Shape-Memory Property and Characterization of Epoxy Resin-Modified *Mesua ferrea* L. Seed Oil-Based Hyperbranched Polyurethane

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ABSTRACT: Modification of existing polymers leads to enhancement of many desirable properties. So, a hyperbranched polyurethane (HBPU) of monoglyceride of *Mesua ferrea* L. seed oil, poly(ε-caprolactone)diol (M_n = 3000 g mol^{-1}), 2,4-toluene diisocyanate, and glycerol with 30% hard segment (NCO/OH = 0.96) has been modified with different amounts of bisphenol-A based epoxy resin. The system is cured by poly(amido amine) hardener at 120°C for specified period of time. Improvement of thermostability, scratch hardness, and impact strength are observed by this modification of HBPU. The differential scanning calorimetry (DSC) results show improvement of melting temperature of the modified systems. The enhancement of tensile strength is about 2.4 times compared with that of the unmodified one. The morphology and structural changes due to variation of epoxy content was studied by scanning electron microscopy (SEM) analysis and Fourier transform infrared (FTIR) spectroscopy. The rheological properties of the epoxy-modified HBPU show the dependence on the amount of epoxy resin. Shape memory study of the crosslinked HBPUs shows 90–98% thermoresponsive shape recovery. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 106–115, 2010

Key words: hyperbranched polyurethanes; high-performance polymers; mechanical properties; thermal properties; rheology

INTRODUCTION

Polyurethane (PU) is one of the most versatile polymers as a range of polymeric systems starting from coating to fibers, including thermoplastic, thermosetting, adhesive, leather, etc.,[1,2] are known to be used in a large scale. This can be done just by variation of composition and structure of its three basic building blocks: macroglycol, diisocyanate, and chain extender.[3] It is also possible to achieve by physical modification, blending or via interpenetrating network formation with other polymers.[4] PU has a number of excellent properties, depending on the structural composition of hard and soft segments,[5,6] which makes it one of the most fascinating polymers of recent times. Epoxy resin, which has good mechanical, chemical, thermal, and dimension stability,[7] possesses strained and reactive oxirane rings. It has a good ability to mix and can cure PU in the presence of a base,[8] and so it is used to modify PUs.

Epoxy-modified linear PU systems are proven to be interesting because of their ease of modification, high flexibility in formulation and improvement of thermostability, mechanical and adhesion properties, and weather resistance.[9] Therefore, it is expected that the epoxy-modified vegetable oil-based hyperbranched PU (HBPU) can also result in significant enhancement of various properties.

The fluctuating price and ever dwindling reserves of crude oil strongly insist researchers to search for alternative potential raw materials.[10,11] So in the present investigation monoglyceride of *Mesua ferrea* L. seed oil (Nahar oil), a nonedible vegetable oil has been used as a chain extender for the preparation of HBPU. Hyperbranched polymers are emerging as advanced potential materials for their unique and inimitable structure and properties. However, the major drawback of these three-dimensional highly branched novel polymers is their poor mechanical strength.[12,13] However, in some recent studies, improvement of mechanical strength has been reported by incorporation of long-chain reactant.[14,15] The currently studied HBPU also has a long chain, containing macroglycol, poly(ε-caprolactone)diol (M_n = 3000 g mol^{-1}).

Again, because of phenomenal combination of soft and hard segments of PUs, they are largely used as

shape-memory polymers in many avant-garde applications such as biomedicals, aerospace, automobile, and smart textile. Such thermosensitive polymers can fix the deformation without external load by cooling and recover the original shape on heating above their transition temperature. Hyperbranched PUs have some added advantage over the conventional linear analogs,[16] and so in the present study, the shape-memory property of epoxy-modified HBPU has been studied. As far as shape memory of epoxy-modified vegetable oil-based HBPUs is concerned, it is the first report to the best of our knowledge.

The authors, herein, wish to report the performance characteristics of epoxy-modified HBPUs at different compositions. The thermoresponsive shape-memory behavior of these modified polymers is also investigated.

EXPERIMENTAL

Materials

Nahar seeds were collected from Darrang, Assam. This seed oil is a nondrying oil available in different countries such as India, Bangladesh, Sri Lanka, and some European countries. It possesses 18 carbon containing oleic (52.3%, one unsaturation at ninth position) and linoleic (22.3%, two unsaturation at ninth and 12th positions) acids as unsaturated fatty acids and 16 carbon containing palmitic (15.9%) and 18 carbon containing stearic acids (9.5%) as saturated fatty acids. Glycerol (Merck, Mumbai) and poly(ε-caprolactone)diol (PCL, Solvay Co., Korea, $M_n =$ 3000 g mol^{-1}) were used after drying at 40°C under vacuum for 4 h. Lead monoxide (S.D. Fine Chemical Ltd., Mumbai) and 2,4-toluene diisocyanate (TDI, Sigma Aldrich) were used as received. N,N-dimethylformamide (DMF, Merck, Mumbai) was dried over CaO, vacuum distilled, and kept in 4A-type molecular sieves before use. The epoxy resin, a glycidyl bisphenol-A-based epoxy (product of epichlorohydrine and bisphenol-A) with epoxy equivalent of 182–192 g/equivalent and poly(amido amine) hardener (Ciba Geigy, Mumbai) were used as supplied. The viscosity of poly(amido amine) hardener is 10,000–25,000 mPa s, and the amine value is 6.6–7.5 equiv/kg. Other reagents are reagent-plus grade and used without further purification.

