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Effect of nanozeolite 13X on thermal and mechanical properties of Polyurethane nanocomposite thin films

ABSTRACT

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Polyurethane/zeolite 13X nanocomposite films were fabricated using solution casting method. The synthesized nanocomposite films were structurally characterized using SEM, TGA and tensile analysis. SEM images showed appropriate distribution of nanocrystalline zeolite particles within polyurethane matrix. Better thermal stability of nanocomposite films in comparison to neat polyurethane was shown in TGA analysis. The tensile analyses were carried out for neat polyurethane (PU) and nanocomposite PU/zeolite 13X films. Adding 5 wt. % of nanozeolite 13X into the polymer matrix caused tensile strength to increase but by increasing zeolite content to 10wt. % and 20wt. % tensile strength decreased. Also, comparison of young's modulus of samples showed that the young's modulus and thus stiffness of composites increased with increasing the zeolite content. Strain at breaking point of nanocomposites decreased by increasing the zeolite content, as well.

Keywords: *Polyurethane; Zeolite 13X; Young's modulus; Nanocomposite; Tensile; Thermal.*

INTRODUCTION

In recent years, polymer/inorganic nanocomposite materials have attracted the attention of scientists due to the many superior properties [1-5]. They usually occupy the combined properties of organic polymers (e.g. flexibility, ductility, dielectric) and inorganic materials (e.g. rigidity, high thermal stability, strength, hardness) [3]. Therefore, they could be widely used in many fields such as plastics, rubbers and coatings. Generally, there are two typical kinds of organic-inorganic nanocomposites depending upon the strength or level of interaction between organic and inorganic phases: those involving physical or weak phase interaction, e.g., hydrogen bonding, van der Waals bonding, or simple mechanical mixing, and those possessing strong chemical covalent or ionic-covalent bonds between the organic and inorganic phases [3].

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Many polymer nanocomposites have been studied over the years. Due to the excellent comprehensive properties, polyurethanes (PU) are the most commonly used polymers [4]. However, the applications of PU are limited by some shortcomings such as poor heat resistance. Compared with PU, PU/inorganic composites have better properties such as tensile strength and heat resistance [1, 4-5]. It has been shown that the properties of composites depend on many factors like structure of inorganic particles; affinity and dispersion in PU. Polyurethanes are rubbery in room temperature. These polymers are usually composed of multi-phase segments, a polyether or polyester soft segment and a hard segment. Soft segment contain flexible ether and/or ester linkages and hard segment is formed by extending a terminal diisocyanate with low molecular weight diol or diamines. Incompatibility between hard and soft segment causes to microphase separated structure [6-10].

Nano particles such as zeolite, TiO₂, silica and ZnO have been introduced to modify polyurethane matrix [1, 3-4]. Zheng et al. reported that polyurethane/ZnO nanocomposites with 5 wt% ZnO nanoparticles have shown approximately 40 % decrease in the Young's modulus and 80% decrease in the strain at fracture in comparison with polyurethanes and in the case of polyurethane/Al₂O₃ nanocomposites with 5 wt% Al₂O₃ nanoparticles about 30% decrease in the Young's modulus were observed [4].

Zeolite is a kind of porous inorganic particle with strong hydrophilicity and polarity, which has a generally regular crystal surface made up of Si, Al and O. Zeolite 13X is a large-pore and high-capacity adsorbents. In addition, its pore size is 13 Å for center pore and 7.4 Å for other pores.

In this study, we focused on the preparation of polyurethane/zeolite 13X nanocomposite thin films and their mechanical and thermal properties. Polyurethane / zeolite 13X nanocomposite with physical or weak phase interaction was prepared. Up to date there are no reports about mechanical properties of polyurethane nanocomposites with high nanoparticle content. Thus polyurethane nanocomposite films with various zeolite content (5, 10 and 20 wt%) were prepared and the effect of high amount of zeolite on the properties of nanocomposites was investigated.

EXPERIMENTAL

Materials

Commercial thermoplastic polyurethane was obtained from API. *N,N*- dimethyl formamide (DMF) were purchased from Merck. Table 1 shows the properties of polyurethane and zeolite 13X.

Table 1. Properties of used commercial polyurethane and zeolite 13X

Material	Product code	Density (g/cm ³)	Hardness [A]
Poly (ester urethane)	Apilon 52-A6505	1.17	65
Zeolite 13X	283592 SIGMA-ALDRICH	1.47	-

The number of atoms in unit cell (B3C2N3NTs) was 32, 40, 48, 56, 64, 72 and 80. Monkhorst–pack mesh of k-points (1×1×6) is used for sampling the one-dimensional Brillouin zone during geometry optimization. The number of k-points was determined from convergence tests.

