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Chapter 16

“Nanoreinforcement” of Thermoplastic Elastomers

J. Karger-Kocsis

1. Introduction

Polymeric nanocomposites (organic/inorganic hybrid materials) have attracted considerable interest in both academia and industry. This is due to the outstanding properties achieved at low “nanofiller” content (usually less than 5 wt%). The nanocomposites contain inorganic fillers the size of which, at least in one dimension (thickness), is in the nanometer range. In contrast, traditional fillers and reinforcements have a lateral dimension of the order of micrometers ($> 5 \mu\text{m}$). Albeit the term “*nanocomposites*” was introduced recently, some of their components are natural products, while others find industrial application since more than half a century (carbon black reinforcement of rubbers). Like traditional fillers and reinforcements, the nanoparticles can be grouped according to their shape and aspect ratio (length-to-thickness ratio), and one can distinguish one- (*e.g.*, carbon nanotubes), two- (*e.g.*, layered silicates) and three-dimensional (*e.g.*, nanoparticles, zeolites, mesoporous glasses) versions.

The unexpected beneficial behavior of nanocomposites is due to filler/matrix and filler/filler interactions. Owing to the huge specific surface of well dispersed nanoparticles, it is often quoted that the properties of nanocomposites are controlled by interface/interphase characteristics. The distinction between interface and interphase depends on whether or not this region has a finite thickness. Polymer nanocomposites are already commercialized, *e.g.*, films of improved barrier properties and low-density injection moldable resins with high heat distortion temperature. Although the structure-property relationships in nanocomposites are poorly understood, the

reader may get useful information to this topic from some recent monographs [1–7]. It should be noted that few reviews are devoted to nanotube reinforcement, and more works describe the incorporation of spherical nanoparticles. On the other hand, the overwhelming majority of the R&D works is dedicated to the use of modified layered silicates.

Nanoreinforcement strategies have been exhaustively adopted for polymers of both thermoplastic and thermoset types. Interestingly, thermoplastic elastomers (TPE) are scarcely studied. This may be due to several reasons, as pointed out in this chapter. Therefore, the aim of this chapter is to draw attention on possible property improvements *via* nanoreinforcement instead of summarizing the related achievements with TPEs. Most of the nanomodification work has been performed on thermoplastic polyurethanes (TPUs). The author is convinced that the related knowledge may serve as a guide for other TPEs, as well. For this reason, strong emphasis is put on the polyaddition-type TPEs, rather than on polycondensation ones. (TPE-based nanocomposites are discussed also in Chapter 14.)

2. Concepts and realization of nanoscale reinforcements

Composites are defined as materials consisting of two or more distinct *components* with an interface between them. This definition is mostly used for materials containing reinforcements, which are characterized by a high aspect ratio. This is the case of one- and two-dimensional particles. Particles with a low aspect ratio (the aspect ratio of a spherical particle is 1) are termed fillers, as their incorporation in the matrix is usually accompanied by both cost reduction and property degradation (strength, toughness). The distinction between *filler* and *reinforcement* is arbitrary in many cases even for macro- and micro-composites, and hardly practicable for nanoparticles. The stress transfer from the “weak” matrix to the “strong” reinforcement occurs *via* the interface and there are many analogies between macro- and nanocomposites. The challenging question is whether the reinforcing effect can be amplified by using nanoscale particles instead of traditional microscale (considering one lateral dimension) ones. The answer is positive. It was demonstrated in several papers that the property profile achieved by adding 30–40 wt% filler (spherical chalk, platy talc) or 10–20 wt% reinforcement (discontinuous glass fiber) can also be realized by dispersing 4–5 wt% layered silicate ([1,2,6] and references therein). It was also shown that effects usually caused by reinforcements could also be achieved by well dispersed spherical nanoparticles, which are appropriately bonded to the matrix [4]. Since layered silicates serve predominantly as nanoreinforcing materials for polymers [1,2,6,8], it is worth to briefly show their action and potential.

