VAMAS Technical Working Area on Polymer Nanocomposites (VAMAS TWA-PNC)
Utracki, L. A.

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National Research Council Canada / Conseil national de recherches Canada

Canada

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Origin of the present TWA-PNC proposal

- Development of nano-particles filled materials was described as one of two principal topics for materials research in Canada [*Canadian Challenges in the 21st Century: Materials R&D in Canada,* LA Utracki at the 2001 VAMAS SC Meeting, Gaithersburg, USA].
- In the discussion that followed LAU proposed formation of a TWA that would focus on standardization problems of ***polymeric nanocomposites*** (PNC). During the 2005 VAMAS SC meeting (Teddington, UK) LAU repeated the proposal. Following that meeting, a proposal was put forward to NRCC/IMI consortium members, PNC-Tech.
- New TWA-29 "*Nanomechanics Applied to SPM*" was recently formed [David Mendels]. Its purpose is characterization of nanomaterials "by harmonization of existing methods and practices". The active project as well as the proposed ones aim on determining the spring constants of the atomic force microscopy (AFM) cantilevers.

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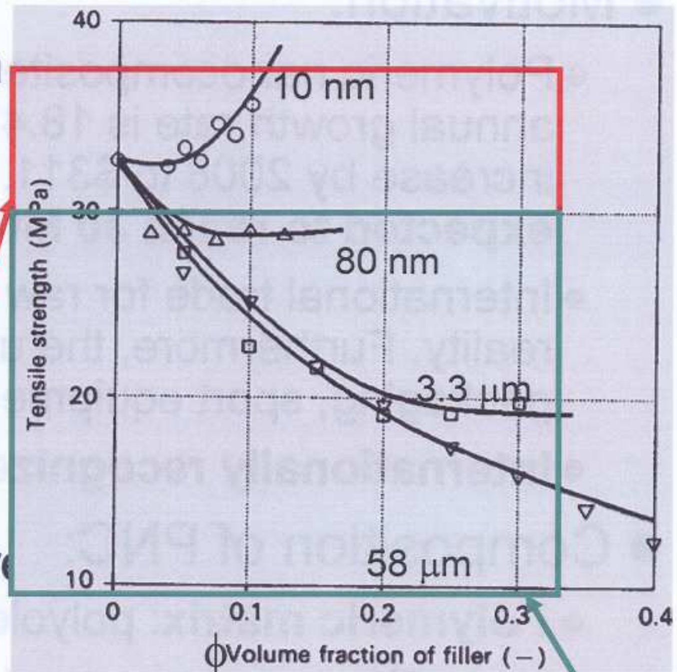
Nano-nomenclature

- **IUPAC nomenclature:** ***nano-morphology*****:** $d \leq 2$ **nm;** ***meso-morphology*****:** $2 < d \leq 50$ **nm (for nano-particles); above – micro (non-reinforcing).**
  - **Matrix**: Any polymeric substance
  - **Dispersed phase:**
    - Solids: clay, mica, metal, glass graphite, boron, carbon or metal oxide fibers or nanotubes, etc. Particles size in the Figure are (from top) d = 10, 80, 3300 and 58,000 nm; **reinforcing limit is 50 nm** [Pukanszky, 1990].
    - Liquid: other (immiscible) polymer
    - Gas: a chemical or physical foaming agent



no adhesion :

$$\sigma / \sigma_p = 1 - a\phi_f^{2/3}$$

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Need for TWA-PNC

- Motivation:
  - Polymeric nanocomposites are new, high volume commercial materials. Their annual growth rate is 18.4%. Sales in the USA in 2004 were $195 million, to increase by 2008 to $311. **By the year 2020 the world production of PNC is expected to reach 30 Mton/year worth over US$65 billion**.
  - International trade for raw PNC between Japan, N. America, and Europe is a reality. Furthermore, the use of PNC in finished parts (*e.g.*, in the transport, packaging, sport equipment industries) is growing rapidly.
  - **Internationally recognized standards for PNC testing do not exist**.
- Composition of PNC:
  - **Polymeric matrix**: polyolefins, polyamides, polyesters, elastomers, etc.
  - **Nanofiller**: mainly natural or synthetic clays, nanotubes and particles
  - **Concentration**: usually 2 to 5-wt% nanofiller
  - **Processing:** it controls on the PNC performance and manufacturer profit
  - **Advantages**: improved rigidity, strength, barrier properties, dimensional stability, heat stability, heat distortion temperature, flame retardancy – **all obtained with marginal increase of material density!**

