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Synthesis and characterization of polyurethane/bentonite nanoclay based nanocomposites using toluene diisocyanate

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Abstract−Polyurethanes (PUs) prepolymers blended with bentonite nanoclay and without bentonite nanoclay were prepared by the reaction of toluene-2,4-diisocyanate (TDI) and hydroxyl terminated polybutadiene (HTPB), and the chain was further extended with 1,4-butane diol (1,4-BDO) to get final polyurethane nanocomposites (PUNC). A mixture of polymer and bentonite clay enriched in montmorillonite (MMT) was formed in solution polymerization, in which MMT dispersed depending on interaction of MMT with polymer chains. The molecular structure of the monomers and the prepared PU nanocomposites was confirmed by FTIR. A series of PUNCs were prepared by varying the percent compositions of bentonite nanoclay into the PU matrix. The existence of the clay in to the PU was confirmed by scanning electron microscope (SEM). SEM images verified the good dispersion of the bentonite nanoclay in PU matrix.

Keywords: Polyurethane, Nanocomposites, Bentonite Clay, FTIR, SEM

INTRODUCTION

Polyurethanes (PU), as a unique content type of polymers and having a special place in the materials-properties array, are recognized for their physical property and substance framework connections because their qualities can be easily tailored by the difference of their architectural elements. Their customary application fields include the aerospace, surface coatings and automotive industries, elastomers, foams, adhesives, fibers, varnishes and sealants [1]. Polymers can be modified for better and critically important interfaces. Polyurethane elastomers (PUEs) are possibly the most versatile classes of polymers as they can be molded, injected, extruded, recycled [2] and can be easily modified by varying the diisocyanate structure [3] and chain extender (CE) length using α, ω-alkane diols [4,5]. Synthesis, characterization of UV-curable and waterborne polyurethane dispersions [6,7], effect of blocked polyisocyanate based PU composites [8] and PU/natural rubber blends [9,10] have been studied comprehensively. Bio-based hyperbranched PU [11-14], PLA-based hybrid bio-composite [15], PP/nitroxide-mediated radical graft polymerization of styrene [16] and influences of clay type, content and dispersion state on PET/clay nanocomposites [17,18] have been documented in the established literature. A large number of reports on the use of reinforcing materials in polyurethane acrylate copolymers are available [19,20]. It has been found possible to improve many properties of polyurethanes by incorporating fillers. For example, calcium carbonate, aluminum hydroxide, kaolin, titanium dioxide, zinc oxide, and silica were used to improve mechanical properties [21]. Modified clay has been used as a filler to improve the mechanical properties [22]. Recently, PU/clay nanocomposite has attracted increasing interest. Compared with pure PU, the tensile strength increased by 120% and the elongation at break increased by 100%, and its fatigue life increased more than six-times [21]. These interesting results urged us to examine the effect of clay on the PU microstructures.

Polymer nanocomposite is a class of hybrid materials composed of an organic polymer matrix with dispersed inorganic nanofillers, which have at least one dimension in nanometer range [23]. The four main strategic processes for preparing polymer/layered silicate nanocomposites are exfoliation-adsorption, in situ intercalative polymerization, melt intercalation and template synthesis [24]. Exfoliation-adsorption in emulsion with Na^+-montmorillonite (Na^+-MMT), known to readily delaminate clay in water has been studied to promote intercalation of water insoluble polymers. Studies by Lee and Jang showed that only intercalated nanocomposites were obtained in systems polymethylmethacrylate (PMMA) [25], polystyrene (PS) [26], styrenecoacrylonitrile (SAN) [27-29] and epoxy [30]. Bandyopadhyay and Giannelis [31] have analyzed how the silicates affect the polymerization reaction in the cases of montmorillonite and fluoro-hectorite. Their results showed that well-exfoliated nanocomposites could be prepared and the dispersion was somewhat better in the MMT-based nanocomposites. The incorporation of MMT will definitely improve the mechanical properties of the prepared material. Taking these antecedents into account, the aim of the present study is to synthesize high-performance TDI based PU nanocomposite by incorporating bentonite nano-clay. Note that no report is available on the preparation of such material using the aforesaid components. The effects of bentonite clay contents on the morphological pattern and structure of the TDI based polyurethane nano-

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composites have been investigated and discussed.