Layered silicates of natural (clays) and synthetic origin possess a layer thickness of *ca.* 1 nm. The lateral dimension of this platy (disc-shaped) reinforcement may reach several micrometers. However, the aspect ratio of clays (bentonite, montmorillonite) is usually less than 300. Isomorphic substitution of higher

valence cations in the silicate framework by lower valence ones renders the layers negatively charged. This negative surface change of the layers is counterbalanced by alkali cations located between the clay galleries. They can be replaced by a bulky cationic organic surfactant (termed *intercalant*) by ion-exchange reactions. By this treatment, the initially hydrophilic silicate becomes organophilic. At the same time, the interlayer spacing (basal or *d* spacing) also increases. To reach an interlayer distance greater than 1.5 nm seems to be necessary in order to facilitate the intercalation with the polymer molecules. *Intercalation* means that the initial interlayer spacing increases, but a still well detectable long-range order remains between the layers. In the case of *exfoliation*, the individual layers are dispersed in the matrix without any structural ordering (Figure 1).

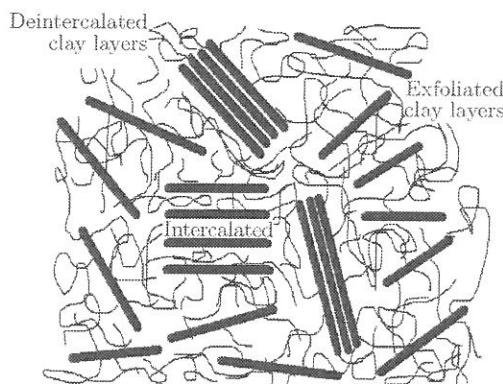


Figure 1. Scheme of the dispersion stage of layered silicates in polymers

What is the driving force of intercalation? Intercalation is governed by thermodynamic and kinetic parameters. This holds for all kinds of intercalation (in the melt, *via* solvents, *etc.*) and in all kinds of hosts (two-dimensional layered stack, three-dimensional framework). It is intuitive that the polymer molecules penetrating in between the silicate layers lose their conformational freedom, which is equal to entropy loss. On the other hand, for a molecular dispersion, the Gibb's free energy term should be negative. Note that the organophilic silicate layer can be regarded as a stiff polymer backbone to which molecules of the cationic tenside are tethered ("brush molecules" composed of inorganic and organic parts [8]). The entropy loss from the side of the bulk polymer molecules enhances the free energy instead of causing its reduction. An overall entropy gain may occur, however, when taking into account the organic intercalants tethered to the clay layers. Their conformational freedom may be strongly enhanced by intermingling and entangling with chains of the bulk polymer. This is the possible scenario from the entropic point of view (*i.e.*, resulting in entropy increase). Further, energetically favored interactions may take place between molecules of the intercalant and the bulk polymer. These interactions

(H-bonding, chemical reactions, acid – base and dipole interactions, *etc.*) may reduce the enthalpy term and thus the overall free energy, as well. All these aspects should be considered when selecting the proper “organophilization” of the layered silicate for a given polymer. It is worth noting that positively charged layered inorganic systems are also available. They can be made organophilic by anion exchange using suitable anionic surfactants (*e.g.*, [9]). However, according to the open literature, such nanoparticles were less used to reinforce polymers and definitely not yet adopted for TPEs.

There are several ways to produce nanocomposites (*e.g.*, [10]). The related strategies are so versatile that they cannot be easily grouped. In this chapter, the production methods will be discussed on the example of TPU nanocomposites containing layered silicates. The related production methods are grouped as follows: (i) *in situ* techniques (polymerization, sol-gel chemistry), (ii) solvent-assisted methods (solution, latex), and (iii) melt compounding.

As emphasized above, the concept of nanoreinforcement is far less practiced for TPEs than for thermoplastics [1,2,4,6,8], thermosets [1,2,8,11] and even for traditional rubbers [3,12]. This remark holds especially for addition and condensation TPEs. On the contrary, considerable amount of work was done on olefinic and styrenic TPEs. What is the reason for paying little attention to the nanoreinforcement of TPEs? This is likely due to the fact that the properties of addition and condensation TPEs can be tailored upon request *via* the related synthesis. Recall that this was also the major argument for their less explored blending with other polymers. A further analogy with blending is that markedly more reports addressed the nanoreinforcement of TPUs compared to poly(ether amide) and poly(ether ester) block copolymers (see also Chapter 15).

