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THE EFFECT OF ORGANOCLAY ON THERMAL AND MECHANICAL BEHAVIOURS OF THERMOPLASTIC POLYURETHANE NANOCOMPOSITES

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Polyurethane nanocomposites films were successfully synthesized by solution casting method using commercial organo modified clay- Cloisite 25A (C25A). The nanocomposite were prepared at different ratios of clay and obtained as a tough film. They are labeled as 1%, 3%, 5%,and 7%, polyurethane clay (PUC) nanocomposites. Pure and PUC nanocomposite were characterized using infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscope (SEM) , thermo gravimetric analysis (TGA) tests. The results X-ray analyses showed that the clay produced the exfoliated nanocomposite in all cases with disappearance of the characteristic peak corresponding to the d-spacing of the organoclay. Morphology of the PUC nanocomposites was characterised by SEM and it reveals the formation of exfoliated structure and good interaction of polymer matrix with fillers. FT-IR analysis confirm that C25A has good compatibility with polyurethane . The mechanical properties of nanocomposite were studied as a function of clay loading and the improvement in strees-strain property of this he tensile strength and young's modulus of polyurethane nanocomposites increased with increasing clay percentage.

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1. Introduction

Nanocomposites derived from organic and inorganic entities interacting at the nanometer level have enriched the field of material science. Recently, the field of polymer/clay nanocomposites has drawn great interest because they exhibit improved thermal [1], barrier [2], mechanical [3] and flame retardant properties [4] at low clay content compared to pure polymer and conventional filled composites. The main reason for these enhanced properties in the nanocomposites is caused by the very high aspect ratios (10-1000) and large surface area of exfoliated clay particles and the strong interfacial interaction between the silicate platelets of 1nm layer thickness and the polymer matrix [5, 6].

Montmorillonite (MMT) is most widely used layered silicates for preparation of polymer-clay nanocomposites because it has a huge cationic exchange capacity (80-120 mequiv/100gm). It consists of layers separated by Vander Waals gaps called galleries. These interlayer are occupied by metal cations which make it difficult to disperse MMT in a polymer matrix. Replacing the metal cations with an alkylammonium cation is well-known method to improve the dispersion of the MMT in a polymer matrix [7-9]. Among nanofiller that could be added to polymeric matrices, organo-modified clays were most frequently utilized because of their relatively low cost and high effectiveness.

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Polyurethanes (PUs) are unique polymer materials with a wide range of physical and chemical properties. 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 [10,11]. However, PUs also have some disadvantages, such as low thermal stability and low mechanical strength, etc. To overcome these disadvantages, a great deal of effort has been devoted to the development of nanostructured polyurethane (PU)/ montmorillonite. In the last few years, many efforts have been made for the improvement of the thermo-mechanical properties of elastomeric polyurethanes by the introduction of small amounts of inorganic nanostructured materials [12-14].

In the present work, we report the synthesis and characterization of polyurethane/ clay nanocomposites material by using different amounts of C25A clay. In order to assess the effect of the clay loading and of the polymer–filler interaction on the microstructural and thermo-mechanical properties of the resulting composites, with particular attention to their thermal degradation resistance and to their tensile mechanical response under impact conditions.

2. Experimental

2.1. Materials

Polyethylene glycol (PEG_{2000}) and the Potassium salt of hydroquinone sulphonic acid were used as obtained from Aldrich, USA. Tolylene 2,4- diisocyanate, tech., (TDI) 80% was purchased from Sigma Aldrich Chemical Co, USA. Dibutyltin-dilaurate was procured from Fluka Chemical Co and was used as obtained. N, N-dimethyl formamide (HPLC grade) was purchased from Sisco Research Laboratories, Mumbai. Cloisite 25A obtained from Southern Clay, USA was dried in a hot air oven at 80ºC for 6 hours to remove moisture content.

2.2. Preparation of polyurethane clay nanocomposites

Polyethylene glycol was taken along with the calculated quantity of Cloisite 25A in a three necked reaction kettle. TDI was dissolved in DMF; the solvent was added at 50ºC drop wise such that one out of the two-hydroxyl groups in each polyol molecule could react with one molecule of TDI to yield the prepolymer. The reaction was allowed to proceed for 6 hours. The potassium salt of hydroquinone sulphonic acid thoroughly dissolved in the solvent was added drop wise at 50ºC for chain extension. The heating was continued until the theoretical isocyanate content of 4-5% was reached, as determined by the dibutyl-amine method [15] and from the disappearance of IR absorption of NCO group at 2270 cm^{-1}. PUC films were obtained by pouring the emulsion onto a Teflon mold. The mould was demoulded and the films were labeled before storing. To investigate the effect of nanoclay content on the physical properties of PU/clay nanocomposites four concentrations of nanoclay were used: 1.0, 3.0, 5.0, 7.0, wt %.

