

## NANOSCALE PARTICLE REINFORCEMENT BY OLIGOUREA PARTICLES IN POLYURETHANES – A CONCEPT TO CONTROL MECHANICAL PROPERTIES

Vladimir Peshkov<sup>1</sup>, Michael Herzog<sup>2</sup>, Gerhard Behrendt<sup>2</sup>

<sup>1</sup>University of Chemical Technology and Metallurgy,

8Kl. Ohridski, 1756 Sofia, Bulgaria

E-mail: peshkov\_v@abv.bg

<sup>2</sup>Technical University of Applied Science,

Hochschulring 1, 15745 Wildau, Germany

E-mail: michael.herzog@th-wildau.de

Received 10 December 2013

Accepted 09 April 2014

---

### ABSTRACT

We report on a concept to obtain high properties of nanocomposites by incorporating into the polymer matrix nanoscale reactive species to reinforce the structures already at low concentrations. The materials used to study the effect of reactive organic nanofillers on properties of organic - organic nanocomposites were poly(urethane ureas) in which the urethane part consisted of long chain polyether alcohols reacted with 4,4'-diphenylmethane diisocyanate (MDI) and the urea part of oligourea particles produced either by solvolysis of flexible polyurethane foams or by a new method in which an isocyanate prepolymer is reacted with appropriate reagents with simultaneous cleavage of the pre-formed urethane bond. The combination of two polymer networks - a urethane and a urea one - result in extraordinary synergy in mechanical properties. The properties can indeed be tailored by changing the volume fraction, shape, and size of the filler particle.

*Keywords:* nanocomposite, oligourea, isocyanate prepolymer, mechanical properties.

---

### INTRODUCTION

Organic-inorganic hybrids can be treated as a creative alternative for obtaining new materials of unusual features. This is related to their two-phase structures leading to multifunctional materials [1]. A low-temperature process is usually applied to synthesize the structures which provide a wide versatility in the design of the compounds. The nanocomposite sol-gel products such as those used as coating materials are among the examples. The potential of chemistry is to vary the structure of these mixtures and dissociate the various contributions in tailoring both phases and controlling the interfaces. The organic and inorganic phases may be weakly or chemically bonded. This concept is not extensively transferred to organic - organic structures making

It is known, that the real fibre strengths of conventional fibre-reinforced plastics are usually much less than the theoretical one [2]. Different alternative approaches for attaining the ideal properties of fibre-reinforced plastics, molecular composites and self-reinforced blends have been the subject of considerable research in recent years [3]. Molecular composites are homogeneous dispersions of a rigid-rod polymer in a flexible coil polymer matrix, although the term has also been used to describe reinforcements with dimensions of the order of 10 nm, i.e. nanocomposites [4]. Self-reinforcing polymer systems can be treated as an approach to the formation of phase-separated mixtures of thermotropic liquid crystalline polymers and thermoplastic polymers [5]. Such materials are also obtained by incorporating polymerizable monomers into a polymer matrix which “heal” the

polymer to retain its original properties. Here we report another concept of introducing nanoscale particles to adjust mechanical properties of materials. It refers to incorporating oligoureas as nanoscale reactive species [6] aiming to reinforce polyurethane structures already at low concentrations.