3. Nanoreinforcement of thermoplastic polyurethanes

Poly(ether-*b*-urethane)s and poly(ester-*b*-urethane)s are designated as TPUs. Interestingly, nanoreinforcement is considered as a suitable tool for the property improvement of crosslinked polyurethanes. The interest in this development is due to the traditional application of crosslinked polyurethanes (coatings, varnishes, *etc.*) where the modification with nanoparticles may be very promising (*e.g.*, yielding scratch and abrasion resistance). Therefore, it is appropriate to have a look at the related works and adopt the results for thermoplastic grades. Note that the related teaching can be rather easily transferred from thermoset to thermoplastic polyurethanes.

3.1. *In situ* techniques

In situ techniques involve polymerization and sol-gel reactions. In the former case, polyurethanes are produced from suitable polyols and polyisocyanates in the presence of nanoparticles or their sources (*e.g.*, an organoclay with mean particle size initially in the range of a few micrometers). According to the sol-gel route, nanoparticles are produced *in situ* *via* suitable chemical reactions (*e.g.*, [10]).

3.1.1. Polymerization

Petrović *et al.* [13] produced segmented polyurethanes of various soft segment contents (50 and 70 wt%) and reinforced them by incorporating colloid silica (up to 30 wt%). The mean diameter of the spherical colloid silica was 12 nm. It was found that the nanoparticles are evenly distributed in both hard and soft phases. The nanoparticles strongly influenced the spherulitic morphology of the hard phase. The size of the crystalline lamellae decreased and the formation of the spherulite-forming fibrils was suppressed, too. These findings are very important and probably give the answer to the question why crystalline TPEs are not favored for nanoreinforcement. Recall that in both addition and condensation TPEs the hard (crystalline) domains are the “knots” of the physical network structure. A fundamental change in the built-up, crystalline organization of these knots usually has a negative impact on the mechanical performance. This is in conflict with the expected tendency. The basic challenge with the nanoreinforcement of TPEs is to develop a “second” physical network. In the latter, the knots should be provided by the nanoparticles with strongly adhering, immobilized molecules around them. Accordingly, the nanoparticle-induced network should form exclusively in the amorphous (soft) phase. The expected outcome is a dual physical network: a nanoparticle-induced one in the amorphous phase which does not interfere with the development of the inherent physical network created by the crystalline (hard) domains. Unfortunately, this double network, if any, can hardly be established.

In situ polyaddition of polyisocyanates and polyols together with organophilic layered silicates was used to produce polyurethane nanocomposites. Zilg *et al.* ([14] and references therein) used organophilic fluoromica (intercalated with bis(hydroxyethyl)-methyl-dodecyl ammonium cations) as a nanofiller. It was found that this hydroxy-functionalized silicate exfoliates upon shearing in poly(oxypropylene)glycol if the molecular mass of the latter is high enough. The resulting nanoreinforced crosslinked polyurethanes exhibited improved tensile strength and even elongation at break values. *In situ* techniques are preferred to avoid the nanoparticle aggregation. Chen *et al.* [15] found that aggregation is not easy to circumvent due to the high surface energy of nanosilica and its tendency to form hydrogen bonds. Similar results were reported also by Zhou *et al.* [16]. As pointed out before, several works discussed the organoclay reinforcement of slightly or tightly crosslinked polyurethanes (*e.g.*, [17–21]). According to X-ray diffraction (XRD) results, the authors concluded that the organoclay layers were intercalated by the polyurethane molecules [17–21]. Exfoliation of the clay was only observed when the clay intercalant had, in addition to the alkyl chain, also ligands with hydroxyl groups. Even in the case of intercalation, a strong improvement in tensile stiffness and strength of the nanocomposites was observed. Contrary to the expectations, the ductility (strain at break) was less affected. This may be attributed to the “plasticizing effect” of the gallery onium ions (intercalant). “Plasticizing” is due to the intermingling of the molecules of the intercalant with those of the polymer matrix [17]. Thus, nanoreinforce-

ment was often not associated with a shift in the glass transition temperature, T_g , toward higher temperatures (*e.g.*, [20,22]). Such a shift is expected due to the immobilization of adhered polymer molecules (*e.g.*, [15]). On the contrary, the plasticizing effect should result in a T_g shift toward lower temperatures. The position and intensity of the T_g peak depends on the dispersion stage of the silicate. Exfoliation usually results in an intensity reduction and in a shift toward higher temperatures. In a recent paper, Dai *et al.* [23] reported the structure-property relationships of an *in situ* produced organoclay-reinforced (cetyltrimethylammonium bromide intercalant) segmented polyether-polyurethane. The authors found an abrupt increase in the tensile strength and Young's modulus as a function of the organoclay content. In addition, the elongation at break has doubled in the presence of 2 wt% organoclay. This was attributed to the exfoliation of the organoclay on the basis of XRD and transmission electron microscopic (TEM) results.