Instruments and methods

By solvent-extraction method, the oil was collected from the Nahar seeds and it was purified subsequently by alkali refining technique.[17] Fourier transform infrared (FTIR) spectra of the epoxy-modified PUs were recorded after and before curing by a Nicolet (Madison, USA) FTIR Impact 410 spectroscopy using KBr pellets. The molecular weights of polymers were determined by gel-permeation chromatography (GPC) analysis (Waters, USA, Model 515) using tetrahydrofuran (THF) as the solvent, ultrahydrogel column, and polystyrene as the standard. The thermal stability was studied by a Simadzu, USA, thermal analyzer, TG 50 at 10°C min^{-1} heating rate under the nitrogen flow rate of 30 mL min^{-1}. The differential scanning calorimetry (DSC) analysis was performed by DSC 60, Simadzu, at heating rate of 3°C min^{-1} from −50 to 200°C under nitrogen flow rate of 30 mL min^{-1}. The surface morphology of the films was studied by JEOL scanning electron microscope, JSM-6390LV SEM, after platinum coating on the surface. The measurement of specific gravity, sol fraction, curing time, impact resistance, scratch hardness, and flexibility (bending) was performed according to the standard methods.[18–22] The percent of swelling was determined in DMF solvent at two different temperatures (25 and 60°C) under equilibrium conditions. The mechanical properties such as tensile strength and elongation at break were measured with the help of universal testing machine (UTM) of model Zwick Z010, Germany, with a 10-kN load cell and crosshead speed of 20 mm min^{-1}. The X-ray diffraction (XRD) study was carried out at room temperature ($\sim$ 25°C) by a Rigaku X-ray diffractometer (Miniflex, UK). The scanning rate used was 2.0 min^{-1} over the range of $2\theta = 10$–$60°$ for the above study. Ultrasonicator (200S, Heishler, Germany) was used to mix the epoxy resin with HBPU at 45% A power and continuous cycle for 10 min. Rheometric study of the solution of epoxy-modified PUs [20% solid content (w/v) in DMF] was done with the help of Malvern CVO100, UK, with a parallel plate of 20 mm diameter (PP20). The study was carried out at controlled stress of 10 Pa under the variation of frequency 1–100 Hz at 25°C. For all the experiments, the gap size was maintained at 150 μm.

The shape recovery of the samples was measured by first heating at a specified temperature (50, 60, and 70°C) for 5 min, they were stretched to twice the length of the original length (l_0), and the stretched length is denoted as l_1. Immediately, the stretched samples were put in the ice water bath (2–3°C) for 5 min to release the stretch, and the length was measured as l_2. The cooled samples were reheated to the same temperature for the same period of time, and the length obtained is denoted as l_3. The percentage retention and percentage recovery were calculated by the following equations at different temperatures.

$$\%\text{Retention} = [(l_2 - l_0)/l_0] \times 100 \qquad (1)$$

$$\%\text{Recovery} = [(l_1 - l_3)/l_0] \times 100 \qquad (2)$$

TABLE I
Composition and Curing Time of the Modified Systems at 120°C

Code[a] of the cured system	Hyperbranched polyurethane (wt %)	Epoxy (wt %)	Touch-free time (min)	Drying time (min)
MHBPU	100	0	–	–
MHBPU5	100	5	25	60
MHBPU10	100	10	20	55
MHBPU20	100	20	15	45

[a] Indicates the weight percent amount of the epoxy resin.

PREPARATION OF THE HYPERBRANCHED PU AND ITS MODIFICATION WITH EPOXY RESIN

Preparation

The details of the synthesis of the HBPU with 30% hard segment (NCO/OH = 0.96) were reported earlier.[23] 2.5 mol of poly(ε-caprolactone)diol, 1.5 mol of monoglyceride of the Nahar oil, and 6.5 mol of TDI were used in the first stage to prepare a prepolymer, and finally, glycerol of 2.5 mol was added to the prepolymer to get the HBPU in DMF. The polymer was obtained as a solution of 25–30% solid content (w/v) in DMF with 97% yield.

Modification

The HBPU 25–30% solid content in DMF was mixed with epoxy resin (100% solid content) and poly(amido amine) hardener (50% by weight with respect to the epoxy resin) in the ratio as given in Table I. A vigorous and thorough stirring by mechanical stirrer at room temperature for about half an hour followed by ultrasonication for 10 min was performed for proper homogenization of the components. Finally, the modified HBPU films were obtained by solution casting, followed by vacuum degassing and curing at specified time and temperature for further testing and analysis.

Sample preparation for performance studies

The mild steel strips of $150 \times 100 \times 1.44$ mm^3 were coated by the polymer solutions for impact resistance and scratch hardness studies. Similarly, thin strips of $150 \times 50 \times 0.19$ mm^3 were coated for bending test. The coating thickness of the films was found to be in the range of 60–70 μm as measured by a Pentest coating-thickness gauge (Model 1117, Sheen Instrument Ltd., UK). For mechanical test, the casted cured films were cut by the manual sample cutter with dimension as per the ASTM D 412-51T and were stored for 7 days before testing.

