

Polyurethane

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Polyurethane is widely considered as the biggest polymer product which is categorized under plastics. PUs belong to a group of elastomers that are linked to a urethane material with a distinctive feature of being hard and soft parts in the macromolecule. Plastic and modular construction industries produce big quantities of PU wastes in the fabrication process during either processing or utilization of materials.

nanocomposite

physio-thermo-mechanical properties

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1. Introduction

A range of research has been conducted on the ongoing discussion of the effect of chemical structure and annealing of the morphology of polyurethanes (PUs) on experimental and theoretical work on phase-separation kinetics ^[1]. Phase separation is the most crucial reason for the PUs' microphase separation as the powerful hydrogen link between the urethane hard parts ^[2]. The main components of PUs are macrodiol, diisocyanate, and chain extender ^[3]. The chemistry of PU synthesis depends on the reactions of isocyanate. The hydrolysis resistance of PUs and the noting of the diol chemistry on molecular weight stability in water are discussed by Gomez et al. ^[4].

PUs belong to a group of elastomers that are linked to a urethane material with a distinctive feature of being hard and soft parts in the macromolecule ^[5]. In addition, the environmental issue that involves PU recycling was a concern of researchers ^[6]. The synthesis of PU is the main theme of the studies in the field of working towards environmentally based materials such as PU, using the short-chain diol called diisocyanate ^[7]. Polyurethane is widely considered as the biggest polymer product which is categorized under plastics ^[8]. Plastic and modular construction industries produce big quantities of PU wastes in the fabrication process during either processing or utilization of materials ^[9]. The structure and properties of PU parts have been investigated to achieve better biocompatibility and are characterized by surface and bulk morphology ^[10]. Traditionally, PU items are equipped with many organic solvents and free isocyanate monomers ^[11]. In the production of PU foams, catalysts are employed in the polyaddition reaction ^[12]. It has been reported that two simultaneous reactions could occur during PU manufacturing that involves the isocyanates and polyols during gas liberation or a foaming reaction ^[13]. As an example, paints from modified PU are extensively used as topcoats for corrosion and weather resistance. The aliphatic PU is sensitive to acrylic ester comprising hydroxyl which is widely considered as having good adhesion and being aging-resistant ^[14]. These processes involve building up strong hydrogen links of the PU matrix, raising

the rigidity of the matrix, and negatively affecting the relaxation of dipoles [15]. The particles dispersed in aqueous phase dispersion, classified as anionic PU, are binary colloidal systems, cationic, and non-ionic systems [16]. Regarding the nanomaterials, the antibacterial polyurethane activity of composite nanofibers has been assessed in food-borne pathogenic bacteria and staphylococcus aureus, using various techniques [17]. The focus is on the formation of soft, long-chain diol segments, whereas the construction of the hard segment belongs to the microdomain of segmented PU copolymers [18].

2. Polyurethane Composite

The soft segment relative to the hard segment of the lower air-interfacial polymer has made the appearance of PU in polyol structure [19]. The size of the dispersed PU particle reduces the concentration of the ionic group per unit chain length of the PU pre-polymer [20]. On the other hand, the increase of the ratio of hard to soft parts of the PU chains results in increasing the viscosity of the prepolymer [21]. The reduction of the ionic group concentration and the increase in the viscosity could cause a stiffer PU chain, lowering the solubility of the polymer, enhance the phase separation, and make coarse particles at the surface [22]. The above behavioural changes increase the hysteresis values of the quaternized polymers compared to the base PUs. The effect then causes a noticeable rearrangement surface that changes the hydration [23].

PUs are industrially crucial polymers with a range of structures and uses [24]. The acrylics PU polymer is known by a table of Newtonian rheological features [25]. Regarding the aging of the PU film, Sanchis et al. [26] have shown that the PU structure plays an important role in addressing the age issue.

The poor elasticity of the two segmented PUs was caused by their low molecular weight which, in turn, influences the morphology of the segmented PUs [27]. Hetflejš et al. [28] illustrated that the stabilizing efficiency of polymer-linked structures could be compared with that of their low-molecular-weight analogs, physically admixed with the PU. In another field, a sufficient mixing of the fluoro acrylic and PU polymers in the film properties could produce better results [29]. In this regard, it was found that modifying the ratio of PU and polyimide parts results in widening the range of properties from plastic to elastomer of the poly(urethane-imide) [30]. The solubility of the polyimide is enhanced as a result of adding isocyanate-terminated PU prepolymer, making a gelatine solution [31].

3. Thermoplastic Polyurethane Composite

Thermoplastic polyurethanes (TPUs) are linear segmented copolymers composed of hard and soft segments separated by a microphase, which complicates the investigation of its relevant microstructure [32]. The difficulty of this investigation shortening the research of the microstructure to extension behaviour [33]. Thermoplastic polyurethane (TPU) and the thermoset PU are chemically similar to each other; however, they have different features [34]. TPU is characterized by unique physical-chemical properties due to the reformation ability from melting state which makes it elastic, highly flexible, and suitable for many industrial applications [35]. On the other hand, the sensitivity of TPU to oil is smaller than that of thermoset PU, as the latter is easy to tear with abrasive

applications [36]. TPU becomes soft at high temperatures and can hold low pressure, possessing a higher tensile modulus in comparison to rubber [37].

TPU is generally described as “bridging the gap between rubber and plastics” and imparts high elasticity combined with high abrasion resistance, and, hence, becomes suitable to a variety of biomedical applications [38]. TPUs are conventionally not degradable; however, they become susceptible to hydrolytic and oxidative under vacuum [39]. The TPUs’ susceptibility to such degradation causes a problem for long-lasting biomedical implants which exploit designing biodegradable PUs [40].

