

Thermoplastic polyurethane-based nanocomposites reinforced with carbon fillers

Krzysztof STAFIN*, Agnieszka LESZCZYŃSKA, Krzysztof PIELICHOWSKI - Department of Chemistry and Technology of Polymers, Cracow University of Technology, Kraków, Poland

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I. The potential of thermoplastic polyurethane (TPU)

Thermoplastic polyurethane (TPU) belongs to the rapidly growing group of commercially available thermoplastic elastomers [1, 2] which plays an important role in a number of industrial branches. For instance, its composites are commonly used in automotive industry as upholstered elements [3], in footwear industry as shoe soles [4] and also TPU is used in biomedical applications [5–6].

Thermoplastic polyurethane (TPU) is a linear block copolymer of alternating hard polyurethane and soft polyether or polyester segments. Thermodynamic incompatibility of these segments and the arrangement of one or two kinds of segments lead to phase separation and induces rise of elastic and rigid domains [8].

TPU material at low and high temperatures behaves like rubber and thermoplast, respectively. Its chemical structure is without covalent cross-links and thus it can be reprocessed. Crosslinking rubber is characterized by the presence of stable chemical cross-links between the main chains of the macromolecules. It precludes the re-processing of the material. However, in thermoplastic polyurethane the area of rigid domains are stabilizing by transverse hydrogen bonds (Fig. 1).

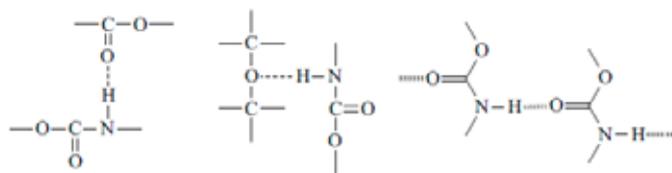


Fig. 1. Hydrogen bonding interaction in polyurethanes [8]

During the heating time above the temperature of hydrogen bonds dissociation in the rigid phase, plastic deformations are occurred and in this way it gives re-processability properties. During the cooling of plasticized TPU, phase separation is formed and microstructures of hard and soft phases are distinguished. The material again behaves as a crosslinked elastomer because of the re-formation of hydrogen bonds [9, 10].

TPU modification by incorporating fillers into polyurethane matrix is an effective way to modify its selected properties, for instance increase the elastic modulus, improve tribological properties [11, 12] and enhance the dimensional stability at elevated temperature. Also reduction of flammability [13] and development of new functional properties, such as electrical conductivity can be noticed [14, 15].

The two phases of TPU significantly vary with the temperatures of phase transitions and due to this, TPU has stable value of the modulus of elasticity in the wide range of temperatures [16–18] (Fig. 2, curve 1 and 2).

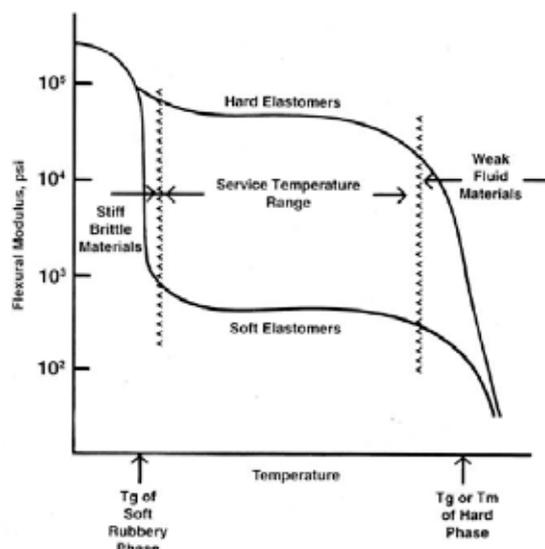


Fig. 2. Modulus-temperature relationships in TPE's [19]

One of the most important contemporary trends in development of new engineering materials, including thermoplastic polyurethanes, is manufacturing of nanocomposites. The primary challenge of this technology is to develop the uniform distribution of nanopowder through the increase of the compatibility between the introduced nanofiller and polymer matrix. The majority literature reports are focused on the incorporation of carbon nanotubes (CNTs). TPU with nanofillers (e.g CNTs) displays for instance significant improvement in the mechanical properties (tensile strength) as well as the gas barrier and fluid resistance.

II. Modification of thermoplastic polyurethane

Besides the type and way of the incorporation of nanofiller into TPI matrix, the properties of attained materials depend on the interactions of nanofiller with both hard and soft segments. Recently, great attention is paid to the uniform distribution of nano-sized powder and the effect of the surface area and particle size of the filler on the organization, dimensions, and sequences of the rigid and soft domains. Therefore, by using nanoparticles it is possible to generate the so-called strengthening effect through reinforcement induced by stiff nanoparticles and alternation of the supramolecular (domain) structure of TPU.