## EXPERIMENTAL

The materials used to study the effect of reactive organic nanofillers on properties of organic – organic nanocomposites were poly(urethane ureas). Then urethane part consisted of long chain polyether alcohols which has reacted with 4,4'-diphenylmethane diisocyanate (MDI), while the urea part of oligourea particles was produced either by solvolysis of flexible polyurethane foams [7] or by a new method in which an isocyanate prepolymer has reacted with appropriate reagents of simultaneous cleavage of the pre-formed urethane bond [8]. The oligourea particles obtained by the former method has diameters between 20 and 800 nm depending on the mode of synthesis with established maxima of particle size diameters of 40, 80, 120, or 320 nm. The maxima of particle size diameters were 8, 12, 20, or 30 nm depending on the ratio of isocyanate and hydroxyl compounds used in the second method. It is to be noted that the size of the oligourea particles cannot be smaller than two former MDI molecules bonded by a urea group with amino end groups where the molecule has a molecular length of 3.9 nm. But three former MDI molecules result in particles of a length of about 6 nm. If such particles agglomerate the particle size increases exponentially. Therefore, agglomeration is kept on the lowest level possible in the course of the synthesis process. In water-blown flexible polyurethane foams, the ratio of isocyanate groups to water (which acts as a bi-functional molecule) is usually in the range of 1 to 4. This results in urea particles of a minimum length of 12 nm but the particle size distribution is between 20 and 300 nm.

The oligourea dispersion polyols produced by the two methods (further details are described in [6]) react with MDI (Lupranol 20 S by BASF) to form films. They are obtained as cast films from a Mathis LabDryer® with a thickness of 200 µm. They are investigated by mechan-

ical tests using a tensile testing machine (Zwick 20S), thermal analysis by differential scanning calorimetry (Netsch) and dynamic mechanical analysis (Myrenne).

## RESULTS AND DISCUSSION

It is known that the nano-effect is determined by the size and the amount of nanoparticles. The effects found with inorganic nanoparticles are limited to a low particle size but such particles are built up of a large number of molecules or atoms. As described above, the lower dimensional limit of the nanoparticles of this investigation is in the range of 5 nm.

When investigating the effect of such nanoparticles amount on the maximum of the distribution curve of 80 nm, the Shore D hardness of the films increases steeply in the range between 1 and 3 % b. w. in the polyol. The curve slightly rises after this beyond 12 % b. w. of the oligoureas in the polyol but a steep increase occurs. This shows that two percolation thresholds occur in the system investigated. The first one is assumed to be a reflection of the so-called nano-effect, while the second is suggesting a phase inversion from a continuous polyurethane to a continuous polyurea matrix. This is due to crosslinking the oligourea particles by MDI to form a continuous highly cross-linked network with an actual glass transition temperature of more than 185°C and a Shore D hardness exceeding 95 (see Fig. 1).

Thus, the question “how nano are the nanocomposites?” described in ref.[9] can be answered to some extent. Based on the calculation of the oligourea dimensions being of at least 5 nm, the nanoscale particles cannot be smaller. They have to be larger. The average of the oligourea length distribution of 4 to 16 structural units provides to calculate the smallest particle size in the range of 10 nm. Some aggregation will also occur under mild or optimum conditions. Thus, the formation of even small aggregates leads to an increase of the particle size to at least 20 nm and more. This is established by AFM investigations where such structures can be seen. In the case of the materials synthesized the nanoscale particles are in the range between 20 and 200 nm. It is established by studying the mechanical properties and DMA that these have the greatest effect even at low concentration

on the properties of the polymers formed.

The model of the morphology developed and the results provides the assumption that the effect of nanoparticles depends generally on the matrix into which they are embedded. In case of metals, several hundred atoms are required to form a nanoscale particle. In the case of simple inorganic molecules at least ten molecules are needed. In the case of macromolecules, such as polymers, lower range nanoscale particles will have a distinct effect on the material properties. It is to be further considered that the mode of interaction between nanoscale particles and the matrix has some effect on the overall structure (morphology and properties). If there are no or few and weak modes of interaction, the effect of the nanoscale particles will be low. In the case of strong interactions, there is a pronounced effect both on morphology and, consequently, on the final properties of the resulting material. This dependence was shown in the case of oligourea nanoscale particles forming a continuous phase in parallel to polyurethane formation. There the urethanes formed connect “hinges” of the larger urea structures and the low reactive polyether polyols forming thus a plasticizing phase. The nanoscale oligoureas have, consequently, a pronounced effect both on the morphology of the synthesized polymers and on their thermo-mechanical behaviour. This is seen in the upper region of oligourea content where the urea particles are cross-linked to a continuous matrix (phase). Annealing at 200°C shows that glass transition temperature ( $T_g$ ) is exceeding 170°C and the melting as determined by DSC is increased to more than 240°C (decomposition of the urethane linkages occurs in this region).