3.1.2. Sol-gel chemistry

The sol-gel route is an interesting alternative in nanocomposite preparation. As aggregation/agglomeration phenomena can be avoided by this technique, it is usually followed when transparent products are targeted. The sol-gel method starts with molecular precursors and results in a nanoscaled metal oxide framework by hydrolysis and condensation reactions (*e.g.*, [10]). The final product is usually SiO_2 , for which various alkoxysilanes are used as precursors. The precursor may be dispersed in some of the polymerizing components, added to a solution containing the polymeric product, by silane functionalization of the related reactants, *etc.* Cho *et al.* [24] produced a nanoparticle-filled polyurethane from a tetraethoxysilane precursor. The mechanical properties (tensile strength, stiffness and elongation at break) were improved by the addition of tetraethoxysilane up to 10 wt%. Beyond this threshold, the stress and elongation at break values dropped while the stiffness remained unaffected. Cuney *et al.* [25] compared the properties of polyurethanes crosslinked either *via* a silica-rich disperse phase (sol-gel route) or by urethane chemistry. Note that the silane compound was introduced in the polymerizing mixture. The aim of these authors was to check whether, for the same soft component, the sol-gel or the polyurethane chemistry is more promising.

3.2. Solvent-assisted methods

3.2.1. Solution technique

In order to obtain polyurethanes with highly regular chains, the polymerization should be carried out in solution. Dimethylformamide (DMF), dimethylacetamide, dimethylsulfoxide, *etc.*, may serve as solvents. Tien and Wei [26] studied the effect of benzidine-modified montmorillonite (MMT) on the hydrogen bonding in the hard segments of TPU. The latter was produced in random one-shot synthesis in DMF. It was established that the H-bonding in the hard

segments was reduced owing to the presence of silicate layers. As a consequence, the morphology of the segmented polyurethane changed considerably. Note that this finding is in line with that of Petrović *et al.* [13]. The extent of the H-bond reduction depended on the amount of the organoclay and its dispersion stage. Chang and An [27] studied the effect of the organoclay intercalant on the TPU properties. The polyurethane was dissolved in dimethylacetamide. Hexadecylamine (primary amine) and quaternary amine compounds (dodecyltrimethyl and dimethyl-hydrogenated tallow-(2-ethylhexyl) ammonium salts; the latter is the intercalant of a commercial organoclay, *i.e.*, Cloisite® 25A of Southern Clay) were used as intercalants of the organoclay. According to XRD spectra and TEM pictures, intercalated structures were found in the nanocomposites containing up to 6 wt% organoclay. The tensile characteristics (strength, modulus, ultimate strain) passed through a maximum depending on the organoclay loading. The maximum was located in the range of 2 to 4 wt%. The best mechanical performance was achieved with a commercial organoclay (Cloisite® 25A of Southern Clay). This is the right place to mention that solution intercalation is often practiced in laboratories. Researchers believe that the best dispersion achievable by this way can be considered as a benchmark for melt intercalation. Han *et al.* [28] investigated the effect of MMT cointercalation in polyurethane nanocomposites. MMT was modified by cetyltrimethylammonium bromide and/or aminoundecanoic acid. The related nanocomposites were produced by solution intercalation of a TPU synthesized by bulk polymerization. The tensile strength, modulus, elongation at break, and tear strength of the plain polyurethane were 10.6 MPa, 5.1 MPa, 1090%, and 2.8 MPa, respectively. In the presence of 5 wt% organoclays of various modifications, these values changed to 13.9–15 MPa, 7–7.1 MPa, 1470–1630%, and 3.6–3.9 MPa, respectively. XRD and TEM results corroborated the onset of an intercalated clay structure. The water absorption was reduced and the thermooxidative resistance improved with the incorporation of the organoclay.