TPU displays a very wide range of properties, ranging from very soft to strong, rigid thermoplastics that depend on the chemical compositions, backbone structures, and resultant microphase morphologies [41]. The 40-year investigation revealed that there are various morphological models for segmented PUs [42]. TPU has become one of the most versatile engineering thermoplastics that have constituted developing more interesting polymers due to specific structures of TPU macromolecules, interphase interactions, and microphase transformations [43]. Several researchers have addressed that blending TPU with nanomaterials enhances its physical properties and toughness [44]. The TPU’s good compatibility with polycarbonate or acrylonitrile butadiene styrene was behind using TPU as a modifier to create new blends [45]. The effect of using special additives can be seen in creating properties necessary to achieve flame retardance, antistatic, and radiation crosslinking ability [46]. Besides, exposing TPU to severe conditions results in significant structural changes depending on the structure and morphology; however, such changes deteriorate the physical properties [47].

4. Properties of Nanofiller–TPU Nanocomposites

The main application of TPU is in the medical field due to its exceptional mechanical properties and biocompatibility. The siloxane-based TPU is one of the most important nanocomposites. TPU nanocomposites were vigorously studied based on the nanofiller aspect ratio, surface modification, and percentage loading. The mechanical properties were increased at an even small amount of loading.

4.1. Morphology Properties of Nanofiller–TPU Nanocomposites

The first-ever successful attempt of dispersion of nanoclays in the TPU matrix has resulted in incredibly high interest amongst the scientific community [48]. It was seen that the morphology of clay platelets plays a crucial role in the improvement of the properties of the clay–TPU nanocomposites. The effect of hard segment content along with the amount of clay on the morphology has been discussed by Xu et al. [49]. Increased hard segment content has been seen to result in an increase of the basal spacing of the clay platelets at a lower clay content. However, the opposition has been observed to occur at higher clay contents, where increased hard segment content reduces the basal spacing. Two varieties of modified montmorillonite (MMT) have been dispersed in the TPU matrix [50]; the first is clay modified with 12 amino lauric acids and the second is clay modified with benzidine. This was done in order to study the effect of the modifier on the morphology and properties of the resulting nanocomposites [50].

Complete exfoliation was observed of up to 5% and 3% for clay modified with 12 amino lauric acid and benzidine, respectively.

4.2. Mechanical Properties of Nanofiller–TPU Nanocomposites

The mechanical properties of modified TPU are extremely important because of the usefulness of modified TPU in many engineering applications. It has been observed that the addition of nanoclay into the PU matrix improves the tensile properties to a significant degree [51]. As an example, adding 10 wt.% of modified clay increases the tensile strength, modulus, and strain at the break by more than 100% [45][49]. Young's modulus of the nanoclay–TPU nanocomposites has previously been seen to increase with the addition of modified nanoclays [52]. Nonetheless, improved Young's modulus coupled with a reduction in tensile strength and elongation at break with the addition of clay has also been reported in previous studies [53]. Besides that, the destruction of hydrogen bonds in the hard segment of TPU due to the incorporation of tethered nanoclays has also been observed [53]. The destruction in H-bonding occurs due to the H-bond formation between the carbonyl group of the TPU and the [–OH] group present on the tail of the modifier to the clay. However, modulus and tensile strength are increased by 110 and 160%, respectively, for the nanocomposite containing 5 wt.% of Cloisite®30B. The reaction of the surface [–OH] group of the MMT with the isocyanate during in situ synthesis, which leads to an improvement in tensile strength, as well as elongation at break, has been observed from experimentation [49].

4.3. Thermal Properties of Nanofiller–TPU Nanocomposites

The thermal stability of the TPU matrix is of great importance since its degradation commences around 230–300 °C. It is important to note that a TPU matrix possesses two glass transition temperatures (T_g) corresponding to the soft and the hard segments, while it is known that the hard segment temperature T_g is not always observed due to the dominance of the soft segment and ordered hard domains [54]. It also appears that the addition of a small amount of tethered clay could increase T_g of the hard segment by 44 °C [55] while a 13 °C rise was observed in the T_g value of the soft segment with the addition of Cloisite® 20A [56]. TPU was found to exhibit two stages of degradation during decomposition. The first stage of degradation relates to the degradation of the hard segment and the second stage of degradation relates to the degradation of the soft segment [57]. In some other studies, a lower T_g of the nanocomposite, as compared to the TPU matrix, has been reported [58]. The thermal stability of the clay–TPU nanocomposite will increase after the complete decomposition of the modifier compared to that of the TPU matrix [59]. An increase in the amount of clay from 1 to 5 wt.% was reported to increase the thermal stability of the TPU matrix from 12 to 34 °C, respectively [55]. The increase in thermal stability with an increase for MMT in the TPU matrix has also been reported in previous studies [49]. The improvement in thermal stability of the clay–TPU nanocomposite was found to be directly connected to the degree of dispersion of the nanoclay in the TPU matrix [59].

5. Conclusions

Controlling the interaction between hard and soft segments through hydrogen linking plays a crucial role in featuring the amorphous structure of PU and the thermally labile thermoplastic polyurethane (TPU), which is chemically similar to PU with a better heat resistivity. TPU has become the most versatile engineering thermoplastic with exceptional mechanical properties and biocompatibility that could be utilized to develop more interesting polymers due to specific structures of TPU macromolecules, interphase interactions, and microphase transformations.

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