TPU reinforced with carbon nanotubes (CNTs)

Carbon nanotubes are graphitic sheets that have been wrapped up into a cylinder. Several types of carbon nanotubes can be distinguished and they are as follows:

- single-walled carbon nanotubes (SWNTs),
- double-walled carbon nanotubes (DWNNTs) and
- multi-walled carbon nanotubes (MWNNTs).

*Corresponding author:

Krzysztof STAFIN – M.Sc., (Eng.), e-mail: stafin@indy.chemia.pk.edu.pl

These structures have attracted much attention because of the presence of peculiar electronic properties which are depended on the shape of molecules consisting of only carbon. The difficult tasks with manipulation and incorporation of carbon nanotubes in polymer matrix are both related to the high molecular weight and the strong intertube forces. These phenomena cause the aggregation of filler nanoparticles, phase separation and result in poor mechanical performance of composites. Increase of the compatibility between TPU and carbon nanotubes can be achieved by the use of surfactant and surface modification of filler, but results are determined by the choice of techniques. In literature, there are many researches on the TPU modification using carbon nanotubes (CNTs). For instance, Sen et al. were the first who investigated the incorporation of single-walled carbon nanotubes into TPU matrix by electrospinning technique. This study indicated that electrospinning is a useful method for producing SWNTs-reinforced nanofibers and membranes with improved mechanical properties. They demonstrated that both the uniform dispersion and the interactions of TPU-CNT can be enhanced by functionalization of carbon nanotubes [20]. Smart et al. investigated the fabrication of TPU nanocomposites incorporating double-walled carbon nanotubes (DWNT) that were functionalized by two-stage reaction procedure. The aim of this functionalization was to increase the hydrophobicity performance of carbon nanotubes. All functionalized CNT provided the superior mechanical reinforcement of composites. However, the greatest enhancement was noticed in tensile strength of DWNT-TPU where the carbon nanotubes were functionalized by reacting with octadecylamine [21]. Deng et al. demonstrated the three-step surface treatment of multi-walled carbon nanotubes (MWCNTs) to enhance the mechanical and transport properties of TPU film. Primary stage of this study was based on treatment with acid followed with hydroxylation of MWCNTs. The third step was grafting isophorone diisocyanate (IPDI) to the MWCNTs. The modifier had similar chemical structure as the hard segments of TPU. The novel covalently attached functional groups enabled the use of carbon nanotubes as the cross-linking agent. These steps of modification showed a remarkable increase of modulus and tensile strength by about 200% and 35%, respectively, compared to the pure TPU [22]. Chen et al. formulated TPU-CNT nanocomposites by extrusion. Previously, carbon nanotubes were functionalized to increase interfacial interactions and uniform dispersion of MWNT in TPU matrix. Homogeneous dispersion of surface modified MWNTs throughout TPU matrix was responsible for the significant improvement in Young's modulus and tensile strength [23].

Graphene-based thermoplastic polyurethane nanocomposites

Nguyen et al. reported the first study in which they evaluated graphene-based thermoplastic polyurethane nanocomposites. Graphene is an one-atom-thick sheet of graphite. Moreover, its structure enables the electron transfer in polymer matrix because of the presence of large π^* -conjugated system. A nanocomposite containing 2 parts of graphene per 100 parts of TPU had an electrical conductivity of 10^{-4} Scm^{-1} [24]. It leads to a 10^7 times increase over the unmodified TPU structure. The major task in this field of technology is to develop strategies for isolating single-layer carbon sheets from graphite. In a polymer matrix, graphene tend to aggregate because of the weak interfacial adhesion between graphene and the neat polymer. Nguyen and co-workers noticed that the technique of TPU-graphene nanocomposite preparation is a way to improve both electrically conducting and mechanical properties. Thermogravimetric analysis showed that the degree of TPU adherence onto the functionalized graphene filler increased when the nanocomposite was prepared by the in situ polymerization method. In this case the nanocomposite containing about 2 wt % of functionalized graphene had an electrical conductivity of $2.07 \times 10^{-3} \text{ S/cm}$ (about 10^8 times higher than that of the neat TPU). Moreover graphene nanofiller allows obtaining the superior

