

Study of Structure and Properties of Thermoplastic Polyurethanes

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Abstract. In the investigation on the effect of clay nano-composite on the structure and properties of thermoplastic polyurethanes (TPUs), the mechanical properties of TPUs had maximum values with 8 wt % clay content. The wide angle X-ray diffraction patterns showed that the glycerol propoxylate had better compatibility with the organoclay than poly(propylene glycol).

Keywords: polyurethanes, thermoplastic polyurethanes, elastomers, clay nanocomposite, glycerol propoxylate

Introduction

Urethanes were the first major elastomers that could be processed by thermoplastic methods. Thermoplastic polyurethanes (TPUs) are derived from three basic compounds: long chain polyester or polyether diols, aromatic or aliphatic diisocyanate, and short-chain diol as chain extender, which in most cases is butanediol. They are characterized by a segmented structure consisting of flexible segments, the polyester or polyether chains, and hard segments, the urethane groups. The hard segments are formed by the addition of a chain extender to the diisocyanate, and the soft segments interconnects two hard segments. At temperatures lower than the order-disorder transition temperature (TODT), the low melting soft segments are incompatible with the polar and high-melting hard segments, which leads to a phase-separated microstructure (Tien and Wei, 2001a).

TPUs come in a wide range of hardness grades. Among elastomers, urethanes have outstanding abrasion resistance, good low temperature flexibility, excellent oil resistance and rank among the best for load-bearing capability. Additives can improve dimensional stability and heat resistance, reduce friction and increase flame retardancy, fungus resistance and weatherability. The polyether types have better hydrolytic stability and low-temperature flexibility than the polyester types. However, mechanical properties of the polyester types are generally higher. The caprolactones offer a good compromise between the ether and ester types.

The morphology of PU determines its mechanical, thermal, and water absorption properties (Garrett *et al.*, 2000; Mark *et al.*, 1988; Miller, 1985; Wang and Cooper, 1983).

The physical properties of thermoplastic PUs are derived from their molecular structure as well as the supramolecular structure formed by interaction between the polymer chains. The

segmental flexibility, the chain entanglement, the interchain forces, and the crosslinking are all factors that influence the properties and determine the use of the end products. With well designed combinations of monomeric materials, PUs can be tailored to meet diversified demands of various applications such as coatings, adhesives, fibers, thermoplastic elastomers and foams (Shokuhi and Ardjmand, 2008a). Hence, they have received wide attention in terms of their synthesis, morphology, chemical, and mechanical properties (Penczek *et al.*, 1993; Szczepaniak *et al.*, 1993). Increasing the strength of PU elastomers without sacrificing its large elongation at break is an important object for elastomeric PU development. The mechanical properties of PU can be modified either by varying PU chemical structure, resulting from step growth polymerization of isocyanate resins with polyols or by dispersing inorganic or organic fillers into the pure PU.

Materials and Methods

Poly(propylene glycol) (PPG1, *Mn* 51000, and PPG2, *Mn* 52000), made by Bayer Chemical Co. Germany under the name of Desmophen, poly- and di-isocyanate (based on TDI and HDI and MDI); made by Bayer Chemical Co. Germany under the name of Desmodur, glycerol propoxylate (GPO3, *Mn* ≈ 3000, made by Dow Chemical Co.), Na-montmorillonite clay (the cation exchange capacity, CEC 5 90-100 mmol/100 g, with a particle size of about 40-70 nm, made by Zhangjiakou Qinghe Chemical Factory), sodium montmorillonite clay (Na-O-MMT), with cation exchange capacity (CEC) of 119 mEq/100 g, was supplied by Coniine Industry Co. (Japan) under trade name Kunipia-F. Styrene was supplied by Aldrich and used after purification by washing with 1M NaOH then drying over anhydrous sodium sulphate followed by distillation under vacuum. Maleic anhydride and ethylene glycol and 1,4-butanediol (from Merck-Schuchardt, Germany); 12-amino-dodecanoic acid, from Aldrich; tetrahydrofuran (THF) (from

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Fluka) and ethanol (from Adwic, Egypt) were used, as obtained without further purification.

In brief, NCO-terminated polymers of MDI and PEG or PPG were prepared in the absence of any catalyst and with various NCO:OH equivalent weight ratios. The reaction process was followed by the removal of absorbed water by azeotropic mixture with toluene and then the water free PEG and TMP mixture was added to the kettle at 60-70 °C and the reaction continued at 70-80 °C for 6 h in N₂ environment. To remove the oligomeric part and the moisture reacted part, MDI was heated and filtered by a cloth before use. The synthesized isocyanate-terminated polymers were reserved in plastic bottles. A part of the polymer was taken in Teflon disc and kept in an oven at 80 °C for 6 h, and then the obtained polymer film was kept at room temperature and humidity for long until complete disappearance of NCO band in FTIR spectrum was observed.

FTIR instrumentation. For the FTIR study, a small and diluted drop of liquid polymers as well as nanocomposites (typically a 1 wt % solution in ethyl acetate) were prepared and coated on KBr disks and stored at room temperature and humidity for a day, before spectral evaluation. To remove the residual solvent, the disks were placed in a vacuum oven at 80 °C for 6 h. The thickness of sample was controlled and kept at the same uniform size. Fourier transform IR spectra (FTIR) were obtained using a Thermo Nicolet Nexus 670 spectrometer. A minimum of 32 scans was signal-averaged with a resolution of 2/cm within the wavelength range of 400-4000/cm.