EXPERIMENTAL

1. Materials

1-1. Chemicals

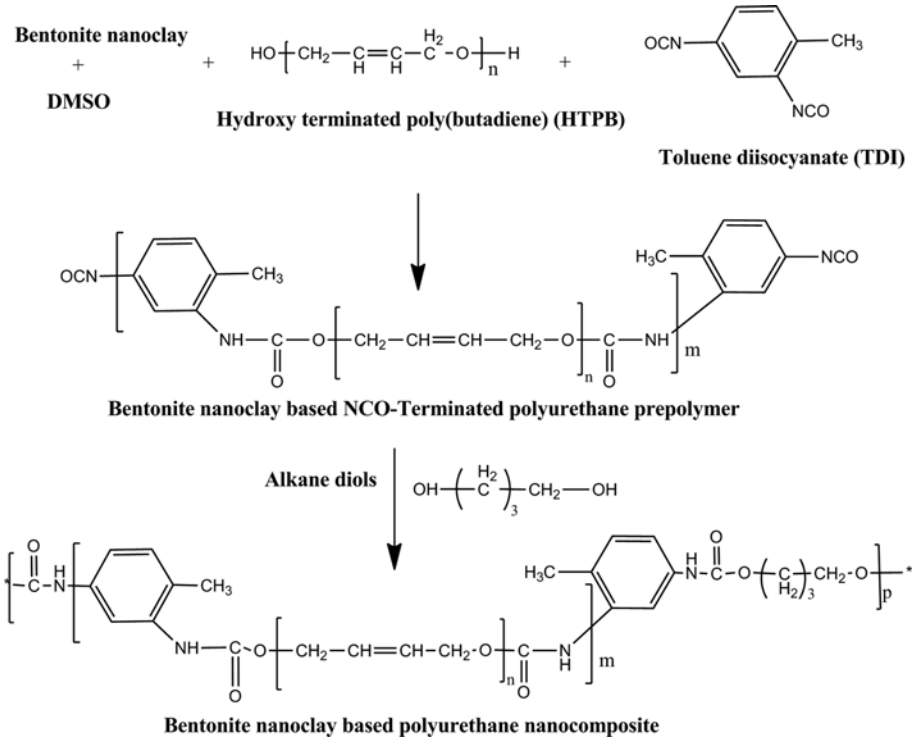
Delite® HPS bentonite (inorganic MMT with highest cation exchange capacity—CEC) was provided by Laviosa Chemica Mineraria (LCM) SpA Italy. The CEC of Delite® HPS as determined in our laboratory was found 74 meq/100 g [32]. Toluene diisocyanate (TDI), 1,4-butane diol (BDO) and dimethyl formamide (DMF) were purchased from Sigma Chemical Co. (Saint Louis MO, USA). Hydroxy-terminated polybutadiene (HTPB) (Mol. wt. 2909) were kindly gifted by National Engineering & Scientific Commission (NESCOM) Islamabad, Pakistan. Its molecular weight was confirmed following the method reported in the literature [33]. The polyol and BDO used in this study were dried at 80 °C in vacuo for 24 h before use to ensure the removal of all air bubbles and water vapors that might otherwise interfere with the isocyanate reactions. TDI and all of the other materials were used as received. All of the reagents used in this study were of analytical grade.

1-1-1. Step 1: Synthesis of Clay Based Polyurethane Prepolymer

The polyurethane (PU) prepolymer was prepared by the step growth polymerization (two-step mechanisms) of polyol and diisocyanate and was extended with alkane diol according to a recommended procedure [1]. For this rationale a weighed amount of bentonite nanoclay with different content (%) and same mole ratio of the prepared material was thoroughly dispersed with the solvent, i.e., dimethyl sulfoxide (DMSO). In a four-necked reaction kettle equipped with mechanical stirrer, heating oil bath, reflux condenser, dropping funnel and N_2 inlet and outlet, clay solvent mixture was placed. The temperature of the oil bath was increased to 60 °C and then 3.0 moles of diisocyanate, i.e., 2,4-toluene diisocyanate (TDI) 99% purity (Mol. wt. 174 g/mol) was added to the clay solvent mixture with continuous stirring for about 1 h at 90 °C. Bentonite nano-clay based PU prepolymer was formed following the addition of 1.0 mole of polyol, i.e., hydroxy-terminated polybutadiene (HTPB) (Mol. wt. 2909) and lasting the reaction at the same temperature for about another 1 h at 100 °C. During optimization of the experimental conditions it was confirmed that the formation of isocyanate (NCO) terminated polyurethane (PU) prepolymer completed in one hour. Fourier transform infrared (FTIR) spectrum of the PU prepolymer was also obtained to confirm the progress of polyurethane (PU) prepolymer reaction. The NCO contents of the PU prepolymer were determined and the experimental values were found close to the theoretical value (experimental value 9.27%; theoretical value 9.29%).