Preparation of polyurethane/zeolite 13X nanocomposite films

Polyurethane films and polyurethane/zeolite nanocomposite films have been prepared by solution casting and solvent evaporation method. In this method a given amount of polyurethanes were added to DMF and stirred for a period of time to obtain 3wt. % solution at 70 °C. Then the solution was casted on a glass plate after filtration and the solvents were allowed to evaporate for a period of 24 h and at 70 °C in air oven. Glass plates were covered with aluminum foil in order to prevent dust particle to contact films and the solvent evaporate more slowly. For complete removal of solvent, the film then were removed from glass plate and dried in a vacuum oven for about 5h. PU/ zeolite nanocomposites were prepared by the same method where zeolites at 5, 10 and 20 wt. % were dispersed into the solvent and stirred for a predetermined period of time and polyurethanes were dissolved in

solvent separately. Then the zeolite suspension was added to the polymeric solution. Poly (ester urethane)/zeolite nanocomposite films with zeolite content of 5, 10 and 20wt. % were prepared. Zeolite content of all nanocomposites is given in Table 2.

Table 2. Composition of the polyurethane/zeolite nanocomposites

Sample	Zeolite content (wt%)
PU	0
PU-Ze5	5
PU-Ze10	10
PU-Ze20	20

Characterization of nanocomposite films

The morphology of the nanocomposite films and the presence and proper dispersion of zeolite particles in polyurethane matrix were studied by scanning electron microscopy (SEM). The degradation temperature have been evaluated by Thermal gravimetry analysis (TGA) using SDTA851e at heating rate of 10 °C/min and the temperature range of ambient to 800 °C. Mechanical properties of composites were carried out on a Zwick/Roell Electronic Universal Testing Machine. Composites were cut into a certain shape before tested.

RESULTS AND DISCUSSION

TGA analysis

In most of the process industries, heat generation become unavoidable and good thermal resistance of the nanocomposite films has attracted the attention of scientists. Thermal behaviour of pure and composite PU was evaluated by thermo gravimetric analysis (TGA). The TGA curves of pure and composite PU films are shown in Figure 1. As shown in this figure decomposition of PU starts from 200 °C and up to 430°C and 80 to 95% of the weight of polyurethane in each sample decreases. Figure 1 also shows that by increasing the amount of zeolite in PU the slope of weight

reduction decreases. This phenomenon indicates that the thermal stability of nanocomposite films increase by increasing the amount of zeolite in polyurethane matrix. The remaining composite's weight after applying heating up to 800 C, increases by increasing the zeolite content in PU and this increment also shows the better thermal stability of nanocomposites. Remaining weight of PU are 6.28% and by addition zeolite content to 20wt% the remaining weight of PU1-Ze 20 increases to 20.66wt%.

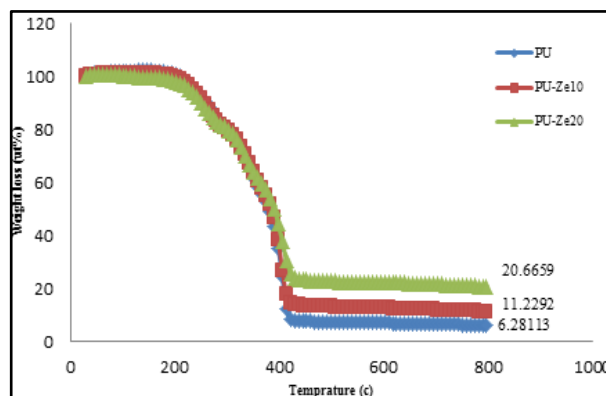


Fig. 1. TGA analysis of pure and composite PU films.

SEM investigations

The SEM images for unfilled- and zeolite-filled polyurethane nanocomposite films are presented in Figures 2 and 3. The presence and nano metric distribution of nanozeolites in polyurethane matrix are evident from the SEM micrographs.

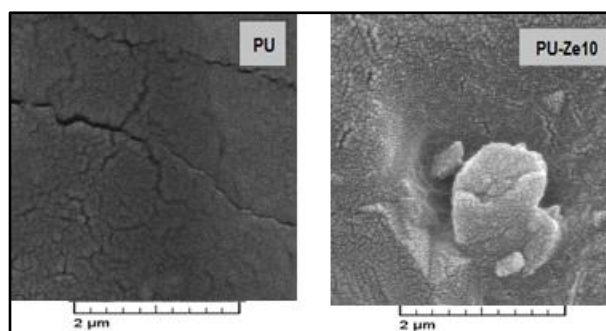


Fig. 2. SEM images of the cross sections of PU and PU-Ze10.