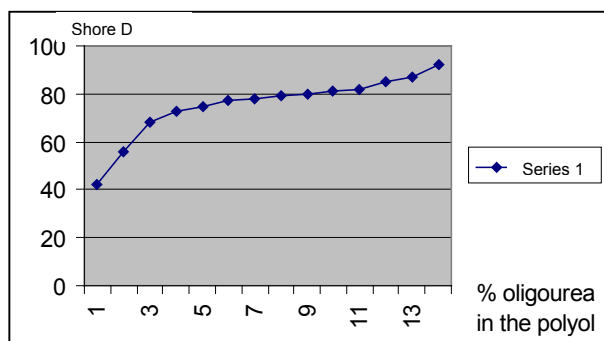


Fig. 1. Dependence of the Shore D hardness on the amount of oligourea particles of 80 nm size in the polyol component.

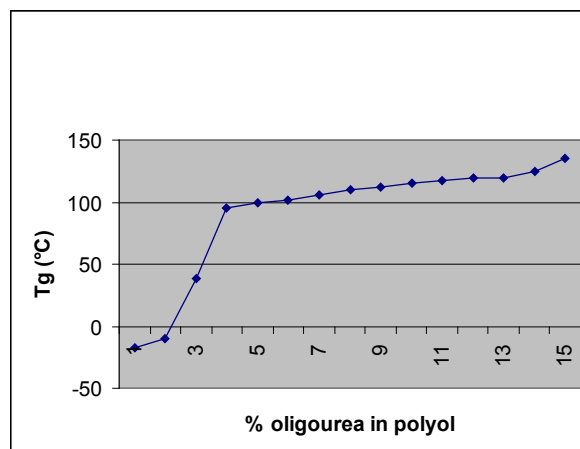


Fig. 2. Dependence of the glass transition temperature (tan  $\delta$  maximum of DMA) on the amount of oligourea particles of 80 nm size in the polyol component.

The effect of the size of the oligourea particles is exemplified when comparing the Shore D hardness curves of the polymer films produced by the two methods. These are oligourea dispersion polyols containing the oligourea particles with a maximum in particle size distribution of 80 nm (see Fig. 1) and a similar polyol prepared with oligourea particles being characterized by a maximum in particle size distribution of 12 nm. In this case, the smaller particles lead to a lower percolation threshold being found in a concentration range of less than 1 % b. w. of the solvated oligourea particles (see Fig. 3). The second percolation threshold defined as a phase inversion is not seen clearly in the curve derived from measurements of the films made of polyols with an oligourea particle size maximum of 12 nm. This can be attributed to the high value of the Shore D hardness

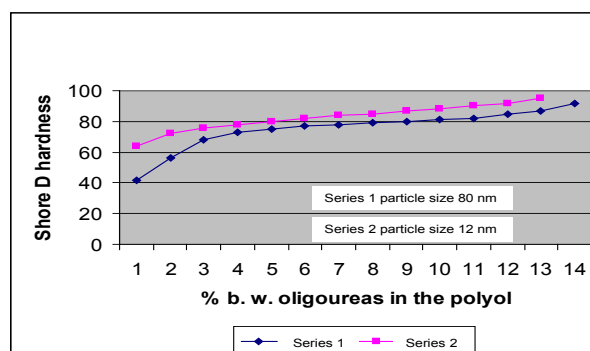


Fig. 3. Dependence of Shore D hardness on the concentration of oligoureas of different particle size in the polyol.

which is close to the upper limit of the method and the measuring instrument.