1-1-2. Step 2: Synthesis of PU Nanocomposites

The polyurethane nanocomposite prepolymer was converted into the final polyurethane nanocomposite (PUNCs) by stirring the prepolymer vigorously and then adding a previously degassed chain extender (alkane diol), i.e., 1,4-butane diol (1,4-BDO) 99% purity (Mol. wt. 90 g/mol) at the last step. When color homogeneity was obtained in the reactant mixture, dispersion of chain extender was considered complete and the liquid polymer was cast onto a Teflon plate to form a uniform sheet of 2-3 mm thick. The synthesized PU nanocomposites were first placed under vacuum for 15 minutes to ensure the removal of air bubbles and to remove the solvent from the synthesized nanocomposites before casting and then were placed in a circulation hot air oven at 100 °C and finally cured for 24 h. The synthetic route for the synthesis of polyurethane is shown in Scheme 1. All the samples were prepared following the formulation given in Table 1. After optimizing the experimental condition,



Scheme 1. General scheme for the preparation of TDI-bentonite nano-clay based polyurethane nanocomposites.

Table 1. Sample code designation and different formation of TDI based PUNCs

Sr. No.	Sample code	Clay[a] (%)	TDI[b] (mole)	HTPB[c] (mole)	1,4-BDO[d] (mole)
1	PUNC1[e]	0.0	3.0	1.0	2.0
2	PUNC2	0.5	3.0	1.0	2.0
3	PUNC3	1.0	3.0	1.0	2.0
4	PUNC4	2.0	3.0	1.0	2.0
5	PUNC5	4.0	3.0	1.0	2.0

[a]Bentonite nanoclay. The contents (%) were calculated on the basis of total weight of the sample
[b]2,4-Toluene diisocyanate
[c]Hydroxy-terminated polybutadiene
[d]1,4-Butane diol
[e]Aromatic diisocyanate base polyurethane nanocomposite

six samples of TDI-bentonite nano-clay based polyurethane nanocomposites (PUNCs) were finally prepared varying the contents of clay. All the synthesized cured samples were then stored for one week at ambient temperature (25 °C) and 40% relative proposed humidity before testing.

2. Molecular Characterization

Molecular characterization of the monomers used in the synthesis, the intermediate compounds and the final material formed at the end of complete polymerization were confirmed using FT-IR spectroscopy. FT-IR spectra of thin films were obtained in the transmission mode using Fourier transform infra-red (FT-IR) spectrometer (Model NICOLET 6700; Thermoscientific, USA). FT-IR scans were collected on completely dried thin films cast on KBr discs from N, N-dimethylformamide (DMF) solution. The spectra covered the infrared region 4,000-500 cm^{-1}; the number of scans per experiment was 16 and resolution was 4 cm^{-1}.

3. Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) studies of TDI-bentonite nano-clay based polyurethane were performed in a JSM-6490A analytical scanning electron microscope (JEOL JAPAN), which was equipped with an X-ray detector for energy dispersive X-ray analysis (EDX). The samples were autocoated on JFC-1500 in an ion sputtering device (JEOL JAPAN) with 290A gold coating. 20 kV voltages were employed for imaging and EDX analysis.