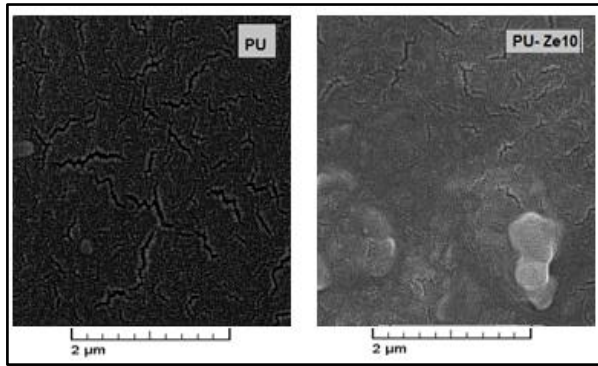


Fig.1. SEM images of the surface of PU and PU-Ze10.

Tensile analysis

As mentioned before in the past researches 3-9 wt% zeolites NaX was added to polyurethane to prepare PU /zeolite NaX nanocomposite. In this study the effect of more zeolite content on the tensile properties of PU/zeolite 13X nanocomposites has been investigated. Representative stress strain curves obtained from the tensile test are shown in Figure 4. As can be seen in this figure by increasing the amount of zeolite to 5wt% tensile strength of composite increases from approximately 10.38 to 10.65 and this phenomenon shows that mechanical resistant of polyurethane improved by addition of 5wt% zeolite 13X. But by increasing the amount of zeolite to 10 wt % and 20wt% the tensile strength decreases to 6.35 and 6.10. Thus the optimal tensile strength achieved at 5wt% zeolite 13 X. Figure 5 also shows the effect of zeolite content on tensile strength of PU nanocomposites.

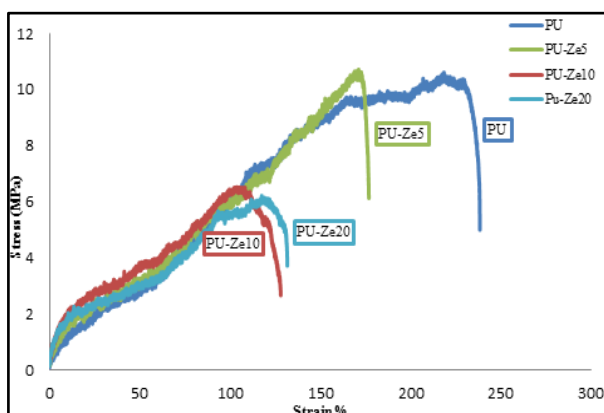


Fig. 4. Stress-strain curves of the of PU/ zeolite13X composites.

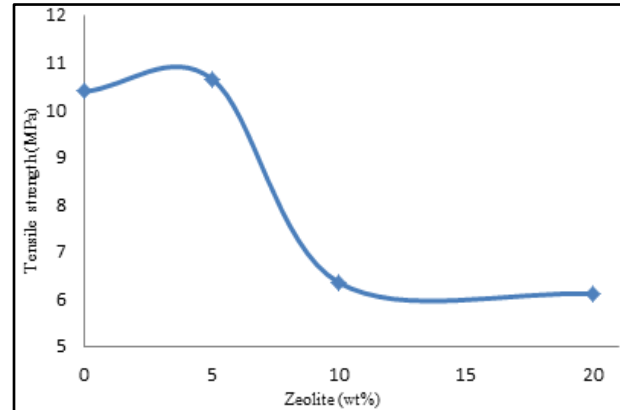


Fig. 5. The effect of zeolite 13X on tensile strength of PU/zeolite 13X nanocomposite films

As can be seen in Figure 4 by increasing the amount of zeolite young's modulus of nanocomposites increase. young's modulus is a measure of the stiffness of an elastic material and is a quantity used to characterize materials and increment in young's modulus shows increase in stiffness and this shows that the rigidity of nanocomposite increase with increasing the amount of zeolite.

Strain at breaking point of nanocomposites decreases by increasing the zeolite content as following order:

$$PU > PU-Ze5 > PU-Ze20 > PU-Ze10$$

CONCLUSIONS

The effect of zeolite 13X on the thermal stability and mechanical properties of PU/ nano zeolite X nanocomposite films was investigated in this study. PU/Zeolite composites were prepared by solution casting method. The structure of samples was characterized using SEM, TGA and tensile analysis. The obtained results from SEM show appropriate distribution of zeolite nanoparticles in the prepared composites. TGA analysis showed better thermal stability of nanocomposite films in comparison with pure polyurethane. Tensile properties of pure and nanocomposite films showed that by increasing zeolite content to 5wt% tensile strength increases and in the zeolite content of 10wt% and 20wt% tensile strength decreases. Also, comparison of young's modulus of samples showed

that the young's modulus and thus stiffness of composites increases with increasing the zeolite content. Also strain at breaking point of nanocomposites decreases by increasing the zeolite content. Therefore, it would be concluded that the PU/ (20wt %) zeolite X has the best thermal stability and the PU/ (5wt %) zeolite X has the optimal tensile strength.

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