RESULTS AND DISCUSSION

The weight average molecular weight and polydispersity of the prepared HBPU (Fig. 1) are 5.28×10^4

g mol^{-1} and 2.42, respectively, as measured by GPC. From the structure of the polymer, it is clear that the polymer is highly branched and possesses large numbers of functionalities. These functional groups may take part in crosslinking reactions during curing with epoxy resin in the presence of poly(amido amine) hardener.[24]

Curing study

The touch-free time (minimum time required by the system to resist impression on touching its surface by thumb) as well as drying time (determined by indenting the cured film by an indenter) was found to be decreased with the increase of amount of epoxy resin and poly(amido amine) hardener at 120°C as shown in Table I. This can be easily understood from the proposed crosslinking mechanism (Scheme 1). The surface —OH groups of the HBPU are crosslinked by the epoxy groups of epoxy resin in the presence of poly(amido amine) hardener.[24] As the amount of epoxy resin and hardener increases, the number of strained oxirane and reactive amino
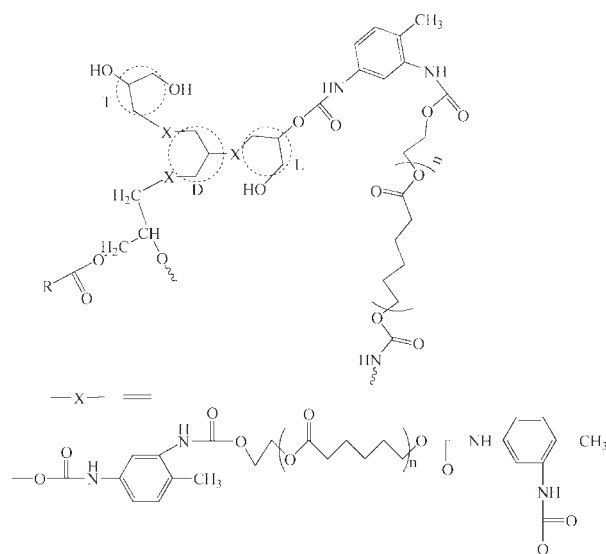
R Mixture of hydrocarbon parts of oleic, linoleic, stearic and palmitic acid

D– dendritic unit, L– linear unit and T– terminal unit

Figure 1 Proposed structure of HBPU.
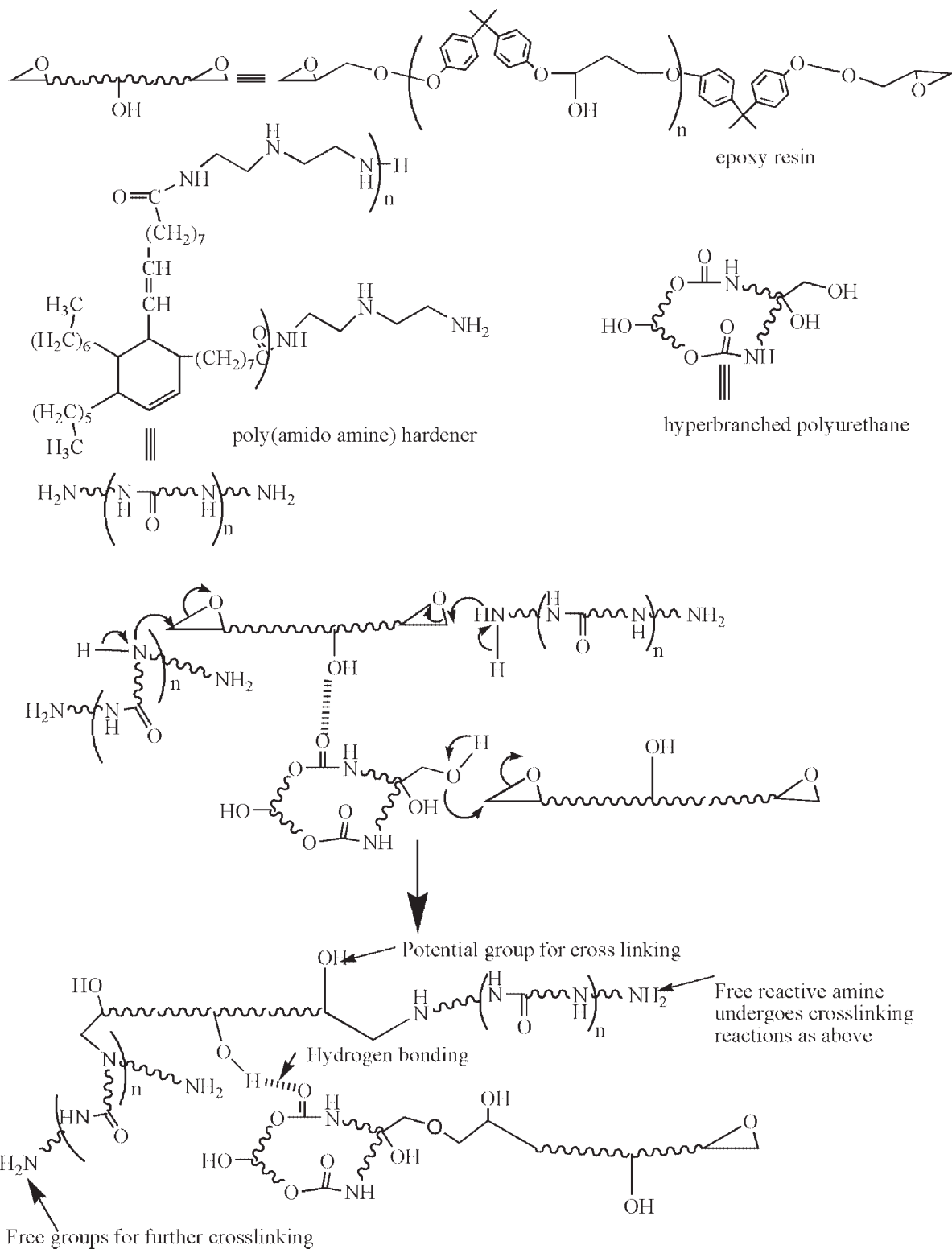
Scheme 1 Proposed crosslinking reactions.