RESULTS AND DISCUSSION

1. Structural Characterization

Fig. 2(a) and Fig. 2(b), respectively, illustrate the FT-IR spectra of toluene diisocyanate (TDI) and hydroxy-terminated polybutadiene (HTPB). The detailed peak assignment of FTIR spectra of TDI and HTPB has been comprehensively discussed in our previous study [34]. FT-IR spectrum of NCO-terminated polyurethane prepolymer (without nanoclay) has also been presented in Fig. 2(c), which clearly indicates that the signal for the OH groups is not present and that of the intensity of NCO groups has been reduced to some extent indicating that isocyanate group has entirely been reacted and a signal for NH units appeared at 3,323.6 cm^{-1} suggesting that polyurethane prepolymer had been formed. The other observed peaks in the FTIR

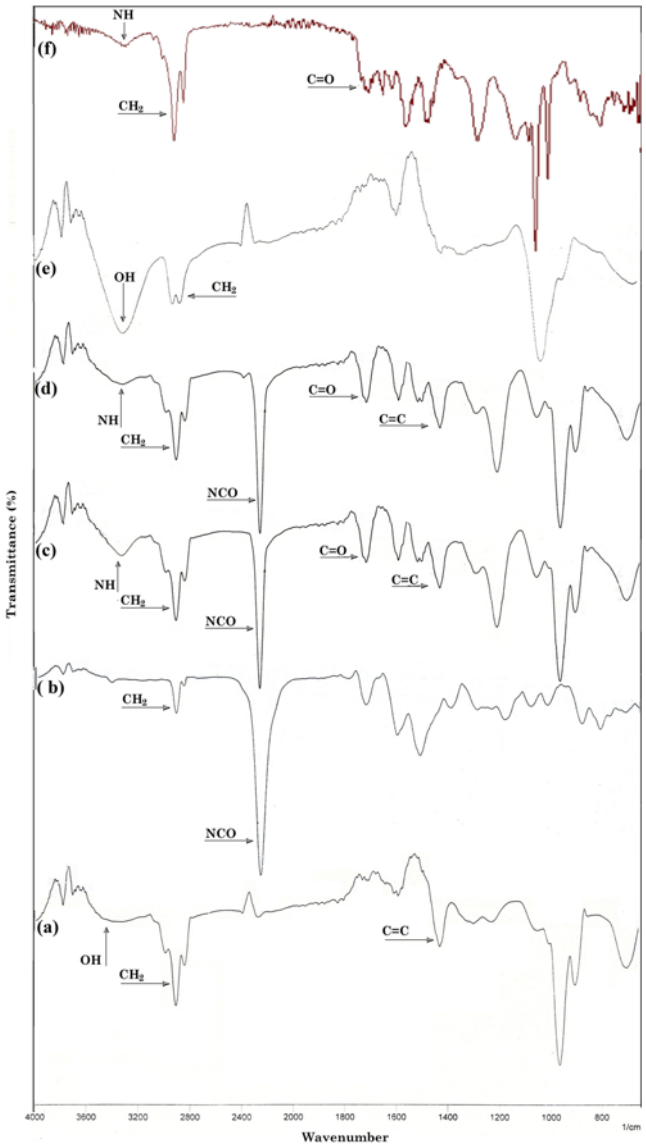


Fig. 2. FT-IR spectra: (a) toluene-2,4-diisocyanate (TDI); (b) hydroxyl terminated polybutadiene (HTPB); (c) polyurethane (PU) prepolymer without nano clay; (d) polyurethane (PU) prepolymer with nano clay; (e) 1,4 butane diol (BDO); (e) Final polyurethane (PU) with nanoclay.

spectrum of polyurethane prepolymer (Fig. 2(c)) were assigned as: 3,074.2 cm^{-1} (C-H stretching of CH_3); 2,913.4 cm^{-1} (CH_2 asymmetric stretching); 2,842.5 cm^{-1} (CH_2 symmetric stretching); 2,265.1 cm^{-1} (isocyanate (-NCO) group); 1,738.1 cm^{-1} (C=O stretching): 1,639.5 cm^{-1} (C=C stretching); 1,529.6 cm^{-1} (C=C stretching due to benzene ring); 1,435.4 cm^{-1} (CH_2 bending). Peaks corresponding to -NH at 3,323.6 cm^{-1} indicate the chemical reaction of the diisocyanate with HTPB, and the observed peak at 2,265.1 cm^{-1} due to isocyanate (-NCO) group indicates the product contains the isocyanate group at the terminated ends. These peaks provide strong evidence for the formation of NCO-terminated polyurethane prepolymer.

