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Research Paper

Synthesis And Characterization Of Ethylene Vinyl Acetate (Eva) / Poly Urethane Acrylate (Pua) Nano Clay Composites

Chemistry

KEYWORDS : Nanocomposies, EVA/ Poly(urethane acrylate), Clay

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ABSTRACT

Ethylene Vinyl Acetate (EVA) / Poly Urethane Acrylate (PUA) nano clay composites were synthesized by solution polymerisation technique in the presence of nanoclay (cloisite 25A) at different weight percentages. The nanocomposites were compression molded and tough films were produced. The phase morphology and physical properties of the nanocomposites were investigated using optical microscope and tensile studies. The hydrogen bonding interaction and micro domain structure of the nanocomposites are discussed based on Fourier-transform infrared spectrophotometer (FTIR), and nuclear magnetic resonance spectrophotometer (FT-NMR). The improvements in the tensile property of the EVA/poly (urethane acrylate) nanocomposites were observed.

INTRODUCTION

In recent years, polymer/clay nanocomposites attracted my researchers to concentrate on polymer composites because of its remarkable property improvements such as enhanced tensile properties, decreased gas permeability, decreased solvent intake, increased thermal stability and flame retardancy in comparison with conventional polymers1. Nanocomposites are a new class of composites having the dispersed particles in nanometer scale. 2-3 Polymer / clay composites are called as nanocomposites due to the nano scale clay. It reported that the morphologies and physical properties for various Urethane Acrylate systems were studied and and reported that reviewed in detail.4-6 EVA is used in applications due to flexibility, low strength and high permeability. The strength and permeability can be modified by adding layered nanomaterials like clay. EVA copolymer based nanocomposites were reported to have enhanced properties.7

The combination of ethylene vinyl acetate copolymer with nanoclay reported to have less crystallinity and has many commercial applications.8 Polypropylene, poly (ethylene oxide), poly (methyl methacrylate), poly (N-vinyl carbazole), polyurethane were synthesized and characterized and reported for enhanced properties.9 Based on this background, nanocomposites of EVA and poly (urethane acrylate) were prepared by solution polymerisation technique and their extent of interaction were investigated using FT-IR, FT-NMR, mechanical and morphological studies.

2. MATERIALS AND METHODS

Commercially available EVA-12 (PILENE 1202), 2 - hydroxyethyl methacrylate (HEMA), azoisobutyronitrile (AIBN), Isophorone-diisocyanate (IPDI) Dibutyltin-dilaurate (DBTDL), Cloisite 25A from southern clay, USA were dried in a hot air oven at 80° C for 6 hours and the moisture contents were removed. Urethane acrylate oligomer was first prepared by reacting 2-hydroxyethyl methacrylate (HEMA) and Isophorone - diisocyanate (IPDI) in the molar ratio 0.02 : 0.01 at a temp 40°c with reflux condenser. Ethylene vinyl acetate was taken in a three-necked reaction kettle and dissolved in chloroform. After swelling of EVA in chloroform calculated quantity of cloisite 25A and 2-hydroxyethyl methacrylate (HEMA) were added. IPDI was added drop wise and Urethane acrylate oligomer was produced. AIBN was used as a radical initiator. The reaction mixture was heated at 85°c for 4 hours under nitrogen atmosphere. The emulsion was poured into a Teflon mould. The EVA/poly (urethane acrylate) nanocomposite film was produced. The experimental was repeated by different weight percentage of nanoclay content.

2.1 FT-IR ANALYSIS

Thin films were cast from the dried EVA/poly (urethane acrylate) nanocomposites over glass plates for FT-IR studies. The films were taken out without distortion and FT-IR spectra were recorded using Nicolet impact 400 FT-IR spectrophotometer.

2.2 FT-NMR ANALYSIS

High-resolution 1 H &13 C-NMR spectra were recorded using a Brucker MSL 300P, 300MHz FT-NMR spectrophotometer. Deuterated chloroform (CDCl3) was used as solvent for recording NMR spectra.

2.3 MECHANICAL STUDIES

Tensile properties were studied using a UTM universal testing machine (Instron-3369, UK). A load of 100N was applied at a cross head speed of 50mm/min. The dumb-bell type specimens, 15 mm wide at the two ends and 10mm wide at the neck with thickness ranging from 1.1 to 2.9mm were used for the investigation. All the measurements were carried out as per ASTM standard test methods.10

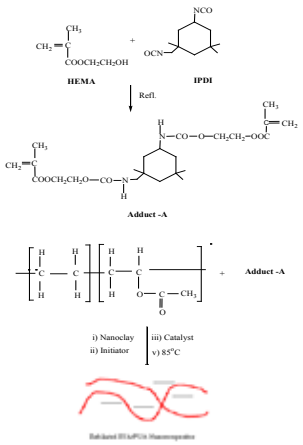
2.4 MORPHOLOGICAL STUDIES

Morphological features were investigated using Olympus BX 50 optical microscope with a magnification at 100x. Nanocomposite films were placed between two thin glass plates and photographs were taken using a Pentax 35 mm camera.

3. RESULTS AND DISCUSSION

Synthetic routes and structure for EVA/Poly (urethane acrylate) nanocomposites are shown in scheme-1. The hydroxyl group of HEMA and the NCO group of IPDI were combined and urethane acrylate adducts were produced and polymerized with EVA, nanoclay and initiator at 85°c for 4 hours to yield the EVA/Poly (urethane acrylate) nanocomposites.

(Scheme – 1)



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The codes and the compositions of the polymer nanocomposites are given in the table-1.