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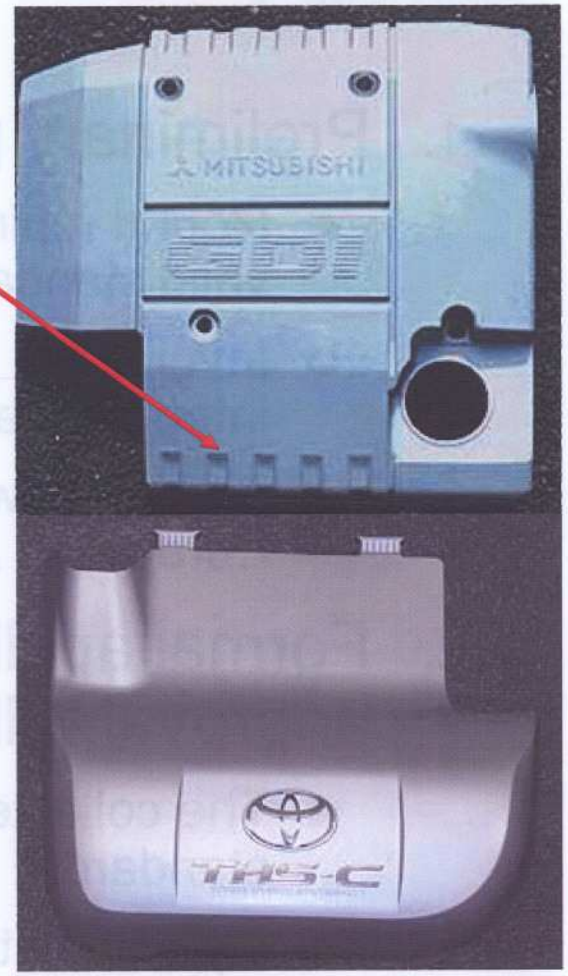
Recent uses of PNC's

- Unitica produces injection-molding grades of PA-6 based PNC used for the production of car engine and converter covers for Mitsubishi & Toyota. The same grade is used for injection molding of rigid base for the electronic control trays & covers.
- Ube PNC is used for rear mirror housing and timing belt cover.
- Bayer manufactures PA-6 nanocomposites for transparent barrier film packaging.
- Kabelwerk Eupen uses EVAc/organoclay for wire & cable applications. Drastic reduction of heat release (flammability) at 3 to 5 wt% clay loading.
- Showa Denko produces PA-66 and POM PNC for improved flame retardancy and rigidity at 0.4 mm thickness. The flex moduli are 30-80% higher, and HDT 30 to 80°C higher, than those of neat resins.
- GMC, Basell, SCP & Blackhawk introduced "step-assist" for 2002 GMC Safari and Chevrolet Astro vans made of PP with 2.5% MMT. By 2004 GMC expanded the use of PNC to body side moldings (Chevrolet Impala-2004) and load floor panels (Hummer H2 SUT).



- Other uses include permeability control, dimension stability, slow aging, etc.

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Formation of TWA-PNC in two steps

1. Preliminary program:
   - Round robin tensile tests of PNC specimens following the locally valid standard procedures (*e.g.*, ASTM, ISO, JISC, etc.).
   - Involve the plastics industry in identifying the true obstacles to international trade posed by the existing standards.
   - Assemble working group mainly from the plastics industry of Europe, N. America, and Asia.
2. Formal application to VAMAS SC for TWA-PNC approval will be submitted if:
   - The collected data will show a need for modification of existing standards
   - Opinion of the plastics industry will favor development of specific standardization methods for PNC.