3. Characterization

Fourier Transform infrared analyses were performed on a Nicolet Avatar –320 FT-IR spectrometer (Nicolet Instruments; Madison, WI) and FTIR- ATR spectra were obtained using a Ge internal reflectance element at an incidence angle of 45º with a HATR – ATR accessory which was placed in the sample compartment of Avatar - 320 FTIR. The thickness of the sample was controlled at the same uniform size. A minimum of 32 scans were signal-averaged with a resolution of 4 cm^{-1} within the 400-4000 cm^{-1} range. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku Miniflex diffractometer (30 kV,10 mA) with Cu Kα radiation (λ = 1.54 Aº) at a scanning rate of 2º/min at room temperature. scanning electron microscopy (SEM) micrographs of the samples were observed on JEOL JEM-5800 with an acceleration voltage of 20 kV. The thermal stability of the synthesised polyurethane clay nanocomposites was determined by Perkin Elmer, TGA 7 system at a heating rate of 20ºC/min. in N_2 atmosphere. The sample were heated from room temperature to 800 ºC. Tensile properties were measured using a UTM universal testing machine (Instron-3369, UK). A load of 100N was applied at a crosshead speed of 50mm/min. The dumb-bell shaped specimens were 15mm wide at the two ends and 10mm wide at the neck with thickness ranging from 1.1 to 3.2mm.The test was carried out as per ASTM D:638 test procedure. Dynamic Mechanical Analysis (DMA) determines elastic modulus (E'), viscous modulus (E") and damping coefficient (tan δ) as a function of temperature, frequency or time. DMA (NETZSCH Proteus) dynamic mechanical analyzer is operated in tensile mode. The samples were machined into specimens of 25 X 5X 0.5mm and scanned from -70 to 150 ^{o}C/min. using 1 Hz frequency.

4. Results and discussion

The structures of the PUC nanocomposites were analyzed by ATR-FTIR spectroscopy which was shown in figure 1. The characteristic absorption peaks of the functional group were detected and monitored during the preparations. In the IR spectra of PU, the –NH absorption peak was observed at 3330 cm^{-1}, due to the hydrogen bonded –NH in the urethane linkage, the carbonyl –C=O stretching peak was shown at 1730 cm^{-1} and 1700 cm^{-1} which were considered to be free and hydrogen bonded carbonyls respectively. The –CH stretching from 2975 to 2888 cm^{-1} remain almost unchanged in the presence of nanoclay particles, indicating that clay particles did not interfere with hydrogen bond formation by urethane –NH groups. The Si-O asymmetric stretching was observed at 1091 cm^{-1}. The peak at 1223 cm^{-1} confirms the presence of ionomer ($So_3^-K^+$) present in the nanocomposites.