The FT-IR spectra of urethane acrylate adduct, EAU, EAU-1, EAU-3, EAU-5, EAU-7, EAU-9, EAU-12. The peak at 1533 cm-1, absent in HEMA and IPDI, was assigned to the NH bending vibration of urethane acrylate produced by reaction of the NCO and OH group. A series of bands around 1390 - 1150 cm-1 were recorded indicating -CH2- bending. The peak at 660 cm-1 was responsible for C-H vibration of aromatic ring. The symmetric and asymmetric stretching of the –CH2 group of urethane acrylate are observed from 3000-2750 cm-1 .A characteristic band at 1721 cm-1, associated with the C° O stretching of acrylate. The peak at 797 cm-1 in IR spectra of the polymer nanocomposites confirmed the rocking vibration of the methylene group. The peak observed at 1050-1300 cm-1 may be related to C=O stretching vibration of ester group.11

From the 1H-NMR spectrum of UA oligomer and EAU, it is clear that the peaks were due to the different kinds of protons ie, δ = 1.0 (H-1H, S, 3H), 4.28 (H-2H, m, 2H), 5.58(H-3H, S, 1H), 6.1 (H-4H, w, 1H) and the protons on phenyl skeletal at δ = 7.25 the formation of NH produced absorbencies at 4.7-5.2 ppm (fig-1).

The tensile strength (TS) and elongation at break (EB) of the EVA/PUA nanocomposites films were increased with increasing clay content (table- 1). The filler particle reduces the molecular mobility of polymer chains, resulting in a less flexible material with a higher tensile strength.12-16 Furthermore, the final conversation of the nanocomposites increased with increasing clay content, resulting in a higher cross-linking density of the polymer matrix with a high tensile strength. The increase in the TS and EB of nanocomposites confirms that EVA-12 was strengthened and toughened simultaneously by the incorporation of 5% nanoclay dispersed homogeneously in the EVA-12 matrix. It was observed that the (TS) and (EB) start to decrease with further increase in the nanoclay content in the composites. This decrease in the TS and EB of the composites may probably be due to the aggregation of the nanoclay particles causing a weak interaction between the nanoclay layers and the EVA-12 chains.17-19 Sample EAU -5 exhibits the highest tensile strength and elongation at break over all the nanocomposites synthesized.

The optical microscope image of EVA clearly shows the presence of nanoclay particles dispersed homogeneously within the EVA matrix as very small white spots. This concludes that the hybrids synthesized were on the nanometer scale.

Table - 1

Composition and properties of EVA/PUA incorporated with clay nanocomposites

Sample code	Mole ratio of HEMA:IPDI	EVA-12 (g)	Nanoclay(g)	Stress Max. load (MPa)	Strain (%)	Elongation (%)	Thickness
EAU	0.005:0.005	7	1.05	0.82	4.38	1.75	1.2
EAU-1	0.005:0.005	7	0.0816	0.65	3.30	1.32	1.2
EAU-3	0.005:0.005	7	0.2598	2.41	3.58	1.43	1.2
EAU-5	0.005:0.005	7	0.4330	5.25	4.57	1.82	1.2
EAU-7	0.005:0.005	7	0.6062	1.33	5.73	2.29	1.2
EAU-9	0.005:0.005	7	0.7794	1.34	2.36	0.94	1.2
EAU-12	0.005:0.005	7	0.0391	4.31	3.70	1.48	1.2

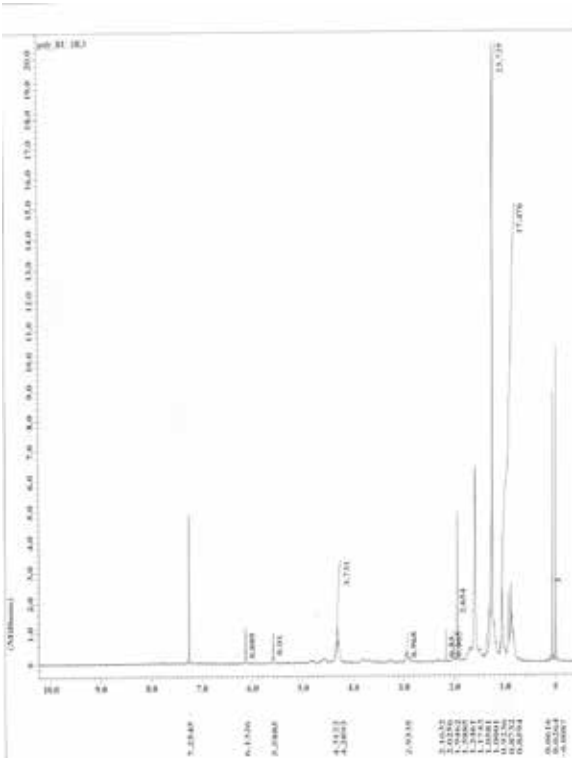

Figure-1

4. CONCLUSION

EVA/Poly (urethane acrylate) nanocomposites were synthesized by solution polymerization techniques. All the nanocomposites were obtained as tough films. The properties of nanocomposites were enhanced with clay content, resulted in a higher cross-linkage with a high tensile strength. The effect of clay interaction on the micrograph and tensile properties of the nanocomposites has been described. Tensile strength and elongation at break increase with increasing clay content. The structural information was carried out by FT-IR, FT-NMR. The peak at 797 cm-1 in IR spectra of the polymer nanocomposites confirmed the rocking vibration of the methylene group. The peak observed at 1050-1300 cm-1 may be related to C=O stretching vibration of ester group.

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