REVIEW ON POLYURETHANE-MATRIX NANO COMPOSITES, PROCESSING, MANUFACTURING AND APPLICATION

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ABSTRACT
This review paper gives knowledge on polyurethane nano composite Processing techniques, and its applications. In addition to presenting the scientific framework for the advances in polymer nano composite research, the review provides a comprehensive discussion on technology, modeling, characterization, and processing, manufacturing, applications on polyurethane nanocomposites.

KEY WORDS: Polyurethane, graphite nanoplatelets, carbon nanotubes, nanoparticles, nanofiber.

1. INTRODUCTION
Polyurethane is one of the most interesting Synthetic materials in Industries, Which has been widely used in adhesives, coatings, Synthetic leather, Construction, automatic applications, etc., Nano Composites are having polymers containing nanofillers [1-2]. The microstructure of nano composites has inhomogeneties in the scale range of nanometers. Nowadays in the application of Polyurethane, researchers start to search for higher performance of polyurethane. Polyurethane based nanocomposites exhibit remarkable improvements in mechanical, dielectric, magnetic, thermal, optical and acoustic properties compared with pure Organic polymers [3-4].

The present paper provides a brief critical review of the literature and some of our resolution polyurethane (PU) nanocomposites studies. Nanocomposites demonstrate often unusual & beneficial for the user properties. Scientific and technical literature report shows the improvement of properties of polymer nanocomposites compared to the pristine polymers.

2. TYPES OF NANOCOMPOSITES
Polyurethane nanocomposites are classified based on its reinforcing materials such as nano particles and nano clays. The main archetype is that a valuable nanocomposite is one with the largest possible surface of nanofiller. Nanoparticles are commercially available from different sources, avoiding aggregation of nano particles and exfoliation of nanoclays is important in synthesis. Nanoparticles tend to aggregate and have very poor dispersion in
polymers [5]. To achieve good dispersion of nanoparticles and yield better compatibility between nanoparticles and polymer matrix, the use of various modification agents, such as trialkoxy, silane, stearic acid, CTAB are recommended for appropriate surface modification of nanoparticles [6-7]. Ultrasonic irradiation is also employed to overcome the disadvantages such as agglomeration of particles [8] and suslick et al., [9] have employed a variety of applications of ultrasound to materials chemistry.

Sols of nanosilica as colloid solutions in water or inorganic solvents are used in the preparation of PU nanocomposites. Fumed Silica (10-20nm) is also successfully disposed in a polymer [10-11]. Clay consists of naturally available layered silicates. The thickness of each layer is ≈1nm and its lateral dimensions are typically within 20-1000nm. The stacking of the layers forms a gallery between layers [12].

The Silicate layers of clay usually contain hydrated Na+ (or) K+, which render them highly Hydrophilic, the silicate layers must be modified to increase their hydrophobicity. The modified Organic clay is known as Organoclay. Exfoliated nano composites with a high aspect ratio demonstrate enhanced properties compared to the same pristine polymers. Thus, the exfoliation of clay nanolayers in a polymer matrix requires polarity match between the clay surface and the prepolymer precursors to allow optimal access to the gallery [13]. The numbers of way to increase a degree of exfo- liation in a nanocomposite, such as in situ polymerization, melt blending, solution blending, sonication, high shear mixing, melt intercalation, and some others [13, 14]. The morphology of nanocomposites is usually studied by X-ray techniques (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [15].

3. PU-NANOPARTICLES COMPOSITES

SiO2 nano particles are widely introduced into polymers to improve the heat resistance, mechanical and electrical properties of polymer resistance, mechanical and electrical properties of polymer materials [16-18]. A new modification agent is introduced, to improve the dispersion and compatibility of nano-SiO2 in PU matrix and prepare a series of PU/SiO2 nano composites. PPG is one of the most popular Polyols in PU industry because of its low cost. Poly Propylene glycol phosphate ester (PPG-P) was synthesized by the esterification of PPG and Polyphosphoric acid (PPA). It is a new polymeric surfactant with –PO (OH)₂ as an anchoring group and PPG as a soluble chain [19].

PPG-P is a new applicable modification agent to synthesis PU nano composites, since it can exhibit good dispersion and compatibility with PU matrix. Nano SiO₂ was then modified with PPG-P and a series of PU/SiO₂ nano composites were prepared via insitu polymerization. The micro domain structure of the pure PU and PU/SiO₂ nanocomposites were shown in fig1. The comparison of the spectra shows that the positions of peaks for the distinctive functional groups are identical with those of the pure PU; which means that the segment structure of the pure PU is not affected by the pressure of Nano SiO₂.
SEM in fig 2. shows that the blank SiO2 nano particles are tightly joined together to form aggregates and most of the nano particles are exposed on the freeze-fractured surface. After surface modification with PPG-P; the surface energy of nano-SiO2 decreases, which increase the stability of the nano particles. Therefore the new particles tend to form finer particles and embedded in the PU matrix, without phase separated.