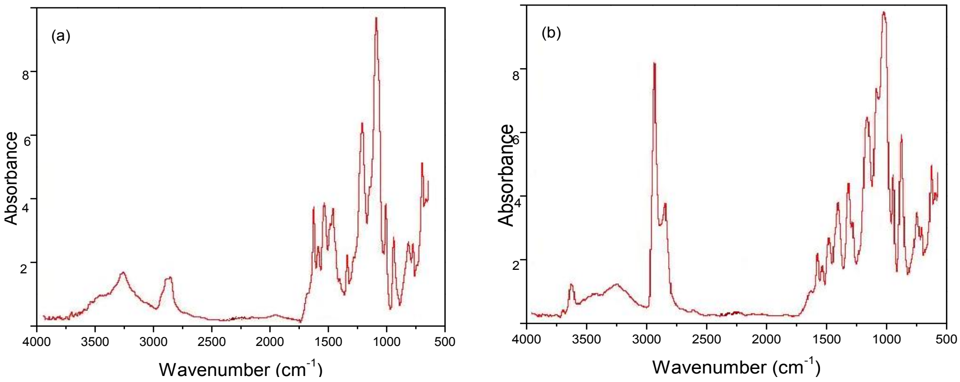

Fig. 1. IR spectras of (a) PolyUrethane (b) PUC-1 nanocomposite

The crystal structure of MMT consists of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge shaped octahedral sheets of aluminium hydroxide. The stacking of layers of clay particles is held by weak dipolar or van der waal forces [16]. The XRD is a powerful technique to observe the extent of silicate dispersion, ordered or disordered structure in the PUC nanocomposites. The figure 2 show typical XRD curves for the organoclay (Closite 25A) and PUC nanocomposites. The d_{001} spacing was calculated using Bragg's equation: $d = n\lambda / 2 \sin \theta$. The nanoclay shown the peak at 4.88° (*d*-spacing = 1.94 nm), but for polymer nanocomposites exhibit almost no peaks in 2θ regions. This may be suggested that the silicate layers of C25A are well dispersed in PU matrix. This can be interpreted as the indication of an exfoliated nanocomposite. This is somewhat unexpected since C25A does not have any special functional groups, which can be thought to be involved in the specific interaction with PUs.

Better clay dispersion (C25A) nanocomposites may be explained in the thermodynamic sense that the balance between platelet spacing caused by the modifier, level of access to exposed silicate surface and the number of unfavorable interactions between the polymer and the alkyl units of modifier play the important role in the polymer layered nanocomposites. This is in accordance with the literature proposed by Fornes et al [17]. The interaction between clay and polymer can be more important than that between modifier and polymer in the clay dispersion, the modifier increase the gallery height and make the layer separation much easier, since the modifier inside the layer weakens the electrostatic force between silicate layers compared to pristine MMT, which may partly explain the better clay dispersion in C25A nanocomposites compared to pristine MMT nanocomposites [18].

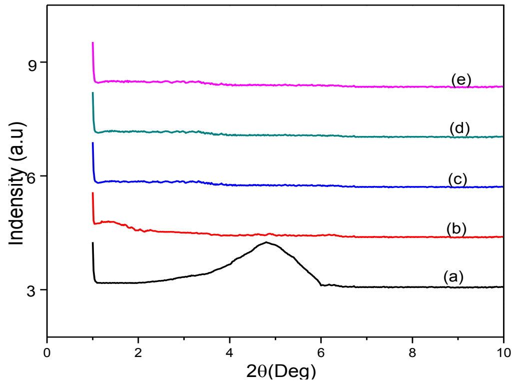

Fig. 2. X-ray diffraction angle patterns for (a) Cloisite 25A (b) PUC-1 (c) PUC-3 (d) PUC-4 (d) PUC-7 nanocomposite

Scanning electron photographs of the polyurethane clay nanocomposites are shown in figure 3. All the clay particle was uniformly dispersed on polymer matrix, the particle surface are coarsely rough. This uneven surface might be due to the high viscosity and the high degree of cross linking of the dispersed phase during the solution polymerization. However, the polymerization system was very stable and there was no macroscopic aggregation. All the particles ranged in size range from ~5 to 100µm.

The thermal stability of the PU nanocomposites were determined by TGA analysis. The representative of TGA thermogram PUC nanocomposites was shown in Figure 4. Thermoplastic PU show two stage decompositions temperature The first stage is mainly governed by the degradation of hard segment and the second stage correlates well with the degradation of the soft segment. The silicate layers can make the path longer for thermally decomposed volatiles to escape [19]. It is clearly observed that the initial stage thermal decomposition temperature is the major and sharp which involve the thermal decomposition of the intercalated polymers, especially the polymers present on the surfaces of the layers of the clay. Clay incorporated PU nanocomposites show enhanced thermal stabilities than thermoplastic PU. The PUC-1 show the initial decomposition at 354.9°C. The thermal stability of the nanocomposites was increased with increase in wt % of the clay. The PUC-5 shows maximum thermal stability.

