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VEGETABLE OIL BASED HYPERBRANCHED AND CONVENTIONAL RESINOUS POLYURETHANE/CLAY THERMOSETTING NANOCOMPOSITES

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Abstract : *Hyperbranched thermosetting polyurethanes have been prepared by pre-polymerization technique using poly(ϵ -caprolactone) diol (PCL) as macroglycol, monoglyceride of *Mesua ferrea l.* seed oil as chain extender, and glycerol as the trifunctional polyol with toluene diisocyanate (TDI) followed by crosslinking with epoxy resin in presence of poly(amido amine) hardener as reported earlier. Similarly, the conventional resinous polyurethane thermoset was prepared by using monoglyceride of the same oil with same isocyanate and polyethylene glycol, and cured by the same system as reported earlier. These polyurethanes were used to prepare PU/clay nanocomposites using different doses of organically modified nanoclay by ex-situ solution technique using industrially used solvent, xylene. The formation of nanocomposites with well-dispersed clay layers is confirmed from FTIR, XRD and SEM studies. Significant improvement of mechanical, chemical and thermal properties of these nanocomposites compared to pristine polymers in both the cases was observed. The results confirmed the advantages of using hyperbranched polyurethane over the conventional polyurethane resin.*

Introduction :

Due to the rapid depletion of petroleum based feed stocks and ever increase of environmental awareness, the utilization of vegetable oils as renewable resources is gaining importance in the field of polymers in addition to other fields. Polyurethane is a versatile polymeric material, which gains popularity that has been sustained as a direct consequence of its structural molecular non-homogeneity (hard and soft segments). Further, this versatility will be more meaningful when it is derived from renewable vegetable oils. Various vegetable oils such as castor, linseed, soybean, canola, corn, sunflower, palm, rapeseed, etc. have been reported to be employed to synthesize different categories of polyurethanes. Oil extracted from the seeds of *Mesua ferrea l.*, a plant available in North East India, is utilized in the preparation of a few polymers from the same laboratory¹⁻².

Highly branched non-linear dendritic polymers like hyperbranched polymers have been received great attention in present time for their unique architectural features and properties. These macromolecules exhibit lots of outstanding properties like high solubility, low melt and solution viscosity, high reactivity, etc. because of the highly functionalized three-dimensional globular non-entangled structure. In addition, single step processes can be adopted to prepare

hyperbranched polymer which indicates its great potentiality for large scale production at a reasonable cost for industrial applications³. A large number of reports are available on the synthesis and characterisation of hyperbranched polyurethanes³. However, there is only a very few scattered reports on the development of hyperbranched polyurethanes from vegetable oils⁴.

Polymer nanocomposites are attracting a great deal of attention from academicians and scientific communities for their versatility in diversified applications. The nano-scale dispersion of inorganic nanofillers particularly layer silicates in organic polymer matrix and almost molecular level interaction between the filler and the matrix make the nanocomposites as one of the frontier materials. The higher modulus, strength, heat resistance, chemical resistance, flame retardancy etc. and lower gas permeability, elongation etc. are due to the synergistic effect between organic and inorganic components in the nanocomposites compared to pristine polymers. However, such improvements in physical and mechanical properties depend on the extent of intercalation or exfoliation between the layered nanofillers and the organic polymer. Even though lot of studies have been carried out on thermoplastic but research on development of thermosetting polyurethane/nano clay nanocomposites are difficult to find. As epoxy can cure and form compatible system with polyurethane, so epoxy cured polyurethanes are finding a growing interest for applications in composites due to the increase of demand for light weight, durable and cost effective compounds for various fields⁵.

In the present study, *Mesua ferrea l. seed oil* (MFLSO) based epoxy modified hyperbranched and conventional resinous polyurethane thermosets nanoclay nanocomposites have been reported at different loadings. The performance like mechanical, thermal, chemical, etc. have been studied for both the systems and compared.