groups increases, which, in turn, increases the rate of crosslinking reaction and thereby forming a three-dimensional network structure. This result is also supported by the other reports, where the conventional PU is cured by epoxy resin.[25,26] This process is accelerated by the presence of aromatic moiety of the HBPU forming active complexes with the epoxy/amino/urethane groups of the system.[27]

FTIR studies further support the crosslinking reaction between HBPU and epoxy resin systems.
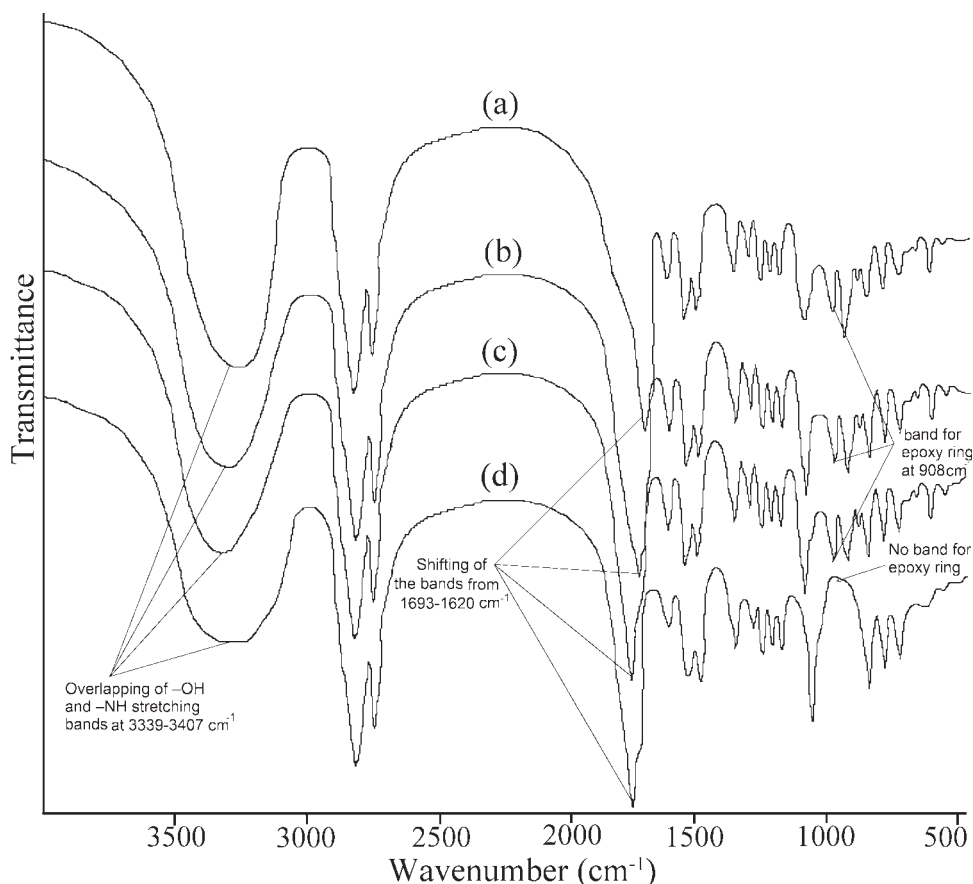
Figure 2 FTIR spectra of the modified HBPUs (a) MHBPU20, (b) MHBPU10, (c) MHBPU5 before curing, and (d) MHBPU10 after curing.

Figure 2 shows the FTIR spectra of epoxy-modified HBPU before and after curing. The characteristic band for epoxy ring[28] was found around 908 cm^{-1} for the epoxy-modified PUs before curing, whereas the same was absent after curing. The other characteristic bands were also observed in the FTIR spectra (Fig. 2). This supports the crosslinking reactions as proposed in Scheme 1.

Generally, free —OH (without hydrogen bonding) and —NH groups show sharp band around 3500 cm^{-1} and >3420 cm^{-1}, respectively. These sharp bands became broad and shifted to lower wavenumber upon H-bond formation.[26] In this present investigation, a broad band appears in the region 3339–3407 cm^{-1}, which predicts the overlapping of —OH and —NH stretching bands[29] as well as H-bonding between epoxy —OH and —NH groups of HBPU. Further, this intermolecular interaction can be proved by the shifting of —C=O absorption band from 1693 to 1620 cm^{-1} in the epoxy-

TABLE II
Physical and Mechanical Properties of the MHBPUs and HBPU

Property	MHBPU5	MHBPU10	MHBPU20	HBPU[a]
Tensile strength (MPa)	16.14 ± 1.29	22.05 ± 2.28	30.20 ± 2.91	6.80 ± 1.73
Elongation at break (%)	550.74 ± 2.87	538.34 ± 2.37	510.52 ± 1.38	721.31 ± 1.17
Scratch hardness (kg)	2.5 ± 0.08	3.1 ± 0.13	4.2 ± 0.08	1.2 ± 0.10
Bending test (mm)	<5	<5	<5	<5
Impact test (cm)	57 ± 1.58	79 ± 1.70	92 ± 1.92	35 ± 1.24
Specific gravity	1.15 ± 0.001	1.16 ± 0.002	1.17 ± 0.002	1.14 ± 0.001
Swelling (at 25°C)	4.83 ± 0.05	1.94 ± 0.03	1.60 ± 0.04	–
Swelling (at 60°C)	32.12 ± 2.16	21.92 ± 2.35	12.68 ± 3.01	–
Sol fraction (%, at 60°C)	37.96 ± 3.02	27.01 ± 2.58	18.04 ± 2.31	–