The FT-IR spectrum of polyurethane prepolymer, obtained by the reaction of TDI with HTPB after incorporation of bentonite nanoclay, is presented in Fig. 2(d). It is clear that the signal for the OH groups disappeared and that of the intensity of NCO groups was

reduced to some extent, indicating that the isocyanate group has entirely reacted and a signal for NH units appeared at 3,324 cm^{-1} suggesting that PU prepolymer (with nanoclay) had been formed. The other observed peaks in the FTIR spectrum of PU prepolymer were assigned as: 3,072.7 cm^{-1} (C-H stretching of C=C-H); 2,913.8 cm^{-1} (CH_2 antisymmetric stretching); 2,843.1 cm^{-1} (CH_2 symmetric stretching); 2,264.5 cm^{-1} (isocyanate (-NCO) group); 1,639.5 cm^{-1} (C=O stretching); 1,513.7 cm^{-1} (-NH deformation); 1,435.0 cm^{-1} (CH_2 bending). Peaks corresponding of -NH at 3,324.0 cm^{-1} indicate the chemical reaction of the TDI with HTPB and observed sharp peak at 2,264.5 cm^{-1} which is due to isocyanate (-NCO) group indicating the product contains the isocyanate group. These peaks provide strong evidence for the formation of NCO-terminated PU prepolymer (with nanoclay). The chain extender (1,4-BDO) was added in the final step to end the polymerization reaction. The FTIR spectrum of the chain extender is presented in Fig. 2(e). The detailed peak assignment of FTIR spectra of 1,4-BDO is presented elsewhere [34]. FT-IR spectrum obtained from the cast film (bentonite nanoclay+TDI+HTPB+1,4-BDO) is shown in Fig. 2(f). By extending PU prepolymer (having bentonite nanoclay) with 1,4-BDO, the FT-IR spectra showed a very strong, new peak at about 1,707 cm^{-1} which was assigned to C=O stretching of soft segment of HTPB. Peaks corresponding to the absorption of -NH, -CO, -CHN were

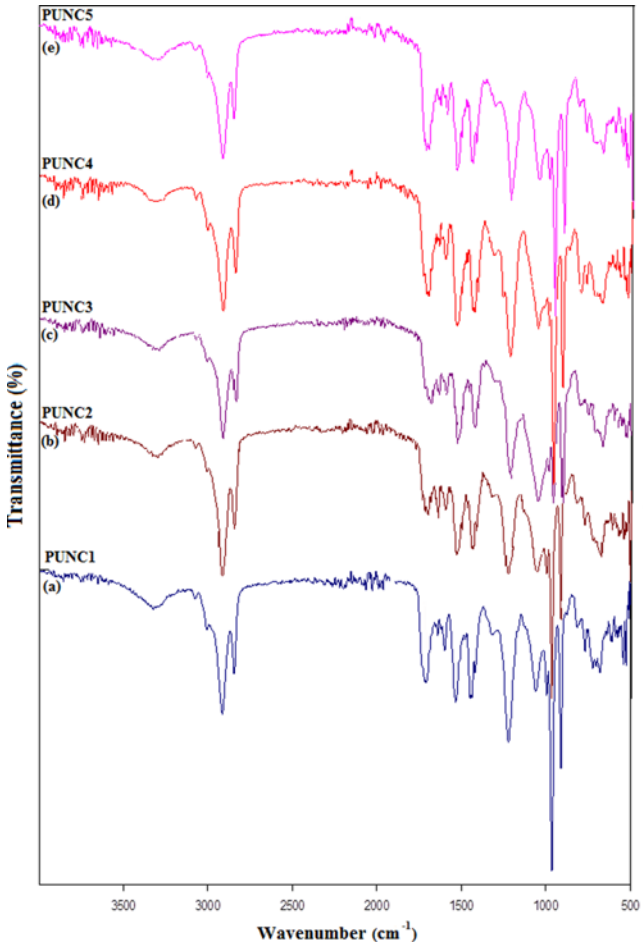


Fig. 3. FT-IR spectra: (a) PUNC1; (b) PUNC2; (c) PUNC3; (d) PUNC4; (e) PUNC5 in scattered form.