Materials and Methods :

Materials

Mesua ferrea l. seeds (Assam, India) were utilized to extract the oil. Poly(ϵ -caprolactone) diol (PCL, Solvay Co., $M_n = 3000$ g/mole), poly(ethylene glycol) ($M_n = 200$ g/mole), and glycerol (Merck, India) were used after proper drying. Organically modified bentonite clay (Sigma Aldrich), bisphenol-A based epoxy resin (viscosity – 450-650 mPas at 25 °C, epoxy equivalent – 182-192 g/eqv) and poly(amido amine) hardener (Ciba Gigy, Mumbai) were used without any further modification. Toluene diisocyanate (TDI) and dibutyl tin dilaurate (DBTDL) (Merck, Germany), xylene and lead mono-oxide (Merck, India) were used as received.

Preparation of polyurethane-ester (PUE)

The polyurethane-ester resin (PUE) with NCO/OH ratio 0.5 was prepared as reported earlier by taking TDI and monoglyceride of *Mesua Ferrea l.* seed oil along with polyethylene glycol (PEG) as chain extender, DBTDL as catalyst and xylene as the solvent⁶.

Preparation of hyperbranched polyurethane-ester (HBPUE)

The hyperbranched polyurethanes was prepared by earlier reported method using poly(ϵ -caprolactone) diol, monoglyceride of *Mesua ferrea l.* seed oil and TDI to prepare the pre-polymer followed by completion of polymerization with glycerol in xylene⁷.

Mixing of PUE and HBPUE with epoxy

The epoxy modified systems were prepared by mixing PUE and HBPUE (35-40 % solid content in xylene) with epoxy resin and poly(amido amine) hardener (50 wt% with respect to epoxy resin) separately in the proportion of polymer:epoxy::50:50 and 80:20 respectively. The mixing was carried out with constant vigorous stirring for about half an hour at (30 \pm 1) °C.

Preparation PUE/HBPUE bentonite nanocomposites

Desired quantity of the bentonite clay particles (1.0%, 2.5% and 5.0% by weight) were allowed to swell in minimum amount of xylene for ca. 3h followed by mixing with the epoxy modified PUE or HBPUE system separately by constant stirring and then homogenized by applying ultrasound with the help of a ultrasonicator for ca. 30 min.

Fabrication of nanocomposite

The thin films of both the series of nanocomposites (PUE and HBPUE based) were prepared by drawing the homogeneous mixture of the solutions on glass, tin and mild steel plates using a micro adjustable thickness gauge (Sheen Instrument Ltd., UK) under ambient conditions. After removal of sufficient amount of solvent under atmospheric conditions, the coated strips were degassed under vacuum at (45 ± 5) °C for 45 minutes to remove the last trace of solvent and volatile compounds. Then the coated nanocomposites were cured by heating at 120 °C in an oven for specified time periods. The cured nanocomposites were kept under ambient conditions for 24h. Then the dried films were peeled off from the glass plates by immersing the plates in warm water. The films were kept in a desiccator under vacuum and stored for 7 days before testing.

Results and discussion :

Characterization :

No noticeable change in characteristic bands has been observed from the FTIR spectra of epoxy cured PUE and HBPUE nanocomposites on incorporation of nano clay. This indicates that the curing mechanism of the polymer was not influenced significantly by nanoclay loading.

The nanocomposite formation was characterized by XRD and SEM analyses. From the XRD patterns, it has been seen that the interlayer spacing of the nanoclay layers increases from 3.5 nm in pure clay to ca. 5.9 nm in PUE nanocomposites (Fig.1). This is due to intercalation by polymer chains into the inter-gallery region of clay layers. Interestingly for HBPUE nanocomposites, no peaks were observed which may indicate the formation of exfoliated structure (Fig. 1). However, the extent of intercalation or exfoliation was found to be not significantly dependent on percent of clay loading.

SEM micrographs were taken to have an idea about the dispersion of bentonite clay into the epoxy modified PUE and HBPUE matrices. The SEM pictures of the fractured surfaces of both the nanocomposites show smooth and systematic patterns which indicate well dispersed clay layers in the polymers.