Choi *et al.* [29] showed an elegant way to use the polyurethane prepolymer (termed by the authors “organifier”) as clay intercalant. Further, to get a better organoclay dispersion, sonication was used. Owing to the clay intercalation with the organifier, the initial intergallery distance was enhanced from 1.18 (Na-MMT) to 2.29 nm. In the corresponding nanocomposites containing up to 5 wt% organoclay, a further small gallery expansion was noticed (*up to ca.* 2.6 nm). Due to the presence of the organoclay, the oxygen permeability was reduced by *ca.* 30% and the resistance to thermal degradation improved. It is worth noting that the gas permeation depends not only on the clay content and its dispersion, but also on the matrix morphology [30]. A strong enhancement in mechanical properties was reported [29]. The tensile strength and modulus of the nanocomposites scattered between 27.2 and 43.2 MPa and the Young’s modulus between 7.2 and 11.4 MPa. This corresponds to a pronounced property upgrade, as the unfilled matrix had a tensile strength of 14.7 MPa and a modulus of 6.5 MPa. The scatter in the above values is due to the organoclay

content (1 to 5 wt%) and sonication time of the solution (0 and 60 min, respectively).

Wang *et al.* [31] used the solution intercalation of an organoclay to get peculiar optical properties. In this case, the clay (saponite) was intercalated with a suitable compound bearing chromophore moieties. Ni *et al.* [32] tried to use an amine-functionalized attapulgite as chain extender (instead of a diamine) in the polymerization reaction. The best mechanical performance was achieved by dispersing 2–5 wt% organophilic attapulgite in the polyurethane.

3.2.2. Latex technique

Organic solvents cause several problems (toxicity, flammability, disposal, recovery, etc.) and for this reason there is a growing tendency to their elimination. A promising way in this direction is to disperse the polymer in an aqueous medium. Polymeric products, including TPUs, can be emulsified and thus brought in a latex form in many cases. There is a further benefit with this strategy: pristine clays and layered silicates, especially those in sodium forms, can be well dispersed in water. Water acts as a swelling agent *via* hydration of the intergallery Na^+ ions. Note that pristine layered silicates (LS) cost markedly less than the organophilic versions. Needless to say that latex intercalation is extensively practiced with rubber latices [12,33,34]. Varghese *et al.* [33,34] produced thermoplastic poly(ester-urethane) nanocomposites by blending the related latex with 10 wt% LS. Similar to solution intercalation, the test films were produced by casting. Figure 2 shows the XRD spectra of the pristine LS along with that of the polyurethane nanocomposite film.

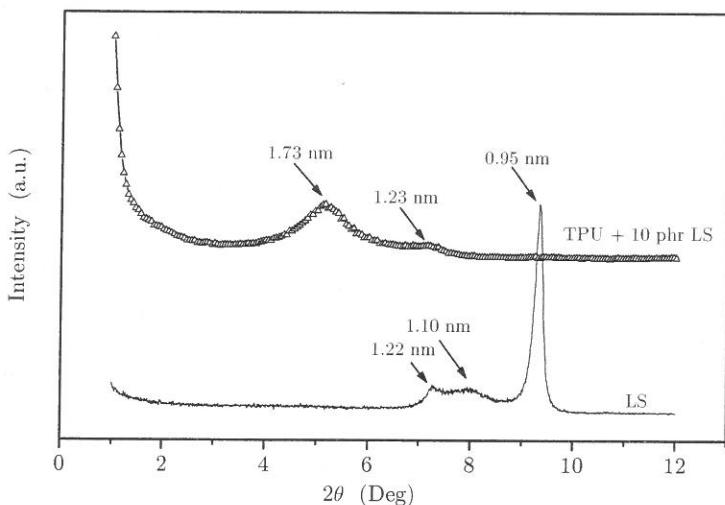


Figure 2. XRD spectra of the pristine layered silicate (LS; Na-fluorohectorite) and cast TPU nanocomposite containing 10 parts per hundred resin (phr) LS

The major peak of the nanocomposite indicates that the intergallery distance expanded up to 1.73 nm from the initial 0.95 nm. This good intercalation was also proved by transmission electron microscopy (TEM) (Figure 3).