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Action plan

- Following VAMAS draft of "best practices" to organize new activities the following steps were taken:

No.	Activity	Action
1	Establish whether there is a "real" need for a new TWA.	Approved by PNC-Tech; Done
2	Create an organizing group.	Done in June 2005 – see below
3	Obtain declaration of support from no fewer than 6 participants from three continents: America, Europe, Japan /Korea.	Contact PNC-Tech members, colleagues from industry &academia, and inform SC of the intentions. Done
4	Run a preliminary project with a few participants. The work expected from each should be <u>about one man-week per year</u>.	Select the preliminary project, e.g., tensile test on specimens prepared at IMI. Done
5	Organize the first pre-TWA meeting in June 2006: 1. Discuss results of the preliminary project, 2. Evaluate the need for TWA, 3. Identify chairperson, co-chairperson, and members of the TWP, 4. Agree on links to SDO, 5. Tormal proposal to SC.	(Afternoon on the 2nd day of the PNC-Tech Spring meeting) Done
6	Submit proposal for new TWA to VAMAS SC, and for 1 – 3 proposals for projects.	Complete the standard forms and send electronically to Secretariat. Sent to Dr. Freiman on 2006.11.09
7	If plan proposes an inter-laboratory testing, TWA 18 on Statistical Techniques for Interlaboratory Studies must be contacted ASAP.	Contact: Dr. Jörg Polzehl, WIAAS Mohrenstr. 39, 10117 Berlin, DE Tel: 30 20372481; Fax: 2044975 e-mail: polzehl@wias-berlin.de

Round-robin tests (RRT)

- Material: commercial polyamide-6 and its PNC containing natural and synthetic clay (3 sets of specimen: PA-6 (Ube 1015B); PNC-1 (Ube 1015C2), and PNC-2 (Unitika M1030CH).
- Dried resins were injection molded into ASTM specimens for tensile and impact tests following Unitika's recommended procedure.
- Vacuum-packed specimens were sent by special courier to members of the round robin group.
- The results were collected by IMI and preliminary Report sent to participants for approval.
- The final report: ***"Mechanical behavior of polyamide-based nanocomposites a round-robin tests of the VAMAS TWA-PNC"*** was finalized 2007.02.28 and sent to participants and SC members.