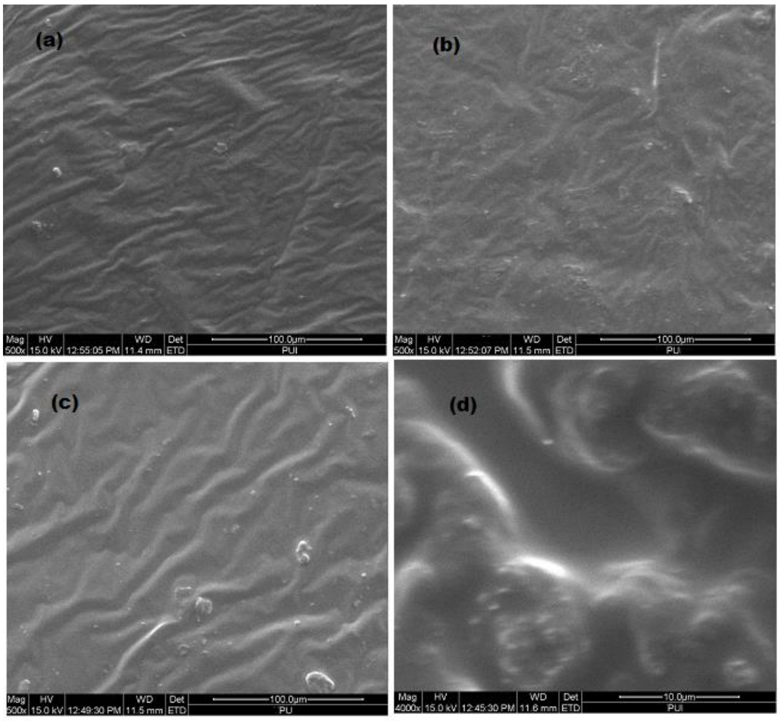

Fig. 3: Scanning electron micrographs of (a) PUC-1 (b) PUC-3 (c) PUC-5 (d) PUC-7 nanocomposites

The second stage is broad in which the weight loss ranging from 42% to17% in the temperature range 448 - 700 ºC. In this stage the complete decomposition of the small organic molecules happens and all the nanocomposites display higher thermal resistance than the pure PU, further decomposition of the rest intercalated polymers, specially the polymers present in the interlayer of the clay or some salts in the interlayer of the clay or interval of the clay minerals loses OH groups and the crystallographic structure collapsed. The PUC-5 nanocomposite show higher thermal stability up to 30ºC, this remarkable enhancement of thermal stability may be due to the highly aromatic nature of the compound synthesized from the aromatic isocyanate, TDI and the aromatic ionic chain extender $\mathrm{Ph(OH)_2SO_3^-\ K^+}$. From this result, it is calculated that over 80% of the initial clay added was quantitatively introduced into the polyurethane matrix.

Table I. TGA data of PUC nanocomposites.

Sample code	First stage decomposition, T_1 ºC [a]	Second stage decomposition T_2 ºC [a]	Residue % [b]
PU	348.18	448.37	15.74
PUC-1	354.9	453.39	15.377
PUC-3	360.7	458.83	15.145
PUC-5	379.85	476.67	21.868
PUC-7	375.59	477.80	22.371

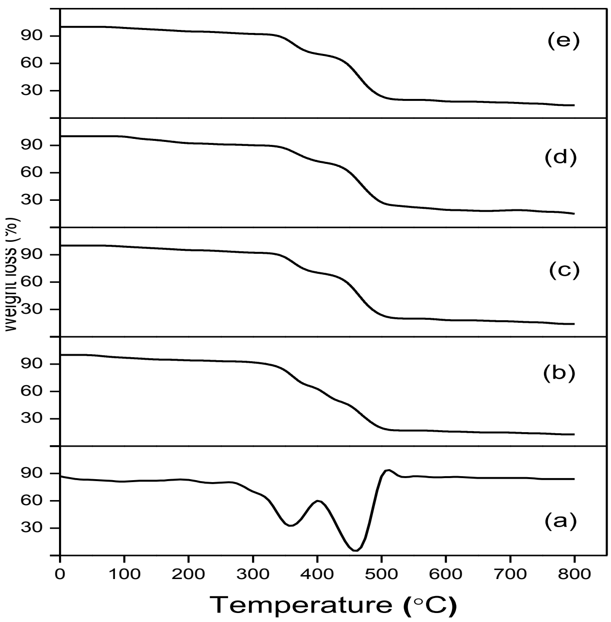

Fig. 4: TGA thermograms for (a) pure PU (b) PUC-1 (c) PUC-3 (d) PUC-5 (e)PUC-7 nanocomposites

The mechanical properties of prepared nanocomposits and their effect of organo clays is summarized in Figures 5 and 6.Tensile strength (TS) and percent elongation at break (EB) test results are listed in table II. From the figure which was shown that the tensile strength and elongation at break increase with increase in the clay content upto 5 wt.% . This is due to that PU is toughened and strengthened by the insertion of clay homogeneously dispersed in PU matrix. Morever the TS and EB start to decrease composite containing 7 wt.% due to the aggregation of clay content causing a weak interaction between the PU and clay layers. young's modulus of the nanocomposites with different clay wt.% are shown in figure 6. Such results indicate that the incorporation of clay might reduce the molecular mobility of polymer chains, resulting in a less flexible material with a higher young's modulus [20].

