHANES: DESIGN, STRUCTURE AND PROPERTIES

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The aim of investigations is to create a new class of high-strength polyurethane constructional materials while using energy-saving technologies.

On the basis of spectral, viscosimetric and computed methods of investigation, kinetic parameters of catalytic and non-catalytic urethane-formation reactions have been determined and regularities of low-temperature curing process for hard polyurethanes have been studied. It has been proven that a regular structure of a polyurethane system is formed as a result of the quickly proceeding reaction of OH-groups of  $N,N,N',N'$ -tetrakis(-2-hydroxypropyl)-ethylenediamine with NCO-groups of multifunctional isocyanate followed by formation of branching hard block-nodes, by subsequent interaction of the forming macro-isocyanate with low-molecular-mass oligodiols, and also, as a result of cross-linking of the polymer on the last stage of its formation.

Complex investigations to ascertain the structure, rheological, physic-mechanical and adhesion properties of polyurethane composites indicate a possibility of controlling the urethane-formation process and the targeted variation of physic-mechanical and rheological properties of multi-component polyurethane systems by appropriate matching of oligomeric mix base's components, of catalysts and ratios between these.

Efficiency of the proposed approach has been demonstrated by the example of specific materials produced as per the low-temperature curing technology featured by the strength (up to 105 MPa), the Young modulus (900–1000 MPa), by glassing temperature (up to 108°C) and by vitality period (4–8 min). Analysis of thermal behavior of the designed material has shown that the polyurethane

composite does not practically decompose while heated up to 205°C. An opportunity in principle to use the new material under severe climatic conditions has been shown.

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# THE STRUCTURE AND PHYSIC-MECHANICAL PROPERTIES OF HARD POLYURETHANES AS INFLUENCED UPON BY THE CURING RATE

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The use of hydroxyl-containing oligomer mixtures as a polymeric base is a promising trend in formation of polyurethanes (PU). In systems comprised of a mixture of hydroxyl-containing compounds featured by different reactivity, several reactions concurrently take place. These reactions differ in reaction rates thus leading to structural heterogeneity of a material. Two catalysts, namely *N,N,N',N'*-tetrakis-(-2-hydroxypropyl)-ethylenediamine which enters into reaction with isocyanate followed by formation of branching hard block-nodes on the first stage, and iron(III) trisacetylacetonate accelerating the cross-linking process on the final stage of the spatial structure's formation, are simultaneously used to selectively control the interaction rate between isocyanate and hydroxyl-containing oligomers [1].

In order to comparatively assess the urethane-formation rate, rheological kinetics of the PU curing process has been investigated and the *k* constants of the reaction rate have been determined using experimental kinetic curves.

Correlation between kinetic parameters of the urethane-formation reaction and physic-mechanical properties of PU has been ascertained: the larger is the *k* constant, the less is the vitality period of the polyurethane composite and the better are strength characteristics of the finished material.

On interaction of hydroxyl-containing oligomers with polyisocyanate (PIC), reaction of NCO-groups takes place not only with OH-groups of an oligomer but also with moisture of the air. This leads to CO<sub>2</sub> emission and to formation of defects in the material. The Roman spectroscopy in the area of C=O valence oscillations (Amide I) has shown that at high curing rates, main reaction of interaction between hydroxyl groups of oligoethers and isocyanate groups of PIC predominantly takes place. At this point, the content of hard urethane



fragments capable of forming strong hydrogen bonds between themselves and simple polyether's oxygen increases.

The conducted investigations have enabled to ascertain that the increase in the urethane-formation reaction rate and, accordingly, in low-temperature curing rate on the one-stage synthesis of the PU based on the mixture of hydroxyl-containing oligomers and PIC leads to producing a material featured by more regular structure and by improved physic-mechanical properties.

*This work was financially supported by the Chemistry and Natural Sciences Department of the RAS entitled "Creation and study of macromolecules and macromolecular structures of a new generation" (project Nr. 12-T-3-1002).*

[1] E.R. Volkova, V.V. Tereshatov, V.I. Karmanov Kinetics of reactions occurring during polyurethane synthesis // Journal of Applied Spectroscopy. 2010. Vol.77. № 5. P.737–740.

# **BIOCOMPATIBLE HYBRID POLYURETHANE- POLY(2-HYDROXYETHYL METHACRYLATE) SEMI- IPN-OXIDE NANOCOMPOSITES: STRUCTURE, INTERFACIAL BEHAVIOR, DYNAMICS, AND PROPERTIES**

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Polyurethane-poly(2-hydroxyethyl methacrylate) semi-interpenetrating networks (PU-PHEMA semi-IPNs) as the biocompatible materials for medical aims were applied [1], and their nanocomposites with artificial nanodiamonds [2, 3] or nanosilica fillers [4] manifesting the enhanced physical properties were developed. In this presentation, two sets of the PU-PHEMA (83/17) semi-IPN-nanooxide composites with 0.25 and 3 wt. % of fumed 3D amorphous silica or crystalline alumina nanoparticles (NPs), with 9 and 25 nm in the average diameter respectively, are considered. Interfacial state in these nanocomposites varied via a presence of hydroxyls (“-OH cover”, native state) or grafted 3-aminopropylmethylsilyl (“-NH<sub>2</sub> cover”), or 3-methacryloyl-propylsilyl groups (“-CH=CH<sub>2</sub> cover”) at NP surface. Native silica surface had the higher hydroxylation degree than native alumina surface. The combined AFM/IR/TSDC/ /DSC /creep rate spectroscopy (CRS [5]) analysis of the structure, dynamics, and elastic properties of the nanocomposites at temperatures from -200 to 1600C was performed.

As shown, silica NPs dispersion in the PU-PHEMA matrix was satisfactory irrespective of a type of their surface state whereas functionalizing of alumina NPs resulted in their larger aggregation. The strong impact of NPs, basically suppression of the dynamics and

temperature-dependent increasing modulus of elasticity as well as the pronounced dynamic heterogeneity in the glass transition were observed. Unlike the majority of works on polymer-3D nanoparticle composites, low content of oxide NPs strongly affected PU-PHEMA matrix under conditions when an average inter-particle distance  $L \gg R_g$  (radius of gyration); thus, suppressed dynamics, increased creep resistance and two-fold increase in elasticity modulus were attained at 0.25 wt.% oxide NPs. This was caused by creating peculiarly cross-linked structures in the nanocomposites due to double hybridization with covalent bonding between PU network junctions (residual isocyanate groups) and PHEMA hydroxyls, and between the polymer matrix and NP surface functional groups. In general, the impact of NPs on the PU-PHEMA matrix properties was controlled by the competitive influence of interfacial interactions and NP dispersion. The first factor was crucial for silica-containing composites where the largest effect was attained with the  $-\text{CH}=\text{CH}_2$  covered NPs due to their copolymerization with HEMA. In contrast, the second factor was crucial and the best result was shown for the composites with untreated alumina NPs.

#### Acknowledgement

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