Synthesis of TPU/clay nanocomposites. The hard segment of the TPU was formed from 4,4 methylenebis (phenylisocyanate) (MDI) and 1,4-butanediol (BD). The soft segment was formed from PTMG. MDI and PTMG were dried in a vacuum oven before use, and BD was stored on 4-A molecular sieve. Both unmodified MMT (Na-MMT) and O-MMT were used after heating at 130 °C for 24 h to remove molecular water in the galleries. The TPU/clay nanocomposites were prepared by an *in situ* polymerization method; the molar ratio of MDI/BD/PTMG was 4 : 3 : 1 and was denoted as MBP431. The nanocomposites were synthesized by a two-step reaction. In the first step, PTMG was reacted with an excess of MDI at 85 °C for 2 h to form a prepolymer end, capped with isocyanate groups. In the second step, clay dispersed in freshly distilled dimethyl acetamide was added to the prepolymer at room temperature; then, the chain extender (BD) mixed with dibutyltindilaurate was added. The chain extension reaction was carried out at 85 °C for 2 h.

Results and Discussion

Improvement in TPUs properties. Montmorillonite clays include all clay minerals with an expanding structure, except

vermiculite, and also the high alumina end member of the group. Members of the montmorillonite group of clay minerals vary greatly in the mode of formation. Alkaline conditions and the presence of magnesium particularly favour the formation of these minerals which occur in various modes in the soils, bentonites, mineral veins, marine shales, and as alteration products of other minerals. Recently formed sediments have a fairly high content of montmorillonite.

TPUs have some disadvantages, such as low thermal stability and low mechanical strength, etc., (Table 1). To overcome these disadvantages, a great deal of effort has been devoted to the development of nanostructured PU (PU)/montmorillonite (MMT) composites in recent years (Tien and Wei, 2001b; Chen *et al.*, 2000).

A wide variety of fillers, including talc, mica, and wollastonite, have been applied in TPU formulation to reduce cost and to increase the rigidity (Varma *et al.*, 1985). However, addition of filler frequently results in reduction in the elongation at break. In recent years, polymer/clay have attracted great attention both in industry and academia, after the Toyota group developed clay/nylon 6 nanocomposites with excellent mechanical properties (Solarski *et al.*, 2005), creating interest in the use of clay as a reinforcement material for polymers (Rhoney *et al.*, 2004). These composites exhibit remarkable improvement over the conventional microcomposites in various properties such as mechanical strength, heat resistance, gas permeability and flammability.

Table 1. Some advantages and limitation of TPUs in all forms

Advantages	Limitations
Excellent abrasion resistance, wear resistance, and tear strength	Narrow hardness range compared to other TPEs
High tensile strength	Low upper service temperature limit
High dynamic load-bearing capacity	Susceptible to hydrolytic attack by acid and base solutions and by pure water at elevated temperatures
Low coefficient of friction	Limited resistance to halogenated solvents
Good U V, weathering oxygen, and fungus resistance	Can be "tricky" to process; TPUs are more sensitive to temperature and shear than other TPEs
Good resistance to non-polar fluids	Must be dried before processing

TPU clay/nanocomposites. Thermoplastic and thermosetting nanocomposites were reported to exhibit unusual properties such as improved stiffness/strength/toughness balance, improved heat distortion temperature, strong barrier properties, and flame retardancy (Ma *et al.*, 2001; Pinnavaia and Beall, 2000). Since the development of the nylon/MMT nanocomposite (Usuki *et al.*, 1989), a large number of new polymer nanocomposites have been investigated (Shokuhi Rad and Ardjmand, 2008a; Biasci *et al.*, 1994). Most of the polymer/clay nanocomposites were based upon glassy polymers with high glass-transition temperatures, such as PMMA, PS, SAN and epoxy, and studies of rubbery polymers have rarely been reported.

Pinnavaia and Beall (2000) focussed on compatibility between organoclay and polyols. They found that the montmorillonite clay, exchanged with long chain onium ions (carbon number ≥ 12), had a good compatibility with several polyols commonly used for synthesizing PU.

Tien and Wei (2001b) reported preparation of completely exfoliated PU/clay nanocomposites by *in situ* polymerization using 12-aminolauric acid and benzidine. Pattanayak and Jana (2005) reported that exfoliated nanocomposites of TPUs can be prepared by some unique method resulting in remarkable increase in tensile strength and modulus along with optical clarity when compared with pure PUs.

Zilg *et al.* (1999) reported that TPU nanocomposites containing synthetic fluoromica could simultaneously increase their tensile strength and elongation at break. Chen *et al.* (2000) synthesized a novel segmental PU/clay nanocomposite via poly (ϵ -caprolactone)/clay (PCL/clay) route. They reported that the mechanical properties were enhanced by introducing a small amount of PCL/clay in the composite.

However, the composite was transformed from an elastomer to a plastic as the amount of PCL/clay in the composite was increased (Jang *et al.*, 2005).