TGA Curves of PU/SiO2 nano composites with different surface treated SiO2 contents (3%, 5%, 10%), thus the thermal stability of PU/ SiO2 (surface treated) is better than PU/SiO2 (blank) is shown in fig 3. The first weight loss step, from 100 to 200°C is attributed to the loss of residual water and organic solvent. It is clear that the samples shows very good thermal stability before 200°C and decompose around 250°C in air gas. The second weight loss step, about 300°C, might be starting the decomposition of the hard segment of polyurethane. The third weight loss step, about 400°C might be attributed to the decomposites of the staff segment of PU. It is obvious that in the mass range 3-10 wt%, the thermal stability of polyurethane increases with increasing nano-SiO2 content due to more interaction between nano-SiO2 particles and macro molecular chains [20].
The nano composites of polyurethane / TiO2 were synthesized through a simple and convenient Ultrasonic wave dispersion process. The mixture of nanoparticles of PU/TiO2 and KH 550 was irradiated under Ultrasonic radiation for 30 min at 30°C. Cooled to room temperature, Centrifuged and dried in vacuum at room temperature for 6hrs. The Transmission electron microscopy and SEM micrographs of the fine TiO2 nano particles and PU/TiO2 nano particles are shown. From fig.4 (a) it can be clearly seen that the nano particles have some aggregates, whereas fig. 4 (b), fig.5 with size of about 30-35 nm consists of the very uniform particles. The nano particles dispersed in PU matrix on nano scale be seen clearly, which indicates the formation of nano composites [21-22]. As expected, the nano particles homogenously distributed in the polymer through the ultrasonic technique.
X-ray diffraction curves of the polymer, nano particles and composite is as shown in fig 6(b). PU is amorphous and does not exhibit any anisotropic behaviors [23]. The most of the characteristic peaks at 2θ values of anatase TiO2 are kept intact can be seen in fig 6(a&c). The average size of the nano composites is calculated to be 30-35 nm according to the Debye-Schemer formula. The ultrasonic irradiation reduces the crystallite size of anatase due to the generation of many localized hot spots in the solution by the ultrasound irradiation. Thus, the homogeneous formation of a large number of seed nuclei, leading to a smaller particle size [24-25]. TEM and SEM measurement also agree with this statement.

The infrared emissivity values at wave length of 8-14μm of all the samples are tested, that the pure polymer and TiO2 posses high emissivity values of 0.945 and 0.925 respectively. Polyurethane has high infrared emissivity value, because of strong absorbability at infrared wave band [23]. TiO2 has high infrared emissivity value due to the high refractive index. Conversely, Pu/TiO2 composites has the lower infrared emissivity value (0.538) than both of its components, the decrease of infrared emissivity of the nanocomposites is due to direct consequence of the interfacial interactions.
4. PU-ORGANOCLAY COMPOSITES

The properties of PU with Organoclay were studied [1-2]. PU was prepared by the following procedures: i] distribution of clay in polyol with a subsequent reaction with diisocyanate; ii] Interaction of PU with clay in Organic solvent with a subsequent evaporation of solvent; iii] Reaction of diisocyanate with hydroxyalkyl groups of Organic modifier in the clay with a subsequent reaction with Polyol.

A PU nanocomposite with 1-6 wt% of clay shows peaks on XRD patterns with a distance between galleries (basal spacing) in the range of 1.6 - 3.2nm. It is possible to conclude based on XRD and SEM and other spectroscopy, that polymer intercalated into the organoclay is not exfoliated, and organoclay is not homogeneously dispersed in a PU matrix [24]. Many composites with added non-exfoliated clay still demonstrate improved mechanical and physical properties and thermal stability, lower permeability of dioxide compared to the pristine PU [24]. At the same time presented data of property vs organoclay level are not simple in a series of similar nanocomposites: it can be a curve with a maximum (minimum), it can be a permanent decrease or an increase of a property. It is documented that high temperature resistance of PU nanocomposites is higher than that of pristine PU.

PU nanocomposites prepared by solution of Organoclay by polyol, loading of polyol with clay upto 10-20 wt% makes a pourable mixture [25]. The intercalation of polyol into clay in XRD results in an increase with basal spacing from 1.8 -2.3nm to 3.2 -3.9nm and formation of PU results in further increase of basal spacing upto more than 5nm. The latter case may be considered as exfoliation of a clay (or) dispersal of nanolayers, in which the onium ions of the clay were considered as active reagents for coupling with diisocyanate[25]. Loading of PU with 5-10 wt% of clay results in a two-three times improvement of tensile properties of a polymer, which increase of strain-at-break, tensile modulus and tensile strength.

Inorganic fillers are used in PU to reduce formation cost and to increase stiffness, but the improvement in modulus for conventional PU composites are compromised by a sacrifice of elastomer properties. Clay nanolayers aggregated in the form of intercalated tactoids, strength, stiffen and toughen the matrix. The enhancement in strength and modulus is directly attributed to the reinforcement provided by the disperse clay nanolayers. The improvement in elasticity is tentatively attributed to the plasticizing effect of onium ions, which contribute to dangling chain formation in the matrix [25].