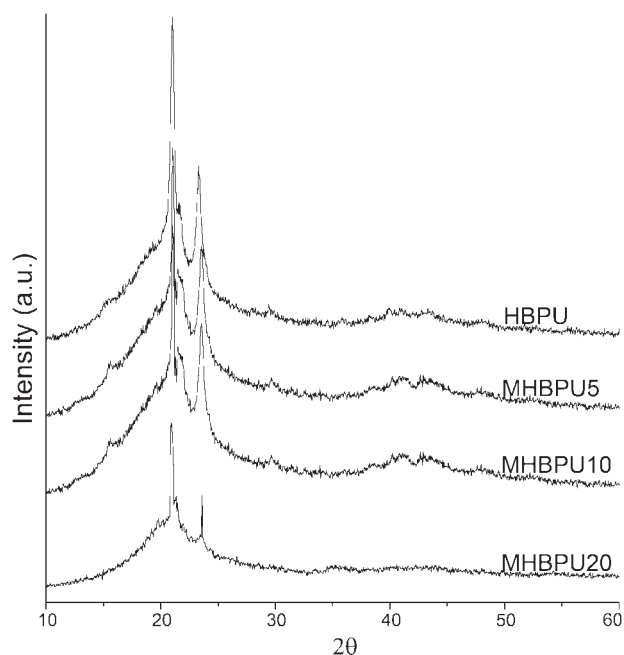[a] HBPU is the unmodified hyperbranched polyurethane containing 30% hard segment.

Figure 3 X-ray diffractograms of all the MHBPUs and HBPU.

modified HBPUs with the increase of the amount of epoxy. Hence, the interactions increase with the increase of amount of epoxy content through the

formation of H-bonding, polar–polar interactions, etc.[7]

Physical properties

The density of the modified HBPUs was found to be higher than that of the unmodified HBPU (Table II). This may be due to the compact structure of the cured HBPUs. It is also observed that with the increase of amount of epoxy resin, the density increases as the compactness increases through H-bonding, polar–polar interaction, in addition to cross-linking density. This is further confirmed by swelling test, wherein with the increase of epoxy content, the network formation increases and the percent swelling decreases (Table II).

XRD study

The presence of crystallinity of the HBPU and the modified HBPUs is confirmed by XRD analysis (Fig. 3). The two diffraction peaks at $2\theta = 21.2°$ (4.19 Å) and 23.4° (3.81 Å) are due to the crystalline PCL moiety in the structure.[30] The positions of these two peaks remain unchanged after modification, though the intensity gradually decreases with the increase of epoxy content, which may be due to the increase of molecular restriction through crosslinking
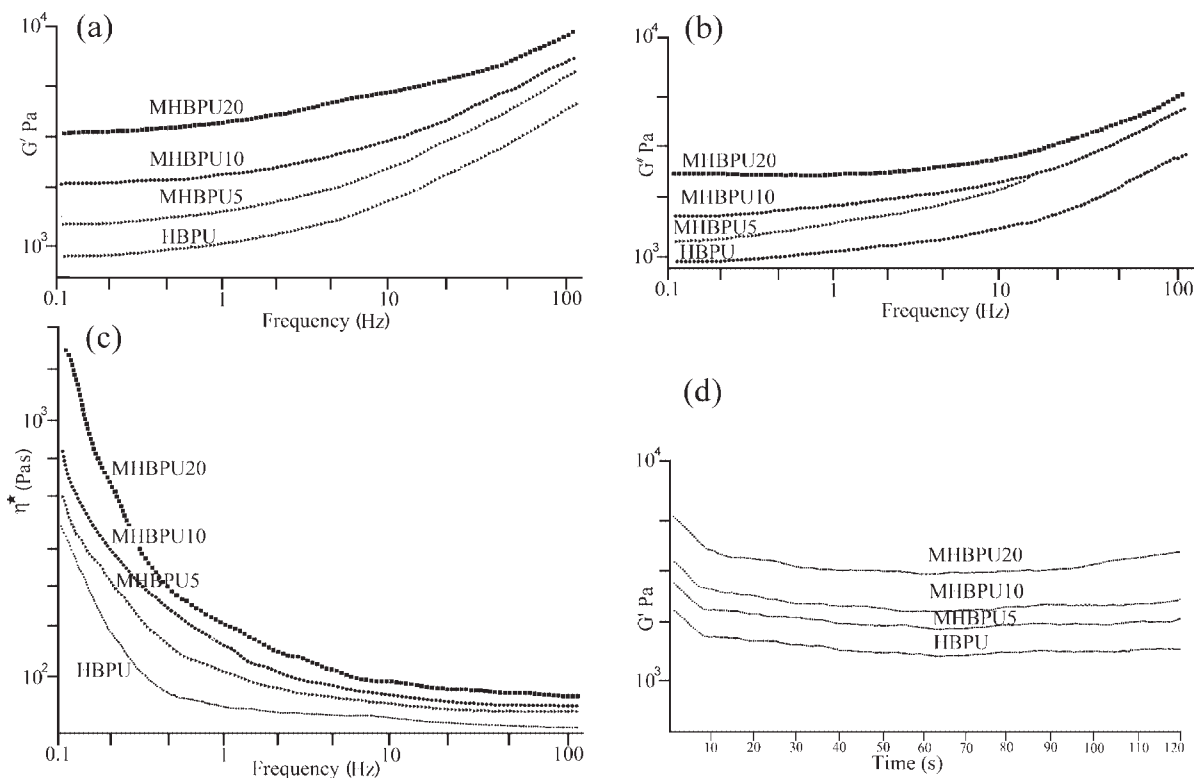