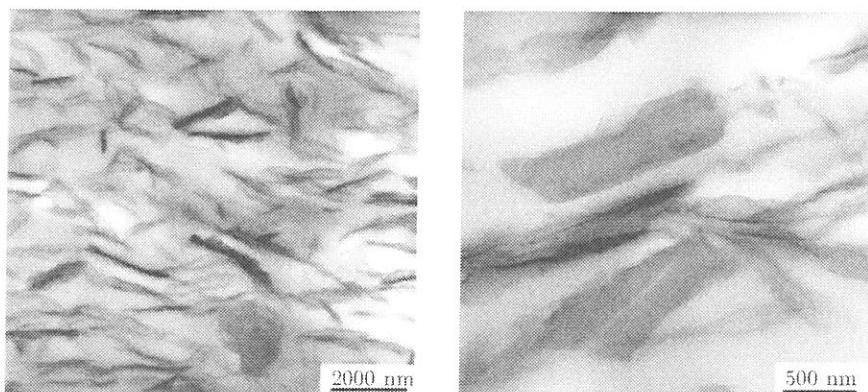


Figure 3. TEM pictures at various magnifications taken from a latex-cast TPU nanocomposite containing 10 phr LS

Figure 3 shows that a part of this synthetic layered silicate (Na-fluorohectorite) is even exfoliated. One can also see in these TEM pictures the very high aspect ratio of this synthetic LS (clay layers displaced from the view plane). The dynamic-mechanical thermal analysis (DMTA) spectra in Figure 4 display how

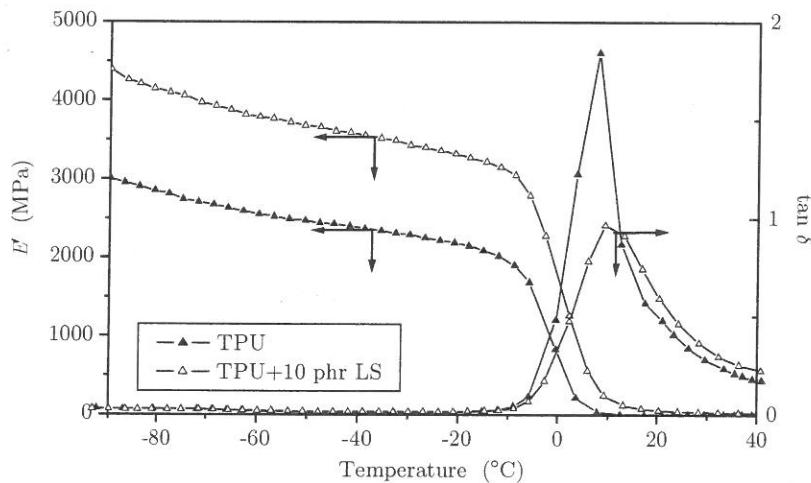


Figure 4. Storage modulus, E' , and mechanical loss factor, $\tan \delta$, as a function of temperature, T , for a latex-cast TPU with and without 10 phr LS

markedly the stiffness below the T_g of TPU was enhanced by the LS incorporation. This, along with the strong reduction in the intensity of the T_g peak in the $\tan\delta - T$ trace, are clear indications of the nanoreinforcement. The reduction in the T_g relaxation is due to the strong interaction between the polymer molecules and the clay layers. This kind of "bonding" reduces the segment mobility of the molecular chains, resulting in a reduction of the T_g peak intensity. The mechanical properties (before and after thermal aging) of the neat and nanoreinforced thermoplastic polyurethane are summarized in Table 1.

Table 1. Tensile mechanical properties of latex-casted TPU films with and without 10 phr LS (Na-fluorohectorite)

Property	TPU		TPU+LS (10 phr)	
	As cast	Aged (70°C, 7 days)	As cast	Aged (70°C, 7 days)
Tensile strength (MPa)	4.0	10.5	15.9	17.9
Tensile modulus (MPa) at:				
100% elongation	0.8	1.1	5.6	7.6
200% elongation	0.9	1.4	7.8	10.7
300% elongation	1.1	1.8	10.1	13.5
Elongation at break (%)	932	772	543	444