A complete exfoliation of nanoclay was observed in PU composites with high concentration of nanoclay (upto 40%), was additionally functionalized with diamine, which served a chain extender PU nanocomposite formation [26]. Tensile strength and elongation to break reaches maximum of 5 wt% of nanofiller loading. Another study of PU nanocomposites demonstrates that maximum values of flexural and tensile strengths are obtained at only few percent of clay content [27]. Several PU nanocomposites prepared in [24] were studiedin the range of organoclay loading of 0-8wt%, in which tensile properties shows optimal value at 3-4 wt% loading by different Organoclays. Ultimate strength, initial modulus gas barrier properties and the thermal stability of nanocomposites increased withincreasing clay content [24]. A gradual increase of tensile strength with increase of clay content upto 5 wt% of PU nanocomposites and only slight increase of glass transition temperature (Tg) and also slight increase of thermal stability was observed for PU nanocomposites based on WAXD and TEM that PU intercalated into clay galleries [28].
Organically-treated synthetic fluoromica, which is a layered silicate as well, of different size, has a modest effect on the properties of PU nanocomposites. Exfoliated in asolvent inmodified clay laponite as a hydrophilic compound interacts with polyol in PU, where as in PU with hydrophobic soft segments like polytetramethylene oxide clay interacts with hard urethane links [29]. Thus, a decrease toughness and elongation to break is observed in hydrophilic compound, whereas in hydrophobic compound an increase of the same properties is observed. Such a study gives a better understanding of the nanoclay effect of PU nanocomposites properties. The PU nanocomposites demonstrated an increase in the elasticity, decrease in damping property, significant increase in thermal stability but also a decrease in tensile modulus. Hysteresis results indicate that energy dissipation increases with an Organoclay concentration increase [30].

PU nanocomposites with photo initiator (PI) 2 hydroxy-2-methyl-1-phenyl propane-1-ones (Darocur 1173) were prepared [31]. This PI PU nanocomposite was dispersed in polymer sable resins. Such initiator manifested high efficiency. XRD and TEM demonstrated formation of intercalated and exfoliated UV cured nanocomposites with many good characteristics [31]. PU as well as number of other polymers can demonstrate shape recovery after temporary applied stress. PU nanocomposites demonstrated the lowest relaxation rate after removal of a stress 1wt% of organoclay. The studied PU nanocomposites manifested the highest degree of clay exfoliation nanoclay at 1wt%, PU nanocomposites with 3 and 5 wt% of organoclay relaxed faster than the pristine [PU] [32].

5. CONCLUSIONS AND PERSPECTIVES

In the present article we aimed to describe the current status of PU nanocomposites research. Colloidal silica and organoclays are the most studied nanofillers which often reinforce PU. The advantage of nano-scale reinforcement is twofold: (1) when nano-scale fillers are homogeneously dispersed in the matrix, a tremendous surface area developed that could contribute to polymer chain confinement, which may lead to higher $T_g$, higher stiffness and tensile strength, increased elongation and an increase of both flexural and tensile modulus, higher HDT, and (2) nanoscale fillers, especially clays, provide an extraordinary zigzag tortuous diffusion path that lead to enhanced barriers for gas penetration for a gas (dioxygen, others), moisture. The enhanced barrier characteristics, chemical resistance, reduced solvent uptake and flame retardancy of clay–polymer nanocomposites originates from the hindered pathways through the nano composite. Usually nanocomposites possess special properties not shared by conventional composites, due primarily to large interfacial are per unit volume or mass of the dispersed phase. Current status of nanoscience and nanotechnology does not allow prediction of the ‘good’ formulations and properties of nanocomposites. Chemist/technologist addresses to the prior art and analogies developing nanocomposites, or runs an exploratory work.

Improved properties of some PU nanocomposites with silica can be obtained under high load of the latter, namely 10–50 wt%. Organoclay can be properly dissolved in the level of 3–10 wt% in order to obtain enhanced performance [27, 28]. One should avoid precipitation (crashing, gel formation) of silica in a nanocomposite. In the case of clay all efforts are made to exfoliate clay in polyol or at least to intercalate polyol into organoclay, and to get a large aspect ratio. The fact of exfoliation can be verified by XRD and by other techniques.

PU can be obtained by two ways: by radiation cure of urethane acrylates oligomers (pre-polymerms) or by dark reactions between diisocyanates and polyols. Radiation cure of urethane
acrylates oligomers, and UV-cure in particular, has all of the known advantages over dark cure (high rate, low energy consumption, etc.). The presence of nanofiller, especially well dispersed nanofiller, does not inhibit photo induced reactions, cf., e.g., Refs [36, 38]. Moreover, photo initiator intercalated into clay galleries, demonstrates high efficiency. To the best of our knowledge, this work was never reproduced. Nanocomposites are expected to revolutionize polymer technology. Time will show if it will happen, or not.

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