The effect of used clay. The effects of clay type, clay content, and PU molecular structure on clay dispersion in thermoplastic PU nanocomposites were studied by Cao *et al.* (2005). It was found that MMT clays exchanged with long chain onium ions (carbon number > 12), had good compatibility with polyol. The extent of gallery expansion of modified MMT is mainly determined by the chain length of the gallery onium ions (Wang and Pinnavaia, 1998). A good dispersion of layered silicate has been found to improve the properties of PU elastomer nanocomposites, such as mechanical properties, thermal stability and gas permeability (Chen *et al.*, 2000). Good dispersion of clays in the PU matrix has been achieved through the modification of MMT with active surfactants containing

more than two hydroxyl groups (Tien and Wei, 2001a). The presence of hydroxyl groups enhanced intragallery polymerization, which in turn led to better clay dispersion. However, the morphology of nanocomposites prepared by this approach was still a combination of exfoliation/intercalation and the method only worked at low clay content, i.e., less than 3 wt %, even for organoclay modified by surfactants with three hydroxyl groups. The exfoliated clay dispersion was only observed at low reaction rates in solution polymerization (Tien and Wei, 2001b). PU foams account for the largest market among polymeric foams, estimated at nearly two billion kilograms in the US alone (Khemani, 1997). PU foams have a remarkably broad range of applications including thermal insulation, cushioning, buoyancy, energy absorption (packaging), etc. Their low density also permits the design of light and stiff components such as aircraft-interior panels, structural shapes (transom cores, bulkhead core, stringers, motor-mounts, etc.), in fibre-reinforced plastic (FRP) for boat building, impact-limiters and crash-pads, composite foam cores, mold-patterns and plugs, sports-equipment core material and composite tooling. Mechanical properties are important considerations for such structural and semi-structural applications. Unlike thermoplastic foams, PU foams are formed by reactive processing, in which polymerization and foam blowing occur simultaneously. Polymer structure must build up rapidly to support the fragile foam, but not too fast to stop bubble growth. For thermoplastic foams, it was found that clay-filled nanocomposites could effectively reduce the cell size and increase the cell density (Han *et al.*, 2003). An exfoliated PS nanocomposite produced a foam with a cell size five times smaller than that of the pure PS foam. Several advantages can be expected in using a PU nanocomposite as the matrix of PU foams. The presence of nanoparticles may improve the mechanical strength of the PU matrix and in turn the strength of the PU foam. Nanoscale-dispersed clay may act as nucleation agents during the foaming process to produce finer cell structure and higher cell density. Furthermore, improved gas barrier properties provide another opportunity for application of nanoclay in PU foams.

An alkylammonium modifying montmorillonite, a natural clay, was intercalated into the polyols to prepare the elastomeric PU/clay nanocomposite by Ma *et al.* (2001). Their research focussed on effects of the clay content and route of clay compounding with polyols on the mechanical properties of the nanocomposites. Various types of polyol with different molecular weights and functionalities were used for preparing PU and PU/clay nanocomposites.

In the present work the ratio of the polyols was kept constant to ensure the same chemical structure of the PU and PU/MMT

nanocomposites. It was found that the mechanical properties had maximum values with the clay content when it reached 8 wt %. The maximum tensile stress and the maximum elongation at break increased two and five times, respectively. The WAXD patterns showed that the glycerol propoxylate had better compatibility with the organoclay than poly(propylene glycol). This corresponded to the formation of a nanocomposite from the clay compounding with glycerol propoxylate that, in turn, resulted in the best mechanical properties. The molecular weight of poly(propylene glycol) seemed to have no obvious effect on the intercalative behavior as explained by WAXD results. However, the nanocomposites from the clay compounding with the low molecular weight polyol route showed better mechanical properties than that from the clay compounding with the high molecular weight polyol route. The synthesis procedures, shown in Fig. 1, were used to synthesize the PU/MMT1 and PU/MMT2 nanocomposites. The polyols of PPG1, PPG2 and GPO3 could be used in constant ratio to ensure that all the nanocomposite samples had the same chemical structure.

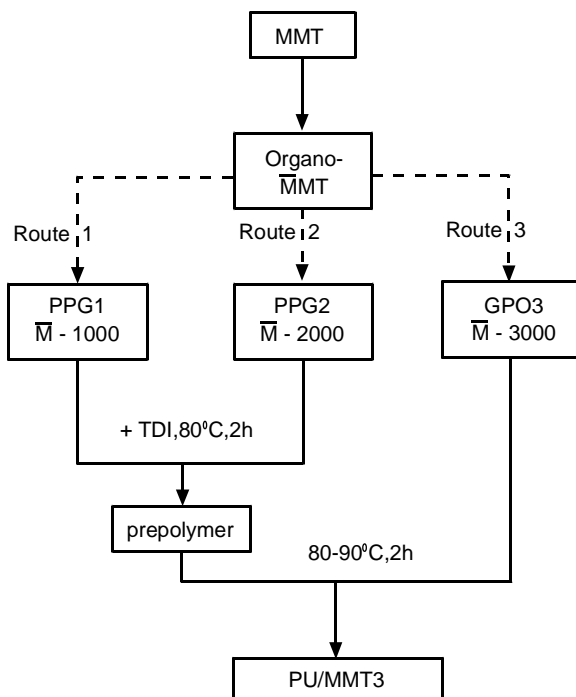


Fig. 1. A schematic diagram of clay compounding route for synthesis of PU/MMT nanocomposites.