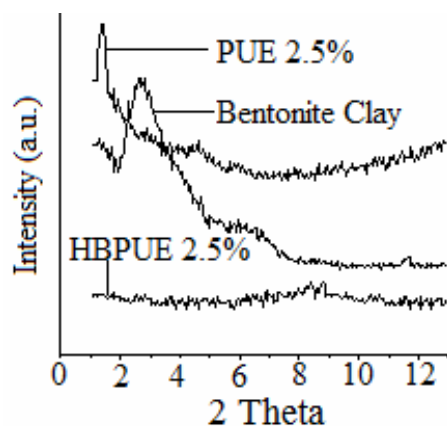


Figure (1) : XRD patterns of the nanocomposites and nano clay.

Performance Characteristics :

The tensile strength (TS) and scratch hardness (SH) of the PUE and HBPUE nanocomposites were found to be significantly enhanced as compared to that of the pristine polymers (Table 1). This enhancement arises mainly from the increase of interactions with bentonite nano clay due to its high surface to volume ratio which increases bridge, tail and loop interactions with the polymer system⁸. However, the values of elongation at break (EB) were found to be decreased with clay content which may be due to the molecular restriction of the polymer chain by bentonite layers. However, the impact strength (IS) values were found to be remained almost intact in nanocomposites (Table 1). Thus the performance characteristics of the HBPUE nanocomposites were found to be better in comparison to the PUE nanocomposites.

The TG analysis of the PUE/HBPUE nanocomposites showed almost one step degradation. All the nanocomposites possess higher thermal resistance than the pristine polymers as indicated by increase in initial degradation temperature of ca. 60⁰C in the PUE nanocomposites and ca. 40⁰C in the HBPUE nanocomposites (Table 2). Furthermore, the weight residue was found to be slightly more for HBPUE nanocomposites (ca. 7-12%) than the PUE counterparts (ca. 6-10%). This high thermostability of the nanocomposites is due to the fact that the motion of the polymer chains in the bentonite layers are more restricted, nano clay causes a thermal barrier and generates more char during the thermal degradation process⁸.

TABLE (1) : Properties of pristine polymers and their nanocomposites

Property	PUE Nanocomposites				HBPUE Nanocomposites			
	0%	1%	2.5%	5.0%	0%	1%	2.5%	5.0%
TS (MPa)	15-18	20-22	25-28	31-33	29-32	34-36	37-41	39-42
EB (%)	20-23	17-19	5-7	3-4	500	440	430	420
IS (cm)	58-61	60-62	62-63	61-64	88-92	90-94	92-96	92-96
SH (kg)	3-5	5-6	7-8	8-9	4-5	8-9	9-10	10-11
Bending (mm)	<3.0	<3.0	<3.0	<3.0	<5.0	<5.0	<5.0	<5.0
Gloss	79-82	78-79	77-78	78-80	79-80	77-78	76-77	76-77

TABLE (2) : Decomposition temperatures and weight residue of pristine polymers and their nanocomposites

Code of nanocomposite	0% decomposition	50% decomposition	90% decomposition	Weight residue at 650 ⁰ C (%)
PUE0%	180	320	515	3
PUE1%	220	325	523	6
PUE2.5%	231	328	532	8
PUE5%	240	332	545	10
HBPUE0%	243	456	593	2
HBPUE1%	247	459	607	7
HBPUE2.5%	255	468	620	9
HBPUE5%	262	472	627	12

The studies on chemical resistance in different chemical media indicate better resistance of nanocomposites than pristine polymers in both cases.

Conclusions :

From this study it can be concluded that the formation of epoxy cured thermosetting polyurethane clay nanocomposites is a pave of enhancement of performance of the polymer. Even very low loading (1-5 % by weight) of nano clay generates significant improvement of tensile strength, scratch hardness and thermostability with the impact resistance intact.

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