Table II. Mechanical data of Polyurethane clay nanocomposites

Sample code	Tensile strength (MPa)	Young's Modulus (MPa)	Elongation at break (%)	Thickness (mm)
PU	6.8	13.6	220	0.21
PU-1	7.6	17.5	280	0.25
PU-3	10.4	20.3	410	0.31
PU-5	14.8	24.4	530	0.28
PU-7	12.3	21.8	480	0.32

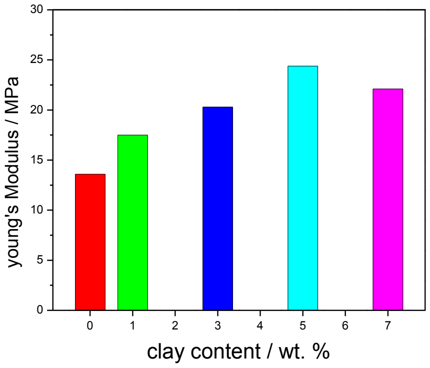

Fig. 5, Effect of clay concentration on young's modulus in PUC nanocomposites.

4.1.Dynamic mechanical measurements

The viscoelastic properties of polymer nanocomposites were determined by dynamic mechanical analysis (DMA) and given in Table III. The DMA measures the response of a polymer to periodic and fluctuating loads and is extremely sensitive to all type of transitions. Dynamic mechanical properties such as storage modulus (E'), loss modulus (E"), and damping factor (tan δ) are of great importance in determining and understanding the behaviour of polymer nanocomposites under these conditions. In the present investigation we could observe that storage modulus of PUC-3. With increase in the percentage of nanofiller loading (3 wt %), the Tg value increases upto -25.2 ºC. This may be concluded that PUC-3 gives maximum dynamic property when compared to other compositions.

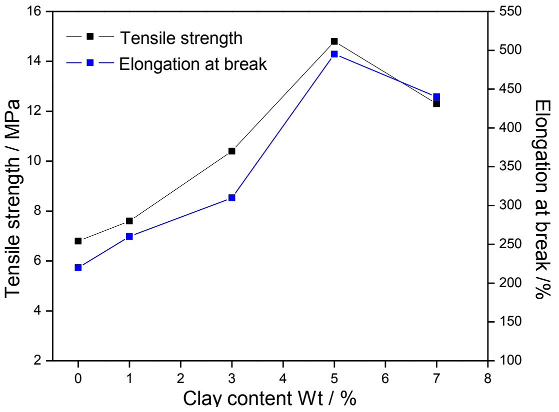

Fig. 6. Tensile strength and Elongation at break versus organoclay in PUC nanocomposites

Table III. The dynamic mechanical data of PUC nanocomposites

Sample Code	E' (MPa)	E" (MPa)	Tg (ºC)	Activation Energy (KJ/mol)	Thickness (mm)
PUC-1	10.7	12.23	-48.9	-457.49	0.25
PUC-3	29.8	1.253	-25.2	-1751.69	0.31
PUC-5	27.0	1.86	-25.5	-323.79	0.28
PUC-7	24.0	8.57	-44.6	-774.23	0.32

5. Conclusions

In this investigation, a series of Polyurethane clay nanocomposites were prepared successfully through solution polymerization techniques. The synthesized PUC nanocomposite were characterized by FTIR, XRD, and SEM. IR results confirmed that Polyethylene glycol and TDI was polymerized. XRD and SEM analysis proved that the synthesized nanocomposite were exfoliated structure and homogeneously dispersed in the polymer chain. Based on TGA results exhibits that all the nanocomposite have higher thermal stability compared to PU polymer. Mechanical studies indicated that tensile strength and elongation at break increases with increasing clay content, while young's modulus also increases. The preparation of these PUC nanocomposite may be further used in gas barrier and flame retardant applications.

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