The reactions that occurred during the TPU/clay nanocomposite syntheses by proposed method are shown in Fig. 2.

Effect of clay on the order-disorder transition of TPU. TPU is a segmented block copolymer having thermoplastic elasto-

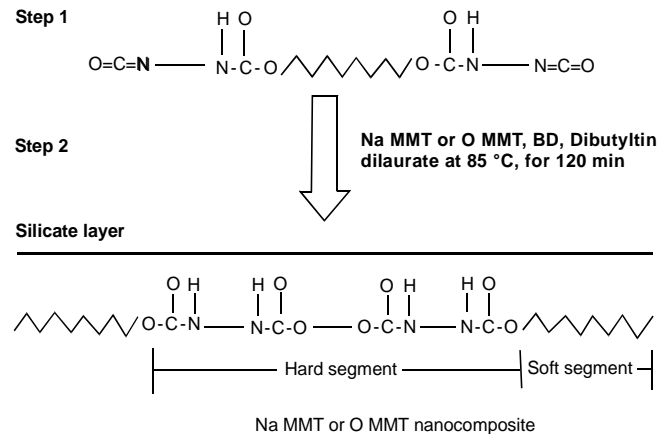


Fig. 2. Synthesis route for the TPU/layered silicate clay nanocomposites.

meric characteristics. The hard segments (formed by MDI) form domains that are dispersed in a continuous matrix of the soft, rubbery segments formed by PTMG segments.

Due to the dissolution of the hard domains in the soft matrix above order-disorder transition temperature (TODT), it was important to maintain the phase-separated structure during various TPU processing operations. On transformation from the homogeneous state to the phase-separated state, most hard segments aggregate and form hard domains in the soft matrix. Typically, PU is extensively hydrogen-bonded, with donor being the NH group of the urethane linkage and acceptor being the carbonyl group of the urethane linkage of the neighbouring polymer chains. Since the hard segments contain urethane groups, they can form hydrogen bonds with other hard segments inside the hard domain, and the formation of hydrogen bonding can be a strong driving force for phase separation. Therefore, one can monitor the extent of phase separation by following the change in the degree of hydrogen bonding. The order-disorder transition, sometimes called the microphase separation transition of the TPU and its nanocomposites with O-MMT were studied by FTIR and DSC methods. Fig. 3 and 4 show C=O stretching peak region in the FTIR spectra of pure TPU and TPU/clay nanocomposite.

Mechanical properties of TPU. The mechanical properties of pure TPU, TPU/Na-MMT nanocomposites, and TPU/O-MMT nanocomposites are displayed in Table 2 and the stress-strain curves are shown in Fig. 5.

The tensile strength and ultimate elongation values of TPU/clay nanocomposites decreased with the addition of Na-MMT or O-MMT. However, a significant improvement in the Young's modulus values was observed with increasing the levels of both Na-MMT and O-MMT. The same trend was observed

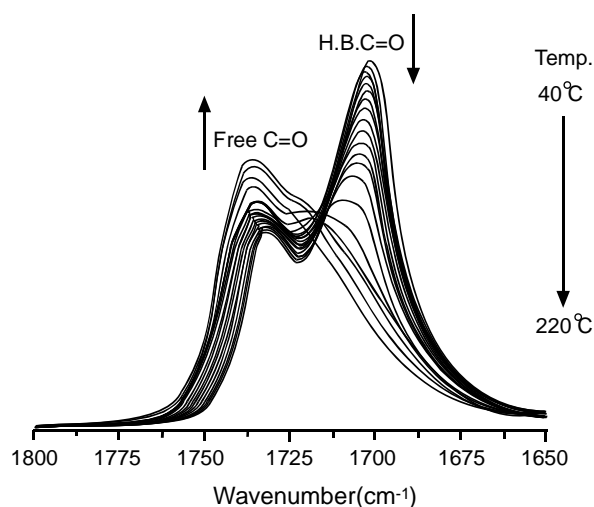


Fig. 3. (Top): FTIR spectra of the C=O stretching peak of the pure TPU at various temperatures; (Bottom): relative fractions of two carbonyl peaks plotted as a function of temperature along with the DSC thermogram (solid line).

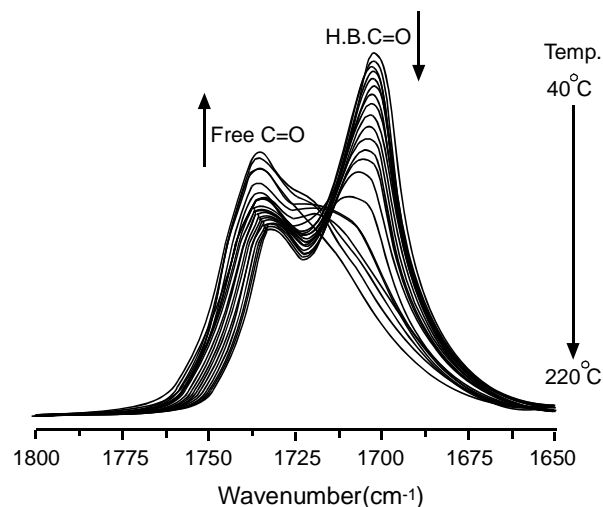


Fig. 4. (Top): FTIR spectra of the C=O stretching peak of the 1 wt % O-MMT/PU nanocomposite at various temperatures; (Bottom): relative fractions of two carbonyl peaks plotted as a function of temperature along with the DSC thermogram (solid line).

for TPU/layered silicate clay nanocomposites by Finnigan *et al.* (2004). Interestingly, O-MMT caused a larger reduction in the tensile and elongation properties than Na-MMT. Meanwhile, the enhancement of Young's modulus caused by O-MMT was higher than that caused by Na-MMT. This appeared to be due to enhanced interaction between TPU and O-MMT.