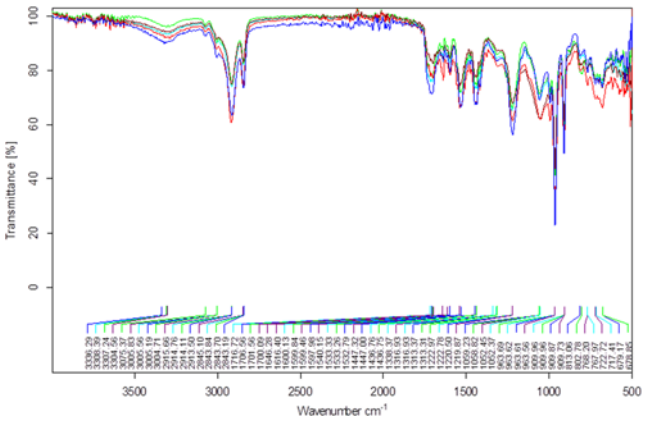


Fig. 4. FT-IR spectra of PUNC1, PUNC2, PUNC3, PUNC4 and PUNC5 in merged form.

observed at 3,289.3 cm^{-1}, 1,707.1 cm^{-1} and 1,637.8 cm^{-1}, respectively, which indicates the new synthesized product has -NHCOO group. FTIR spectra showed characteristic bands of urethane groups at 3,289.3 cm^{-1} (N-H stretching). The other peaks observed were assigned as: 2,845.4 cm^{-1} (CH symmetric stretching vibrations of CH_2); 2,917.5 cm^{-1} (CH asymmetric stretching vibrations of CH_2 groups); 1,707.1 cm^{-1} (C=O bond); 1,637.8 cm^{-1} (NH deformations); 1,589.1 cm^{-1} (CH_2 bending vibration); 1,540.1 cm^{-1} (CH bending vibration); 1,311.8 cm^{-1} (CH_2 wagging). The FT-IR spectra of polyurethane nanocomposite prepared by the incorporation of bentonite nanoclay and reaction of TDI and HTPB and further extended with the 1,4-BDO, fabricating polyurethane nanocomposites varying nanoclay percentage (i.e., 0.5%, 1.0%, 2.0% and 4.0%) are shown in Fig. 3(a)-(e), respectively. The observed peaks in the spectra of PUNC2 to PUNC5 (Fig. 3) imply that the reaction was completed and the predesigned bentonite nanoclay based polyurethane nanocomposite was formed. For comparative study, merged FT-IR spectra of polyurethane nanocomposites sample synthesized by varying bentonite nanoclay contents are presented in Fig. 4. There is no variation in chemistry of all the synthesized polyurethane nanocomposites sample; all the relevant peaks are overlapped on each other, which provides evidence about the similar chemical structure of the synthesized samples. FTIR spectra thus obtained support the proposed structure of the final polymer (Figs. 3 and 4). Note that the N-H group in polyurethane could form hard-hard segment H-bonding with the carbonyl oxygen and hard-soft H-bonding with the ether oxygen. The stronger hard-hard segment H-bonding acts as physical crosslink, leading to difficult segmental motion of the polymer chain, which results in a more significant phase separation between hard and soft segments. The phase separation improves mechanical properties of polyurethanes but reduces the flexibility and solubility.

2. Scanning Electron Microscope (SEM) Analysis

Spectroscopic methods including FTIR, UV/VIS, NMR etc. mainly emphasize the interpretation of molecular structure, but not the morphology of the polymers, whereas polymer morphology provides a great deal of information about the dispersion of the fillers in the nanocomposites and microcomposites. SEM techniques present a distinctive chance to directly visualize the morphology of the nanocomposites. The SEM images of PU nanocomposites without nanoclay (PUNC1), PU nanocomposites with 1.0% nanoclay (PUNC3)