3.3. Melt compounding

Melt compounding is a very attractive way to produce commercial nanocomposites. Major arguments for this claim are the available industrial compounding facilities and the environmentally friendly preparation. Albeit the intercalation/exfoliation phenomena during melt compounding obey also the thermodynamic and kinetic rules, there is a further parameter which strongly affects the clay dispersion in nanocomposites. This is linked to the locally emerging shear and elongational flow fields. Extensive shear and elongational stresses peel apart the silicate layers, as shown in several works (*e.g.* [2,6,35]). It should be born in mind, however, that the thermal stability of the usual organoclays is limited. Results obtained by melt compounding did not meet the expectations at all. The author's group studied the effect of commercial organoclays intercalated with primary (octadecylamine modified montmorillonite, Nanomer® L30P of Nanocor) and quaternary amine compounds (intercalant methyl-tallow-bis(2-hydroxyethyl) ammonium salt, Cloisite® 30B of Southern Clay) on the mechanical performance of TPUs of various hardness values. The poly(ether-*b*-urethane) (PEBU) and poly(ester-*b*-urethane) involved in this extrusion compounding exhibited Shore A80 and Shore D65 hardness values. Albeit the XRD spectra suggested intercalation with Nanomer® L30P and exfoliation with Cloisite® 30B in PEPU (Figure 5), only slight improvements in the mechanical

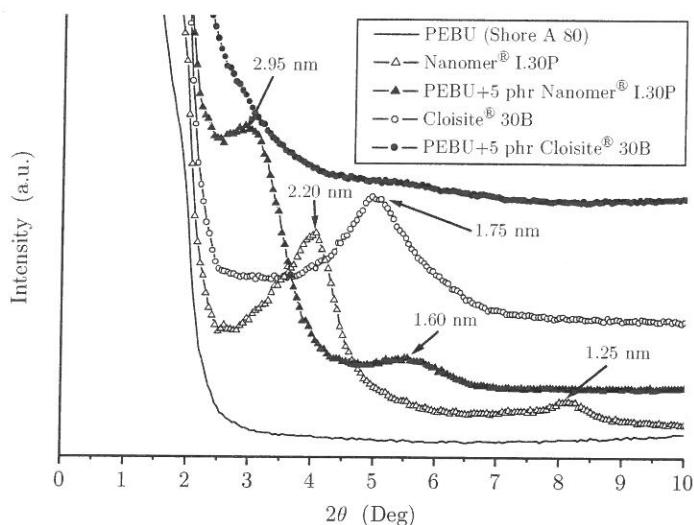


Figure 5. XRD spectra taken from the organoclay powders in reflexion and from the melt-compounded PEBU nanocomposites containing 5 phr organoclay in transmission mode

performance were achieved. The possible exfoliation with Cloisite[®] 30B was due to its hydroxyl functional intercalant. The effect of the organoclay was, however, far more prominent for the low-hardness polyether-based TPU than for the high-hardness polyester version. For the latter TPU, practically no improvement in the mechanical performance was found. On the contrary, the DMTA traces of the nanocomposites with a PEBU matrix showed some stiffness enhancement, however, mostly above the T_g (Figure 6) [36]. Recall that an efficient nanoreinforcement should yield a considerable stiffness increase also below the T_g of the matrix (as shown in Figure 4).

Reasons for this moderate (if any) property improvement are discussed in the exhaustive work of Finnigan *et al.* [37]. The authors produced TPU/organoclay (Cloisite[®] 30 B) nanocomposites by melt blending (twin-screw extrusion) and solution intercalation. Note that not only the extrusion compounding, but also the selected commercial organoclay were similar to those in our work [36]. A further analogy with our earlier work was the broad hardness range of the polyether-type TPU selected (Shore 80 A and 55 D). The published results, namely that the tensile strength and elongation values were not improved in contrast to the Young's modulus, also agree with ours [36]. The most interesting result of Finnigan *et al.* [37] was that the mean molecular mass of the TPU significantly decreased upon both solvent (during which sonication was used) and melt intercalation. This was attributed to effects of the sonication (solution method) and thermal/thermooxidative degradation (melt compounding), respectively. DMTA, differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS) measurements revealed a strong alteration in the