Effect of polyol molecular weight and functionality on intercalative behavior. In order to study the effect of molecular weight and functionality of the polyol on the intercalative behaviour of the nanocomposites, a constant amount of organo-MMT was intercalated with PPG1, PPG2 and GPO3, to obtain PU/MMT1, PU/MMT2 and PU/MMT3 nanocomposites, respectively.

Table 2. Mechanical properties of the TPU/Clay nanocomposites

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
MBP431(PU)	68.3	1420	24.1
1 wt % Na-MMT/PU	51.2	1180	24.4
3 wt % Na-MMT/PU	34.8	980	28.6
5 wt % Na-MMT/PU	37.1	998	49.1
1 wt % O-MMT/PU	28.6	990	26.2
3 wt % O-MMT/PU	27.9	660	46.3
5 wt % O-MMT/PU	31.0	575	53.3

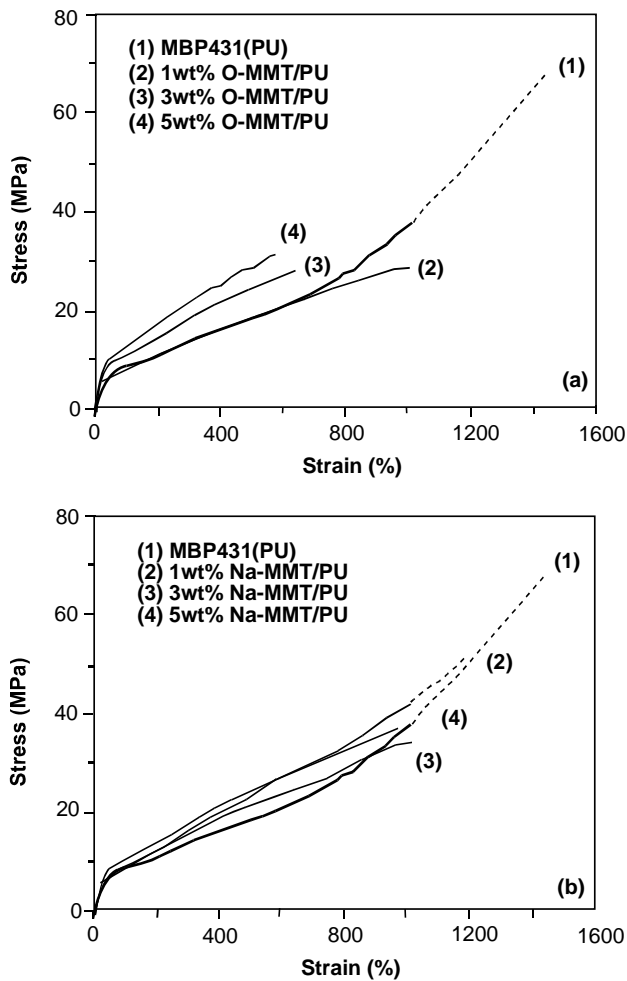


Fig. 5. Tensile stress-strain curves of TPU nanocomposites containing (a) O-MMT and (b) Na-MMT.

Fig. 6 shows that the WAXD patterns of the PU/MMT1 and PU/MMT2 nanocomposites are more complex than that of the PU/MMT3.

Besides the characteristic peaks at 4.6 and 4.0 nm, PU/MMT1 and PU/MMT2 have diffuse diffraction peaks at 2.2 and 1.9 nm, respectively, which is close to the diffraction peak of the organo-MMT (Fig. 7). These results suggest that the GPO3 has superior compatibility with organo-clay and is more easily intercalated into the clay layers than PPG1 and PPG2. From this observation, we expect that the PU/MMT3 nanocomposite would have the best mechanical properties. Since the WAXD patterns of PU/MMT1 and PU/MMT2 nanocomposites show no obvious differences, it appears that the molecular weight of the polyols had no effect on the intercalative behavior.

Effect of clay content on the mechanical of the study of the effect properties of the nanocomposites. The experimental results of the clay content on the tensile mechanical proper-

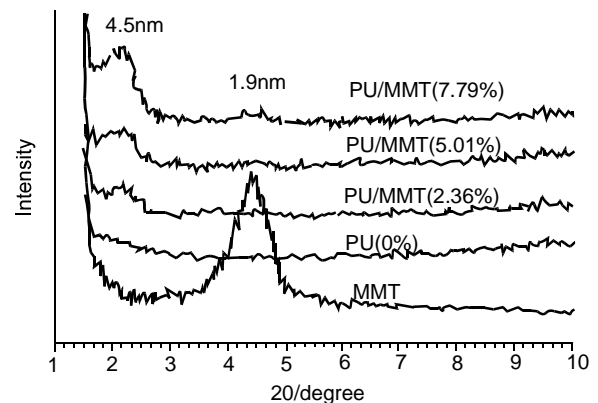


Fig. 6. Effect of polyol molecular weight and functionality on WAXD of PU/MMT nanocomposites with a constant clay content of 5 wt %.