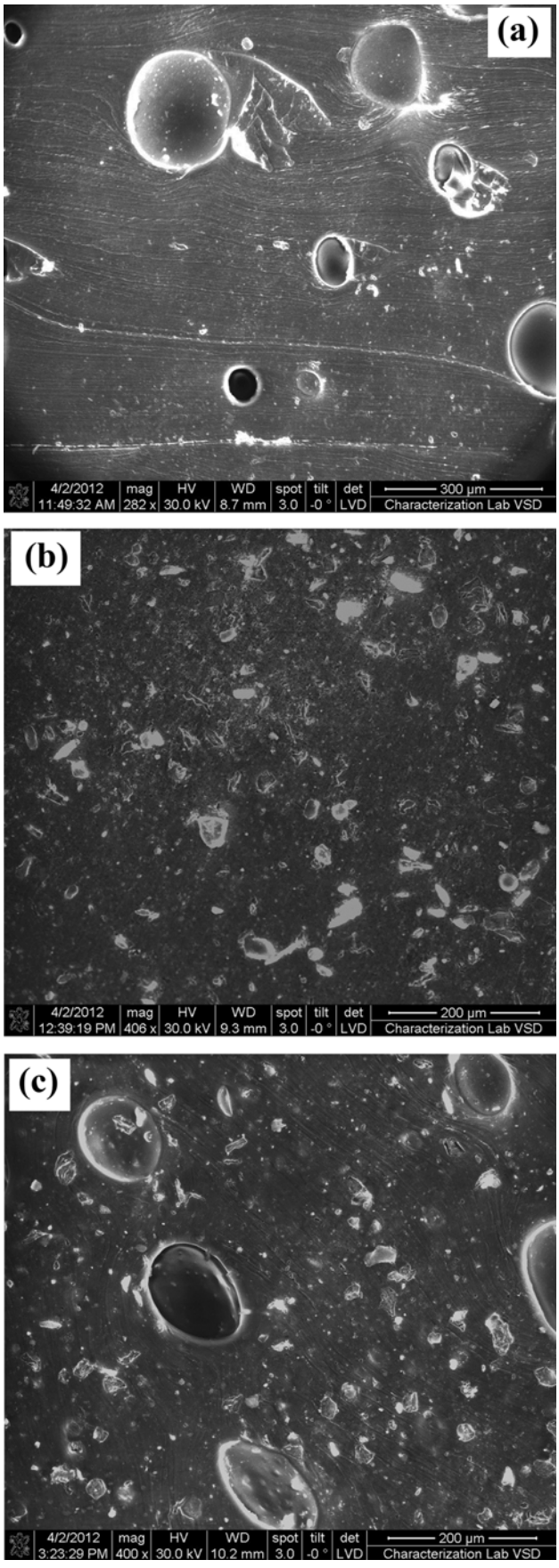


Fig. 5. Scanning electron microscope (SEM) images of (a) PUNC1; (b) PUNC3; (c) PUNC5.

and the SEM images of PU nanocomposites with 4.0% nanoclay (PUNC5) are presented in Fig. 5(a), (b) and (c). SEM images of the prepared PUNCs provided a detailed view of morphology and nanoclay dispersion in the polyurethane matrix presented in Fig. 5(a), (b) and (c). From these SEM images it is possible to study the pattern of aggregates of bentonite nanoclay in the polyurethane matrix taken at different magnifications. It is evident from Fig. 5 that the nanoclay has dispersed in the polymer matrix, which is perhaps due to good interaction between the polyurethane and the nanoclay. When the percentage of bentonite nanoclay increased from 1.0% to 4.0% by weight, the SEM images of sample PUNC3 and PUNC5 provided a detailed view of morphology and nanoscale dispersion, hence clarifying the presence of enhanced level of exfoliation. Homogeneous spatial arrangement within the PU polymer matrix and distribution of the clay is observed in the form of complete exfoliation of the nanoclay platelets. This homogeneity in dispersion of the bentonite nanoclay contents in the PU matrix will certainly help to improve the mechanical properties of the prepared blends. The clay is easily identifiable in the presented images.

CONCLUSION

Toluene-2,4-diisocyanate (TDI), bentonite nanoclay, hydroxyl terminated polybutadiene (HTPB) and 1,4-butane diol (1,4-BDO) based polyurethane nanocomposites (PUNC) were prepared. A mixture of polymer and bentonite clay enriched in montmorillonite (MMT) was formed in solution polymerization, in which MMT dispersed depending on interaction of MMT with polymer chains. FTIR spectroscopy confirmed the structure of monomers and the progress of the reaction. The SEM images confirmed the good dispersion of the bentonite nanoclay in PU matrix.

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