### **The nano effect**

One of the applications of nanomaterials is connected with reinforcement of composites, wherein small additions of nanomaterials lead to large enhancements of the mechanical properties [10]. There are extensive studies on composites where a polymer matrix is reinforced by a single nanomaterial such as carbon nanotubes or graphene platelets. Additionally, binary combinations of nanodiamond, few-layer graphene, and single-walled nanotubes are used to reinforce polyvinyl alcohol [10]. The mechanical properties of the resulting composites show extraordinary synergy improving the stiffness and hardness. The addition of such nano-material is in any case based on the formation of inter-particle or intermolecular interactions which result in the formation of a physical network with the polymer matrix. Another material of this type also showing such a combination is the formation of polymer nanocomposites reinforced with lower volume fraction of nanoceramics and carbon with peculiar and fascinating properties and unique applications [11]. The incorporation of nanoceramics such as layered silicate clays, calcium carbonate or silica nanoparticles arranged on the nanometer scale of a high aspect ratio and/or an extremely large surface area into polymers improves significantly their mechanical performances. The nanocomposites properties depend definitely on the chemistry of the polymer matrices, the nature of the nanofillers and the way in which they are prepared. The uniform dispersion of physically bonded nanofillers in the polymer matrices is a general prerequisite for achieving desired mechanical and physical characteristics [11].

When the nano-particles are not only physically but also chemically bonded into the polymer matrix, the properties depend additionally on the strength of the bond and their thermal or thermo-mechanical behaviour. It is shown, that the nanoscale network synthesised of urethane and urea moieties forms a network of chemical bonds in which the urethane bonds are the weakest. They undergo changes with temperature increase. When poly (urethane urea) is formed, a mixed network of chemical

and hydrogen bonds is established. This leads to phase segregation so that isocyanate hard domains and the chain extender as soft domains of the polyether part are formed. Several rearrangements occur with temperature increase until the system reaches the thermodynamically most stable physical state. At temperatures exceeding 150°C the urethane bonds of secondary alcohols and isocyanate groups start to decompose to release the original components. The isocyanates resulting from this decomposition may again undergo two different reactions – they may react with the formation of isocyanurates as additional cross-linking species or they may further react with free amino groups of the oligourea particles. Thereby the polyurea content is increased in the urethane matrix. The changes in the soft and hard domains can be observed by dynamical mechanical investigation. It leads to the conclusion that it is possible not only to control the mechanical properties but also the thermal stability or the self-healing abilities of poly (urethane urea) by proper choice of the building blocks in the material.

The temperature increase will change the morphology of the material so that at a certain composition a phase inversion will occur. Thus, the former morphology being determined by the two phase structure of urethane and urea matrices with the urethane matrix forming in itself a two-phase morphology of the said domains changes into a morphology which is dominated by the urea matrix forming a continuous and thermally highly stable network. In spite of the known glassy character of urea polymers and their extremely low flexibility such material derived from nanoscale oligourea particles will remain flexible; even at a Shore D hardness of more than 90 the elongation at break is in the range of 3 to 8 % resulting in a extremely hard, very smooth and highly flexible material which makes it a primary candidate for high quality coatings with improved properties [12].

The flexibility in selecting appropriate nano building blocks allows to design novel materials properties and to optimize them for each desired application. Substantial progress is made in the development, processing and microstructural aspects of the polymers reinforced by low-level loading of nanomaterials. Structural and morphological changes in the polymers induced by na-

nomaterials lead to significant enhancement in several aspects of their mechanical properties. Understanding the synthesis–structure–property relationship of nanocomposites is vital for the development of advanced polymer nano-composites with enhanced mechanical strength, stiffness, thermal properties, protection properties (e. g. anticorrosion), and toughness for structural engineering applications.