mechanical properties of composite [25]. Kim et al. performed synthesis of the functionalized graphene layers from graphite oxide via thermal reduction and chemical treatments. Even 1 wt% of graphene made the polyurethane electrically conductive and improved the mechanical and gas barrier properties significantly [26]. Whereas, Wu et al. presented a simple and effective route to improve both mechanical and dielectric performance by hyperbranched aromatic polyamide functionalized graphene sheets. It has been demonstrated that the functionalized graphene-based TPU composite has both higher tensile and yield strength. It remains at nearly the same strain at break when compared with the composites with graphene oxide, ethylene diamine-modified [27]. Huang et al. fabricated a novel self-healing material, using few-layered graphene (FG) and thermoplastic polyurethane (TPU) which not only exhibits a mechanically enhanced properties, but also can be repeatedly healed by various methods including infrared (IR) light, electric and electromagnetic wave with healing efficiencies higher than 98% [28]. The improvement of interfacial interactions in polymer nanocomposites is frequently a complex problem since chemical surface modification of nanoparticles also varies its thermal or mechanical properties. The final effect is not easy to predict without carrying out a broad research program. For example Liang et al. compared the performance of isocyanate modified graphene and sulfonated graphene in TPU matrix and surprisingly found that the former caused significant reduction of thermal stability as compared to the latter. Moreover, isocyanate modified graphene/TPU nanocomposites vs. sulphonated graphene nanocomposite was much poorer in terms of mechanical strength and the shape recovery rate was also inferior [29].

Expanded graphite-based TPU

In the current age of electronic devices and multiple sources of electromagnetic fields spread all over the public and private spaces the shielding materials, other than metals, are demanded on the market. The electromagnet shielding of nanomaterials is currently explored research area. It was demonstrated that nanocomposites of commercial TPU containing 20 wt.% of expanded graphite (EG) showed an average value of -20 dB of shielding effectiveness (SE) for 4 mm thick sample, which made them suitable as shielding material for commercial application. Simulations of metal backed configuration showed that important narrowband electromagnetic (EM) absorption ($> -15 \text{ dB}$) can be achieved at 1 mm thickness, while multilayer structures of 6 mm in thickness were effective in EM broadband absorption ($> -10 \text{ dB}$ between 8.5 and 12 GHz) [30]. In another research by Ye et al. it was reported that the tensile strength was increased by 116.1% when the microwave expanded graphite oxide (wGO) was added to TPU at 3 wt %. Compared with the pristine TPU, the electrical conductivity and thermal conductivity were increased by 72.4% and 6 orders of magnitude, respectively. Moreover, at the GO mass fraction of 2%, the higher microphase separation degree and higher storage modulus at room temperature was observed for wGO/TPU nanocomposites [31]. In research by Quan et. al it was demonstrated that the high strengthening potential of graphite nanoflakes (GNP) is combined with the maintenance of high elongation of elastomer nanocomposite. The nanocomposite that contained 3.9 vol% of GNP (the maximum loading employed in that study), still showed a high elongation at break of over 600%. Due to plate shape the nanofiller was simultaneously acting as a thermal stabilizing agent and intumescent flame retardant [32].

III. Future Trends

The successful preparation of nanocomposites and synthesis of hybrid materials based on TPU indicates that a new group of thermoplastic elastomers should soon emerge on the market of specialty materials. Previous works showed the dependency of the property on the nanofiller concentration and the degree of filler dispersion in form of separated and uniformly distributed

nanoparticles. The future development of nanotechnology still requires the improvement of experimental techniques to better understand the relationship of the nanocomposite properties and nanofiller structure, distribution of additive, polymer phases morphology and conformation of macromolecules in the direct contact with the filler. Thermoplastic polyurethanes have a high mechanical strength and good flexibility. Carbonaceous nanofillers, such as graphene, expanded graphite and carbon nanotubes, have a potential to improve mechanical performance of TPU and simultaneously render new functional properties e.g. electrical conductivity, electromagnetic shielding or flame retardancy. The polymer modifications are becoming more and more commonly used owing to the rapid development of nanotechnology.

It is also necessary to improve the physical and chemical methods of preparation of nanocomposites and the search for solutions to improve the compatibility between a filler and matrix polymer. The basic research and technology development will help to reduce the problem of agglomeration and distribution of nanofiller.

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Krzysztof STAFIN – M.Sc., (Eng.), graduated from the Faculty of Chemical Engineering and Technology at Cracow University of Technology. He is currently a Ph.D. student in the Department of Chemistry and Technology of Polymers at this university. Specialty – Technology of Polymers.
e-mail: stafin@indy.chemia.pk.edu.pl

Agnieszka LESZCZYŃSKA – Ph.D., (Eng.), graduated from the Faculty of Chemical Engineering and Technology at Cracow University of Technology. She is a lecturer in the Department of Chemistry and Technology of Polymers. Specialty – Technology of Polymers.

Professor Krzysztof PIELICHOWSKI – Ph.D., D.Sc., (Eng.), graduated from the Faculty of Chemical Engineering and Technology at Cracow University of Technology. He is the Head of the Department of Chemistry and Technology of Polymers at Cracow University of Technology. Specialty – Technology of Polymers.