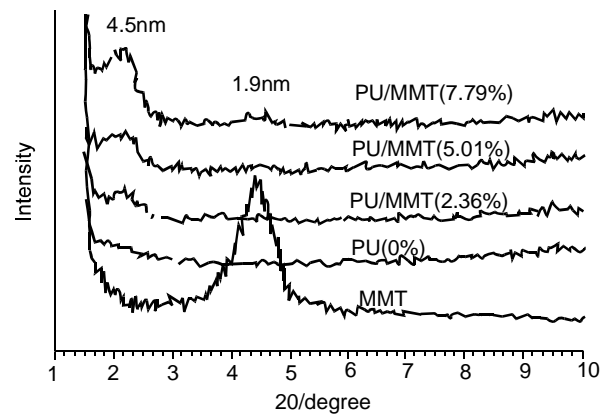
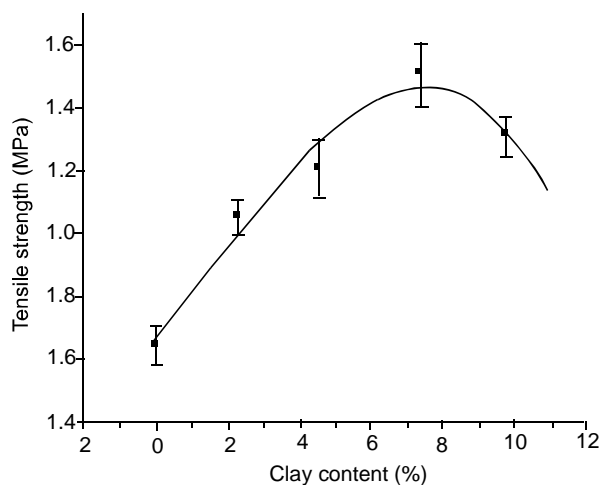


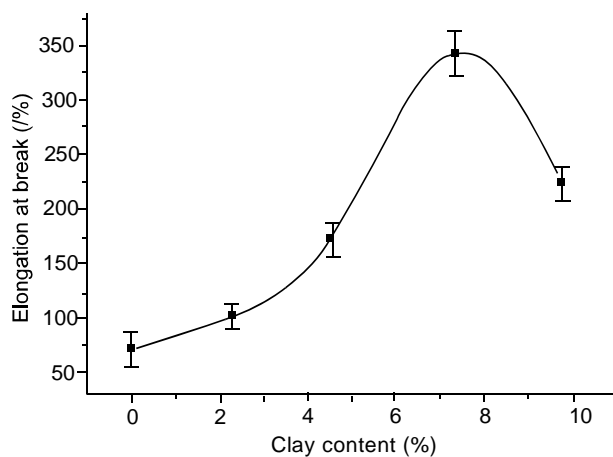
Fig. 7. Effect of clay content on WAXD of organo MMT, PU and PU/MMT3 nanocomposites.

ties of the nanocomposite are shown in Fig. 8. It was found that the clay content had a remarkably effect on the mechanical properties. Both the tensile strength and the elongation at break of the PU/MMT3 increased with increasing the clay content in the range of 0-8 wt %. The maximum values of the mechanical properties were reached when the clay content was 8 wt %. At higher clay content both the tensile strength and elongation at break of PU/ MMT3 decreased. These results could be explained in terms of the interaction between the pure PU and the nanometer clay layers. When the clay content was less than 8 wt %, the nanometer clay layers had a good compatibility and a strong interaction with the pure PU; when the clay content was higher than 8 wt %, the clay began to aggregate, as suggested by the WAXD.

Effect of intercalative way on the mechanical properties of the nanocomposites. The route of the clay compounding obviously affects the mechanical properties of the nanocomposites. As compared to the pure PU, the tensile strength of PU/MMT2 and PU/MMT1 nanocomposites increase by 25



(a)

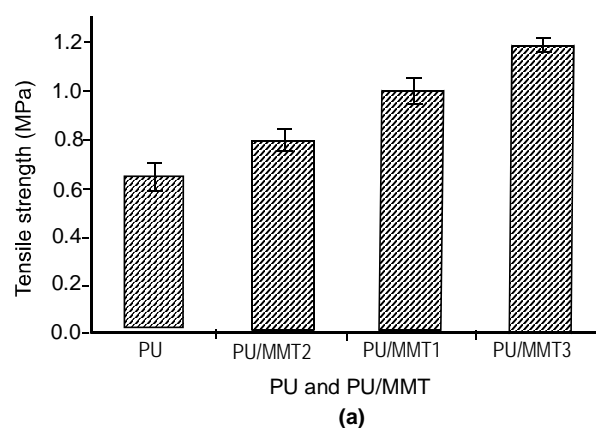


(b)