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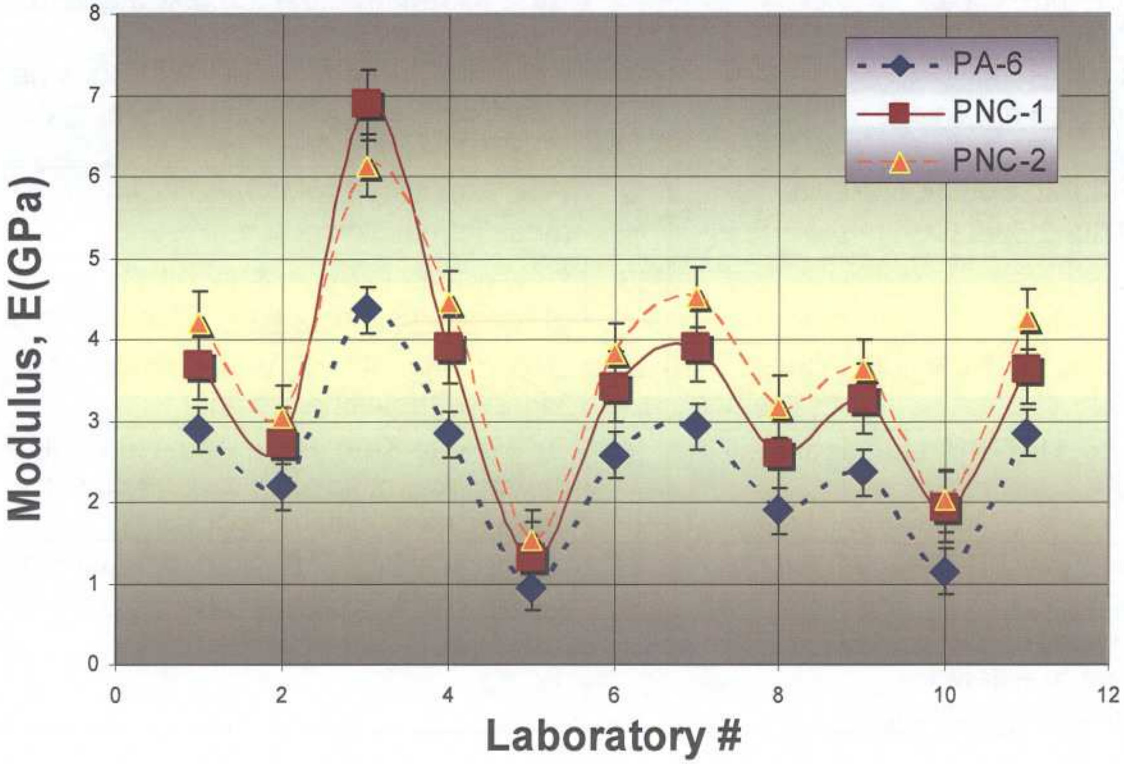
Organizing Committee & Participants of RRT

#	Organizing Committee	#	Participants
1	Dr. M. Berghmans, NOVA Chemicals Corp. berghmm@novachem.com	9	Dr. Robin Winters, Akzo Nobel, The Netherlands, 'Robin.Winters@akzonobel-chemicals.com'
2	Dr. K. C. Cole, NRC/IMI, Boucherville, QC, kenneth.cole@imi.cnrc-nrc.gc.ca	10	Dr. Jürgen Lexow & Dr.-Ing. Volker Trappe BAM, Germany, 'juergen.lexow@bam.de' ; volker.trappe@bam.de
3	Dr. J. Denault, NRC/IMI, Boucherville, QC, johanne.denault@imi.cnrc-nrc.gc.ca	11	Dr. John Blackson, & Dr. Mike Buchmann, Dow Chemical Co, USA; 'johnblackson@dow.com', MEBuchmann@dow.com
4	Dr. L. A. Utracki, NRC/IMI, Boucherville, QC, leszek.utracki@imi.cnrc-nrc.gc.ca	12	Prof. Musa R. Kamal, McGill University, Canada, musa.kamal@mcgill.ca
	Participants	13	Dr. Graham D Sims, & Dr Bill Broughton, NPL, UK, graham.sims@npl.co.uk; bill.broughton@npl.co.uk
5	Dr. Hideki Ichihashi Ube Industries Ltd., Japan '28621u@ube-ind.co.jp'	14	Dr. Eric Vignola, NOVA Chemicals, Canada 'vignole@novachem.com'
6	Mr. Tetsuo Matsumoto, UNITIKA Ltd., Japan 'kj-yasue@unitika.co.jp'	15	Dr. Makoto Kato, & Dr. Arimitsu Usuki, Toyota CRDL Japan, 'makoto@mosk.tytlabs.co.jp'; 'usuki@mosk.tytlabs.co.jp'
7	Prof. Masami OKAMOTO, TTI, Nagoya, Japan; 'okamoto@toyota-ti.ac.jp'	16	Dr. Shuichi KIMATA, Sumitomo Chemical Co., Chiba, Japan, kimatas@sc.sumitomo-chem.co.jp
8	Dr. Alessandro Calogero, CONSORZIO PROPLAST, Alessandria – Italy, 'alessandro.calogero@polial.polito.it'		

Tensile tests 1

- *Tensile modulus as measured in 11 laboratories for three polymeric systems: PA-6, and its two CPNC: PNC-1 and PNC-2*