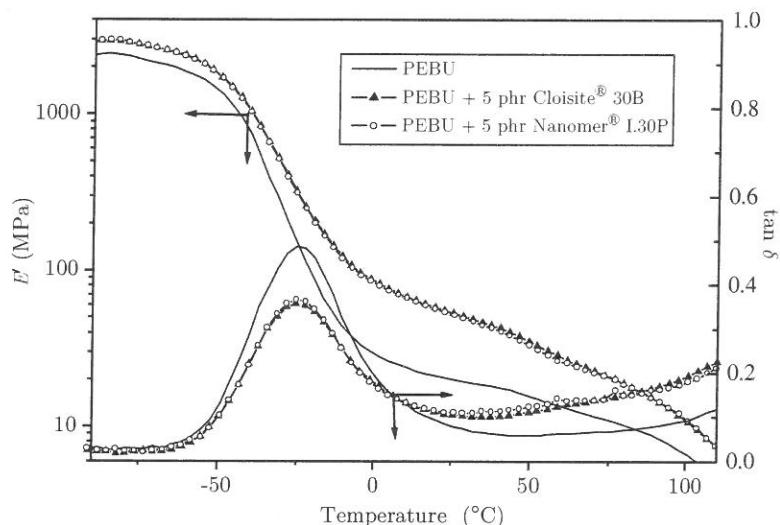


Figure 6. Storage modulus, E' , and mechanical loss factor, $\tan \delta$, as a function of temperature, T , for a melt-compounded poly(ether-*b*-urethane) (PEBU, Shore A 80) with and without 5 phr organoclay; the organoclays contained primary amine (Nanomer® I30P) or hydroxyl functionalized quaternary ammonium intercalants (Cloisite® 30B)

microphase morphology. These findings are consistent with results reported earlier [13]. Ma *et al.* [38] used an organophilic modified rectorite for the melt compounding with a poly(ester-*b*-urethane). For the organophilization of the rectorite, two different quaternary ammonium salts and benzidine were used. According to the authors, the clay was intercalated up to a loading of 5 wt%, while beyond this threshold, clay agglomeration took place. The mechanical properties were improved by clay intercalation and decreased by the onset of agglomeration. Interestingly, the tear strength was less sensitive to the clay dispersion than the tensile properties. Eckel *et al.* [39] emphasized in their work, which covered organoclay-reinforced TPU as well, that the clay dispersion can hardly be characterized adequately solely by XRD. According to the cited authors, the right tool for that is TEM. This claim seems to be of great relevance and is in conflict with the usual belief that XRD traces are good enough to distinguish between intercalated and exfoliated layered silicates (nanocomposites based on TPU are considered also in Chapter 14).

4. Nanoreinforcement of “condensation” thermoplastic elastomers

The author was not able to find reports in the open literature dealing with nanocomposites having poly(ether-*b*-amide) (PEBA) and poly(ether-*b*-ester) (PEE) matrices. This is very surprising owing to several reasons. First, polyamides are those polymers where the nanoreinforcement concept really works, irrespective of whether *in situ* polymerization or melt compounding

techniques are adopted. It is worth noting that the pioneering work at Toyota Central Research Labs was performed also on polyamides (PAs), mostly on PA6 ([1,2,6,40] and references therein). Later, numerous studies were published on organoclay-reinforced PA12 [1,2,6,41,42]. Note that PA12 is the usual crystalline segment in PEBA grades. Second, similar to PAs, thermoplastic polyester-based nanocomposites were successfully produced *via* various intercalation techniques [1,2,6]. This holds also for poly(butylene terephthalate) (PBT) (*e.g.*, [43,44]) which is the usual crystalline block in PEE. Third, numerous reports are available dealing with systems composed of organoclays and polymers with oxyethylene (or similar units) chains (*e.g.*, [45,46]). In addition, poly(ethylene oxide) is a favored polymer for nanoreinforcement *via* the sol-gel route [47]. Note that polyalkyleneoxides form usually the soft segments in the thermoplastic elastomers produced by polycondensation reactions. Thus, there are no arguments against the clay intercalation/exfoliation with such segmented block copolymers. The possible reason behind this lack of interest is the very versatile synthesis of these elastomers *via* which their properties can be tailored in a wide range.

5. Outlook and future trends

As predicted above, the potential of the nanoreinforcement (including carbon nanotubes) will be checked in condensation thermoplastic elastomers in the very near future. A possible driving force in this respect may be linked to coloration issues, since the organoclay would be a suitable carrier for several organic colorants (*e.g.*, disazo compounds). In this way, migration and bleed problems could be avoided. Attempts will also be made to use new types of nanofillers, such as acid-activated Ca-bentonite, anion-exchanged hydrotalcites, boehmites, layered graphites, *etc.* Owing to cost reduction, the sol-gel methods will require cheaper precursors than the presently used organosilane and organotitanate compounds. Nevertheless, the strong competition in respect to property modification between synthesis and nanoreinforcement will remain.

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