Figure 4 Dependence of (a) storage modulus (G'), (b) loss modulus (G''), (c) complex viscosity (η^*) with respect to frequency, and (d) variation of storage modulus (G') as a function of time.
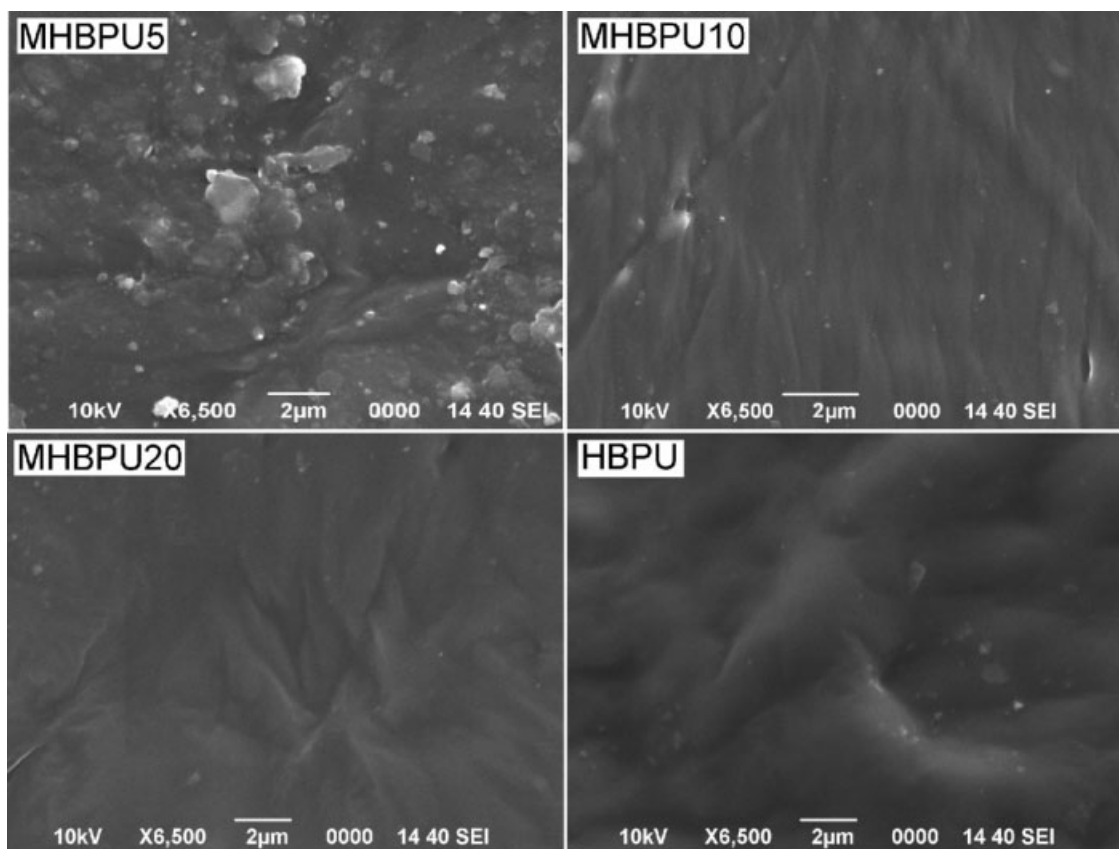
Figure 5 Scanning electron micrographs of the MHBPUs and HBPU.

reactions and also due to the decrease percent of PCL in the matrix.[31]

Rheological study

The frequency dependence of the dynamic visco-elastic properties such as storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) was studied as a function of frequency and time sweep. The G' and G'' were found to be increased monotonically with the increase of the frequency as the amount of epoxy resin increases [Fig. 4(a,b)]. This may be due to the increase of the moduli of the matrix after modification. These increments in the lower frequency region are more, especially for the G' value, which may be due to the pseudosolid-like response of the materials.[32] These curves can be fitted to the Bingham equation for oscillation by the Bohlin curve fitting software. It is observed that the G'' values are independent for the MHBPU5 and MHBPU10 at higher frequencies. The complex viscosity is also increasing with the increase of the epoxy content as it is obvious [Fig. 4(c)]. It was found that the η^* value decreases with frequency, and at the higher frequencies, the value was very low. Thus, shear thinning is observed for