Tensile tests 2

Tensile test results for PA-6, PNC-1 and PNC-2

ABSOLUTE VALUES

	E(GPa)	error	σ (MPa)	error	ε_b (%)	error
PA-6						
Average	2.45 ± 0.89	0.20	63.4 ± 7.4	2.19	225± 138	64.2
Max	4.36	0.95	71.7	11.60	494	150
Min	0.95	0.02	49.0	0.60	22	5.7
PNC-1						
Average	3.39 ± 1.36	0.244	80.6 ± 7.0	1.34	124 ± 79	45
Max	6.89	1.01	87.5	4.72	257	118
Min	1.31	0.04	65.0	0.40	15	1
PNC-2						
Average	3.70 ± 1.2	0.282	84.0 ± 5.9	0.83	22.4 ± 22	6.2
Max	6.13	0.93	92.1	1.96	81.9	27.4
Min	1.53	0.02	72.0	0.47	6.5	0.4

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Tensile tests 3

- The relative values of the tensile modulus, $E_r = E/E_m$, show smaller spread of values, but similar errors as E.

The relative tensile test results for PNC1 and PNC2

PARAMETER	E_r (-)	error	σ_ρ (-)	error	Δ_b (%)	error
PNC-1; Ube PA1015C2						
Average	1.38	0.15	1.28	0.053	-35.6	82.0
Std. dev.	0.13		0.09		28.2	
Max	1.69	0.51	1.52	0.25	-77.8	232
Min	1.24	0.03	1.19	0.02	+12.6	30
PNC-2: Unitika M1030CH						
Average	1.54	0.16	1.34	0.046	-86.2	59.4
Std. dev.	0.11		0.11		18.0	
Max	1.77	0.55	1.59	0.21	-97.2	126
Min	1.39	0.02	1.20	0.02	-36.7	25

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Impact tests

Average values of the impact test data at room temperature (NIRT)

System	NIRT (J/m) ± error
PA-6: Ube 1015B	22.4 ± 5.8
PNC1: Ube 1015C2	18.6 ± 5.1
PNC2: Unitika M1030CH	22.6 ± 5.8
Global average NIRT	20.4 ± 2.9

- There is accepted “wisdom” that PNC have low impact strength.
- The tabulated averages show that within the experimental error PA-6 and its PNC’s have the same resistance to impact.

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Next steps

- The formal application for the SC approval of the new TWA on Polymeric Nanocomposites has been submitted last November, and the group expects that SC will approve it.
- The first meeting of the RRT group will be held at IMI on 2007.06.11 with the following agenda:
  - Pertinent information from the SC meeting
  - Round-Robin tests results (LAU summary, presentations of individual participants, and discussion)
  - Confirm the need for TWA; select the projects
  - Elect chair & co-chair, and formulate operational procedures
  - Draft and submit the project proposal to VAMAS SC.

Conclusions

- An organization for evaluation of a need for new VAMAS TWA has been formed.
- The initial reaction of the international plastics companies and VAMAS SC has been positive.
- Round-robin tensile tests of PNC specimens are completed. Response from participants is favorable – they want to revise the procedures, and work on the relation between nano-filler dispersion and performance of PNC
- **We await the SC decision.**

Clay-containing polymeric nanocomposites (CPNC)

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Two volume, 800 pgs monograph by L A Utracki, NRCC/IMI

Content

- Part 1 Introduction: NC's with ceramic, metallic or polymeric matrix.
- Part 2 Basic elements of polymeric nanocomposite technology:
- Part 3 Fundamentals: Thermodynamics; Thermal stability; Rheology; Nucleation and crystallization; Mechanical behavior.
- Part 4 Technology of thermoplastic CPNC.
- Part 5 Performance: Mechanical properties; Flame retardancy of CPNC; Permeability control.
- Part 6 Closing remarks: Summary; The future.
- Part 7 Appendices
- Part 8 References.

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