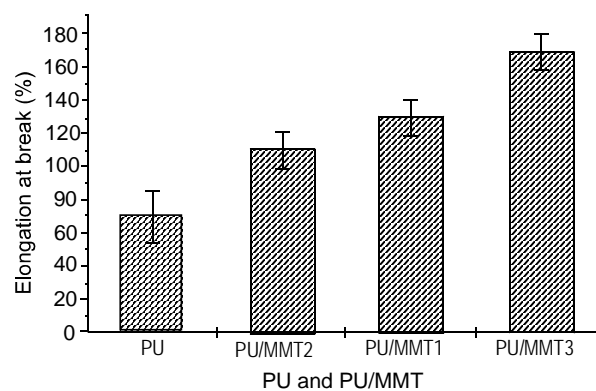
Fig. 8. Effect of the clay content on the tensile mechanical properties of PU/MMT3 nanocomposites.

and 55, respectively (Fig. 9a) and their elongation at break increase by 50 and 80% (Fig. 9b), respectively. The maximum tensile properties were found for the PU/MMT3 nanocomposite, where its tensile strength is about twice that of pure PU and its elongation at break is about 2.5 times that of pure PU. These results can be interpreted by the intercalative behavior of the polyols as shown in Fig. 3. There was a correlation between the mechanical properties (Fig. 9) and the WAXD results of the nanocomposites (Fig. 6). As the characteristic diffraction peak shifted to a smaller angle, the mechanical properties were found to increase in the nanocomposites.

Degradation of TPUs. It is known that TPUs undergo significant structural changes on weather exposure, which have been found to depend on the structure and the morphology of TPUs (Wypych, 1995). These changes lead to a deterioration in



(a)



(b)

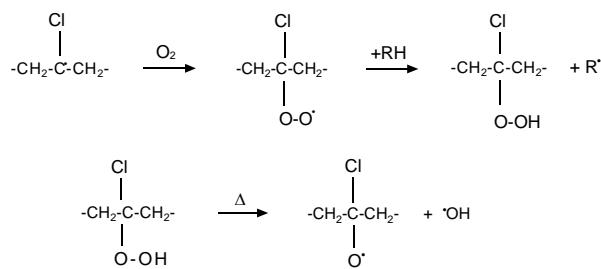
Fig. 9. Effect of clay compounding route on mechanical properties of PU/MMT nanocomposites with a constant clay content of 5 wt %.

physical and mechanical properties; the most published studies have dealt with the processes responsible for degradation and ultimate failure (Hoyle and Kim, 1986).

Proposition for the formation of degradation layer. No reticulation mechanism was found in the literature about the degradation layer; however, by analogy with other polymers, the following schemes could be proposed. The photooxidation of poly(vinyl chloride) (PVC) leads to a radical, $-\text{CH}_2\dot{\text{C}}\text{C}_1\text{CH}_2-$, which reacts according to the mechanism as presented in Fig. 10. The alkoxy radical induces the formation of reticulation points. By analogy with PVC, it could be possible to propose the mechanism in Fig. 10 for TPU. The last radical would cause the reticulation points of the degradation layer.

The polyether photooxidation leads to the formation of an alkoxy radical (Fig. 11), which could eventually induce reticulation points in TPU because the flexible segments of TPU are based on polyether. In polyamides free radicals $\text{R}\cdot$, derived from degradation, involve the abstraction of hydro-

For PVC



For TPU

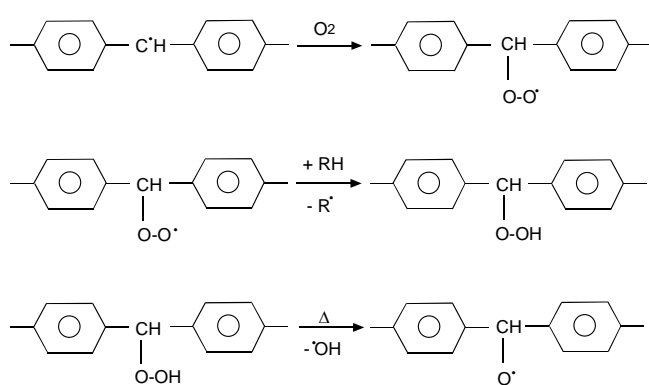


Fig. 10. Reticulation mechanism of PVC [97] and possible reticulation mechanism of TPU.

For polyethers

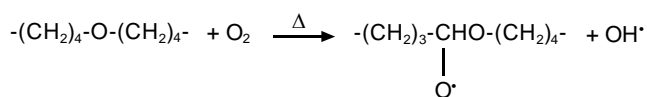
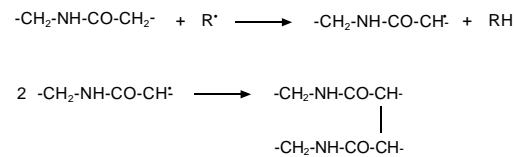


Fig. 11. Reticulation mechanism of polyethers [97].

gen in the α -position from the amide bound, and leads to the formation of reticulation points (Fig. 12). By analogy with polyamides, it could be possible to consider the hydrogen abstraction in the α -position from the urethane group. It would induce the reticulation mechanism given in Fig. 12.

Proposition for the development and stabilization of the degradation layer. *Directly initiated by UV with just sufficient intensity.* Ultraviolet radiation, which goes through the already formed layer, follows the Beer Lambert absorption law i.e. the UV intensity decreases when the layer thickness increases. Consequently, UV could reach a boundary that would be the “nondegraded coating/degradation layer” interface where the UV intensity would be sufficient to cause degradation.