the materials.[33] The G' was also studied at constant frequency (1 Hz) under controlled stress (50 Pa) as a function of time sweep [Fig. 4(d)]. Slight decrease
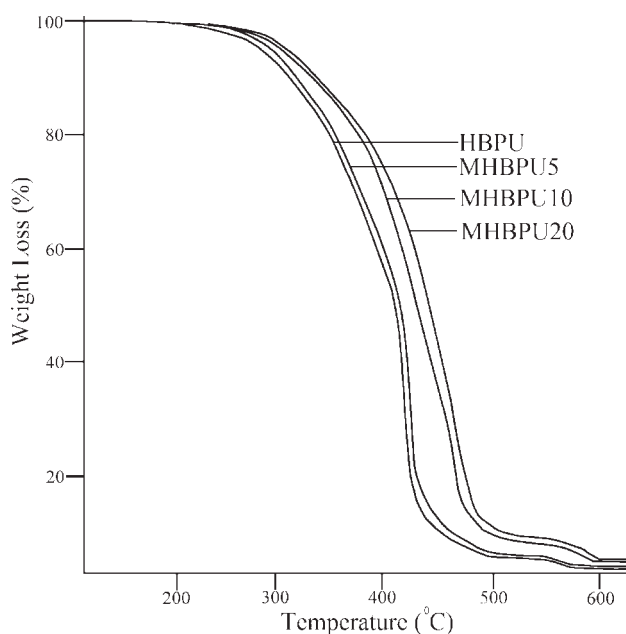

Figure 6 Thermogravimetric thermograms of all MHBPUs and HBPU.

Code	$T_{first\ initial}$	T_{max}	$T_{second\ initial}$	Melting temperature (T_m °C)	Melting enthalpy (ΔH_m J/g)
HBPU	215	420	570	47 ± 0.3	51.8
MHBPU5	225	430	574	48 ± 0.5	48.6
MHBPU10	238	441	582	49 ± 0.2	47.2
MHBPU20	243	456	593	52 ± 0.8	45.1

of the values was noticed, which are not so prominent. This indicates that the structures of the materials might not be changed under the used conditions.

Morphological study

Several factors, such as chemical miscibility of the two components, method of mixing, interfacial interaction, and crosslinking density, affect the morphology of a two-component system at a given composition.[34] Generally, PU shows a good compatibility with epoxy resin.[35]

Among the scanning electron micrographs (Fig. 5) of different compositions, MHBPU20 shows the best dispersion of the epoxy resin in the PU as no phase separation was observed in this blend. However, decrease of the epoxy content in the blends shows phase separation, although it is not so prominent. This is happened because of the good compatibility of the aromatic moieties present in the system through polar–polar interaction between π-bonds of aromatic rings and with other polar groups such as —OH, amino, urethane, and carbonyl in both the polymers.[24,26] Besides these, the confined geometry of HBPU offers improved compatibilizing ability with other components. It is quite obvious to form crosslinked product between hydroxyl/urethane groups of PU and the epoxy groups of epoxy resin in the presence of amine hardener.[24] Thus, the amine hardener also plays role as compatibilizing agent along with its normal crosslinking reactions. Further, the homogenization is enhanced by the possibility of the H-bonding between —C=O of urethane groups of the HBPU with the —OH of epoxy resin. Therefore, as the amount of epoxy with the hardener system increases in the matrix, the interphasic interactions also increase, so the compatibility is improved with the same under the studied conditions.

Mechanical properties

From the Table II, it is observed that the tensile strength of the crosslinked HBPUs increases significantly with the epoxy content. This is because, as the crosslink density increases, the bridges among the chain molecules also increase, which in turn

demand for more stress value for their rapture. The increase of strength is also due to good compatibility and various intermolecular interactions as discussed earlier. The scratch hardness also increases with the increase of the epoxy content, which is again caused by the increase of crosslinking density, H-bond formation, etc. This is also supported by swelling test (Table II) and FTIR study (Fig. 2). Although the modified HBPUs show a considerable hardness, still they have enough flexibility as found by the bending test and elongation at break values (Table II). All the films can be bent to 5-mm parallel mandrel without any difficulty and on average can be elongated about 500%. The long fatty acid chains of oil, ester, and ether linkages of PCL render this high flexibility of the films. The impact resistance of all the films shows excellent result as expected from the tensile strength and flexibility test. The MHBPU20 exhibits the highest impact test, which may be due to the highest strength of the film. The standard deviation for all properties is less than 4, which indicates the uniformity of the results.

Thermal properties

The modification of the PU with epoxy results in significant enhancement in thermal properties of the virgin HBPU. The thermogravimetric analysis of the HBPU with 30% hard segment content and modified HBPUs elucidate the effect of the amount of epoxy
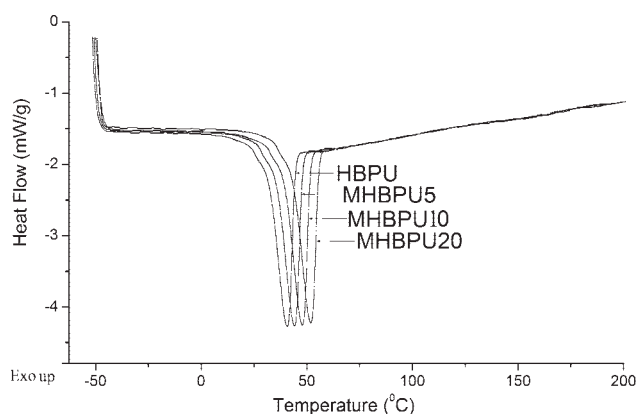