Another aspect should be taken into consideration. With carbon nanotubes (CNT) or graphene platelets or with certain layered silicates a percolation threshold is observed at low concentrations [13], especially in the field of electric properties. The combination of a polyurethane matrix with oligourea particles leads to an improvement in electrical insulation properties. The percolation threshold is found in the concentration range below 1 % b. w. with the smaller particles (e. g. particle size distribution maximum at 12 nm) and in the range of 1.7 % b. w. when the particle size distribution maximum is at 45 nm. It is thus proved that the effect observed with inorganic or carbon nanoparticles can be seen in pure organic nanocomposites as well if the appropriate composition is used to control the structure.

The results presented here suggest a way of designing advanced materials with extraordinary mechanical properties by incorporating small amounts of oligoureas bonded into the matrix. The combination of two polymer networks, an urethane and an urea one, result in extraordinary synergy in mechanical properties. The properties can indeed be tailored by changing the volume fraction, shape, and size of the filler particles [11].

## REFERENCES

1. P. Judeinstein, C. Sanchez, Hybrid organic-inorganic materials: a land of multi-disciplinarity, *J. Mater. Chem.*, 6, 4, 1996, 511-525.
2. G.T. Pawlikowski, D. Dutta, R.A. Weiss, Molecular Composites and Self-Reinforced Liquid Crystalline Polymer Blends, *Annu. Rev. Mater. Sci.*, 21, 1991, 159-184.
3. S.C. Tjong, Structural and mechanical properties of polymer nanocomposites, *Materials Science and Engineering R* 53, 2006, 73-197.
4. D.W. Schaefer, J.E. Mark, eds., *Polymer-Based Molecular Composites*, Mater. Res. Soc. Symp. Proc., v. 171, Pittsburgh, 1990.
5. D. Dutta, H. Fruitwala, A. Kohli, R.A. Weiss, *Polymer Blends Containing Liquid Crystals: A Review*, *Polym. Eng. Sci.*, 30, 17, 1990, 1005.
6. V. Peshkov, G. Behrendt, R. Evtimova, M. Herzog, *New Polyurethanes with a polyurea matrix*, *Wissenschaftliche Beiträge TH Wildau*, 2012, 93 – 102.
7. V. Peshkov, H.-D. Hunger, G. Behrendt, *Neue Polyharnstoff-Dispersionenpolyole und Verfahren zu ihrer Herstellung*, DE-OS 10 2009 000 604 (04. 02. 2009/10. 09. 2009), PCT WO 2009/098 226 (13. 08. 2009).
8. W. Klockemann, H.-D. Hunger, G. Behrendt (Performance Chemicals HGmbH), *Reaktive Sole und Verfahren zu ihrer Herstellung*, DE 10 2012 200474 (13. 01. 2011/19.07.2012); WO 2012/095517 (13. 01. 2012/19.07.2012).
9. D.W. Schaefer, R.S. Justice, How Nano Are Nanocomposites?, *Macromolecules*, 40, 2007, 8501 – 8517.
10. K. Eswar Prasada, Barun Dasb, Urmimala Maitrab, Upadrasta Ramamurtya, C. N. R. Rao, Extraordinary synergy in the mechanical properties of polymer matrix composites reinforced with 2 nanocarbons, *Proc. Natl. Acad. Sci.*, 106, 32, 2009, 13186–13189.
11. R.K.D. Misra, P. Nerikar, K. Bertrand, D. Murphy, Some aspects of surface deformation and fracture of 5-20 % calcium carbonate-reinforced polyethylene composites *Mater. Sci. Eng., A* 384, 2004, 284.
12. R. Langenstraßen, H. Huth, M. Pohl, K.-H. Schmidt, H. Goering, S. Ivanyi, G. Behrendt, *Coatings Prepared from Polyurethane Flexible Foam Recycling Polyols*, Paper presented at Polyurethanes EXPO 2001, Salt Lake City, 2001.
13. A. Battisti, A.A. Skordos, I.K. Partridge, Percolation threshold of carbon nanotubes filled unsaturated polyesters, *Composites Science and Technology*, 70, 2010, 633-637.