For polyamides



For TPU

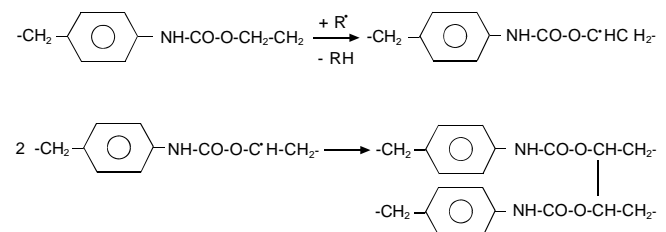


Fig. 12. Reticulation mechanism of polyamides [97] and possible reticulation mechanism of TPU.

By the propagation of radical intermediate species initiated by stronger UV in the layers close to the exposed surface. Initiation of intermediate species on surface and their propagation by reactions in the degradation layer thickness follows a radical mechanism. By means of termination reactions, the concentration decreases when the layer thickness increases. The radical species could thus propagate themselves up to a “nondegraded coating/degradation layer” boundary where the concentration is still sufficient to activate the layer formation. With these processes, the more the layer thickness increases, the more the layer formation rate decreases. The layer thickness is going to increase progressively up to a certain limit. This limit corresponds to the equality of the formation rate of the layer by the nondegraded part and of the degradation rate of the layer by the outside part. Thus a dynamic process is set up, involving a constant thickness of the degradation layer.

Thermoplastic PU coatings. TPU has been in use as a fabric coating material in the textile industry for over 30 years. The first application of TPUs was as a replacement for PVC where the “look and feel” of PVC was of value but the performance of PVC was lacking in areas such as flex properties, plasticizer migration, abrasion resistance, low temperature properties and cleanability.

Thermoplastic PU may be described as the linear structural block copolymer of $(\text{SH})_n$ type, where S is soft and H is hard segment (HS). Due to the wide variety of properties between S and H segment, phase separation may be observed in the final material. Phase separation occurs due to the intrinsic incompatibility or thermodynamic immiscibility between the hard

segments (HSs) and soft segments (SSs). The HSs, composed of polar materials, can form carbonyl to amino hydrogen bonds and thus tend to cluster or aggregate into ordered hard domains, whereas SSs form amorphous domains. The HS acts as filler particle as well as crosslinker to restrain the motion of SS chains. Such a structure was first proposed by Cooper and Tobolsky (1966). Their work and that of Schollenberger (1959), established that segmented PUs consist of high glass transition temperature (T_g) or high melting temperature (T_m) HS microphase separated from relatively low T_g SS. The degree to which the hard and SSs phase separate, plays a vital role in determining the solid-state properties of these multi-block coatings. Properties of thermoplastic PU coatings depend upon several factors such as the composition of soft and HSs, lengths of soft and HSs and the sequence of length distribution, chemical nature of the units composing the polymer, anomalous linkages (branching, crosslinking), molecular weight and the morphology in the solid state. At room temperature, soft macroglycol segments are above their T_g and have easy segmental rotations, which therefore impart the material its rubber-like behaviour or elastomeric properties. On the other hand, hard domains are below their glassy or melt transition temperature and are thought to govern the hysteresis, permanent deformation, high modulus and tensile strength and provide dimensional stability. Compositional variables and processing conditions such as structure of soft and HSs, symmetry of diisocyanate, type of CE (diol or diamine) number of carbon in linear low molecular weight CE, the type (polyester or polyether) and chain lengths of SSs, crystallizability of either segment, thermal history of the PUs and the method of synthesis are known to affect the degree of phase segregation, phase mixing, HS domain organization, and subsequent PU coating properties.

Conclusion

It has been found that MMT clays exchanged with long chain onium ions (carbon number >12) have good compatibility with polyol. The extent of gallery expansion of modified MMT is mainly determined by the chain length of the gallery onium ions. By the study of a TPU/clay elastomeric nanocomposite, it was found that the nanocomposites have maximum mechanical property values with the clay content.

The presence of nanoparticles may improve the mechanical strength of the PU matrix and in turn, the strength of the PU foam. Nanoscale-dispersed clay may act as nucleation agents during the foaming process to produce finer cell structure and higher cell density.

It was found that the mechanical properties had maximum values with the clay content when it reached 8 wt %. The

maximum tensile stress and the maximum elongation at break increased two and five times, respectively. The WAXD patterns showed that the glycerol propoxylate had better compatibility with the organoclay than poly(propylene glycol); this corresponded to the formation of a nanocomposite from the clay compounding with glycerol proxylate that, in turn, resulted in the best mechanical properties.

The tensile strength and ultimate elongation values decreased with the addition of Na-MMT or O-MMT. There was, however, a significant improvement in the Young's modulus values with increasing levels of both Na-MMT and O-MMT.

Besides the characteristic peaks at 4.6 and 4.0 nm, PU/MMT1 and PU/MMT2 have diffuse diffraction peaks at 2.2 and 1.9 nm, which is close to the diffraction peak of the organo-MMT. These results suggest that the GPO3 has superior compatibility with organo-clay and is more easily intercalated into the clay layers than PPG1 and PPG2. When the clay content was less than 8 wt %, the nanometer clay layers had a good compatibility and a strong interaction with the pure PU; when the clay content was higher than 8 wt %, the clay began to aggregate.

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