Figure 7 DSC curves for MHBPU5 and MHBPU20.
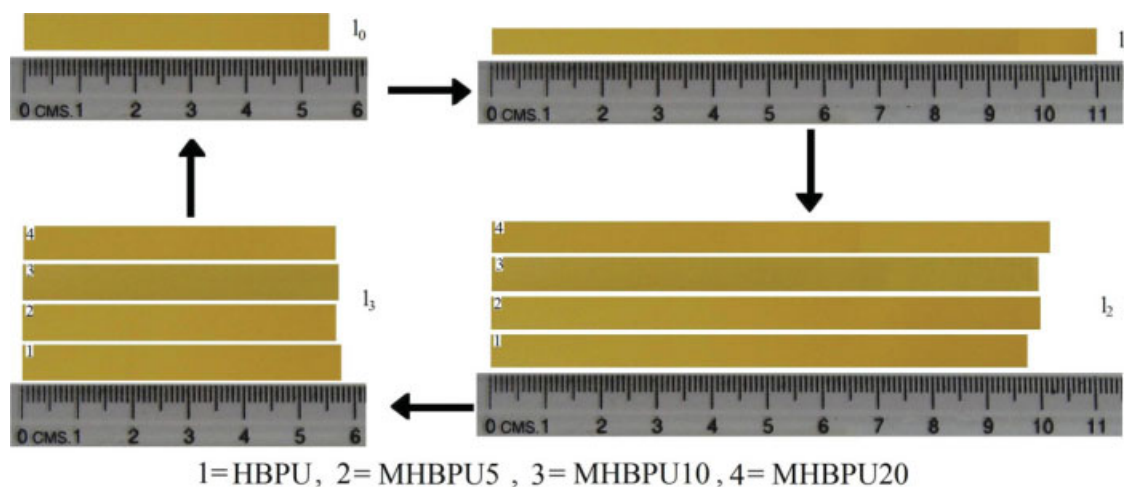
1= HBPU, 2= MHBPU5 , 3= MHBPU10 , 4= MHBPU20

Figure 8 Pictorial diagram of the shape memory behavior of the MHBPUs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

loading on the thermal stability of the system (Fig. 6). For all, the modified HBPUs the decomposition occurs at a range of 225–600°C via a two-step pattern of degradation. The first-step degradation is for the reopening of the allophanate and biuret linkages, which may form during the crosslinking reactions, decomposition of the aliphatic hydrocarbon chains of the oil and epoxy resin, as these bonds are quite thermolabile.[36] On the other hand, the second-step degradation corresponds to the decomposition of the urethane linkages and aromatic moieties of TDI and epoxy resin.[24] An increment of the first initial onset decomposition temperature ($T_{1st\ initial}$), temperature corresponding to maximum rate of weight loss (T_{max}), and the second initial onset decomposition temperature ($T_{2nd\ initial}$) for the modified HBPUs were observed compared with the virgin HBPU (Table III). This is because of the incorporation of the epoxy resin that increases the crosslinking density and thereby bridging the polymer backbone together, which results a "hard material." Thus, the molecular mobility is restricted to a certain extent that causes improvement of thermostability of the modified system.[37]

The melting points with their standard deviations of the modified PU systems are given in Table III. From DSC curves (Fig. 7), the melting point was found to be increased from 47 to 51°C with the increase of epoxy content. This may be due to the formation of compact structure that is formed through different types of interactions as stated earlier.[38] Further, the decrease of the melting enthalpy (Table III) predicts the decrease in the crystallinity, which also support by the XRD result.

Shape memory

A demonstrative experiment for the macroscopic shape memory effect of the modified HBPU network is shown in the Figure 8. The shape memory properties of crosslinked HBPUs were measured at different temperatures, and the values are tabulated in Table IV. All the samples exhibited very good shape recovery of 90–98%, although the influence of epoxy content was very small. The effect of temperature on the shape memory property was also small, although the value increases slightly with temperature. This excellent shape recovery of the polymers may be ascribed to the increased stored energy of system due to an incorporation and uniform distribution of crosslinking in the hyperbranched polymer matrix.[39,40] The small increase of shape recovery with the increase of epoxy content is due to increase of crosslinking density or, in other words, increase

TABLE IV
Shape Memory Data for MHBPUs at Various Temperatures

Code	At 50°C		At 60°C		At 70°C	
	% Retention	% Recovery	% Retention	% Recovery	% Retention	% Recovery
HBPU	69.12 ± 1.82	88.51 ± 1.52	75.92 ± 2.13	91.82 ± 1.02	79.56 ± 1.64	95.62 ± 1.23
MHBPU5	74.23 ± 2.12	90.00 ± 1.10	80.84 ± 2.25	95.36 ± 1.22	85.21 ± 2.41	97.18 ± 1.01
MHBPU10	75.38 ± 2.51	92.13 ± 1.31	81.18 ± 2.35	95.91 ± 1.12	86.15 ± 2.44	98.00 ± 1.03
MHBPU20	77.14 ± 2.41	92.86 ± 1.01	84.20 ± 2.32	96.00 ± 1.13	87.14 ± 2.45	98.50 ± 0.95

of stored elastic strain energy by crosslinking.[41] Thus, while reheating the sample, it can obtain higher recovery stress due to the release of stored elastic strain.[42]

CONCLUSIONS

The modification of the HBPU by the commercially available epoxy resin and poly(amido amine) hardener significantly increases the tensile strength, scratch hardness, impact resistance, and thermal stability. The amount of epoxy resin also has effect on many properties of the modified HBPU. The composition dependence rheological behavior was observed for the materials. The excellent shape recovery and performance characteristics of the modified HBPU indicate the possibility of utilization of these materials as thermoresponsive smart polymers for different advanced applications.

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