

Shape Fixity and Shape Recovery Characteristics of Aliphatic Epoxy-Benzoxazine Shape Memory Polymer

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Abstract

Shape memory polymers (SMPs) are polymers that can fix the temporary shape and recover to the permanent shape by external stimuli. Epoxy resins are an important family of SMPs due to their excellent stability, thermomechanical endurance and the high values of shape fixity. However, epoxide ring opening polymerization required a curing agent which possesses some disadvantages such as high cost, toxic problem to the user and corrosion to the processing apparatus. In this research, novel series of SMPs were prepared from aliphatic epoxy as soft segment and benzoxazine resin (BA-a) as hard segment. Additionally, benzoxazine resin can also function as a curing agent for the epoxy. The composition of BA-a in BA-a/aliphatic-epoxy SMPs was controlled to be in the range of 30 to 50 mol%. Shape fixity and shape recovery as well as essential thermomechanical properties of the BA-a/aliphatic-epoxy SMPs were characterized by dynamic mechanical analysis (DMA) and shape memory test. The results revealed that storage modulus at room temperature of the obtained SMPs was increased from 2.8 GPa at BA-a content of 30 mol% to the value of 4.5 GPa at 50 mol% of BA-a. The glass transition temperature (T_g) obtained from the maximum peak of the $\tan \delta$ was outstandingly increased with an increasing in BA-a content and reported to be in the range of 51 to 140°C. The increment in T_g was also correspond to the raise in the crosslink density of BA-a-modified aliphatic epoxy SMPs. From the shape memory test, all SMP samples exhibited a high value of shape fixity close to 100%. Furthermore, the presence of BA-a content in BA-a/aliphatic epoxy SMPs imparted a greater in recovery stress ranging from 0.25 to 1.59 MPa or about 6 times improvement. These SMPs based on aliphatic epoxy-benzoxazine are highly attractive for shape memory materials to be used in a broader range of applications at elevated temperature and with greater recovery stress.

Keywords : Benzoxazine Resin, Aliphatic Epoxy, Shape Memory Polymer, Recovery Stress

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Introduction

Shape memory polymers (SMPs) belong to a novel class of smart materials developed in the last 25 years. The ability to respond and recover a large deformation with the application of a particular external stimulus by light, humidity, solvents, electric or magnetic fields, ionic strength pH or most typically thermal activation. SMPs have advantages over their shape memory alloys (SMAs) such as high elastic deformation (strain up to more than 200% for most of materials), low cost, low density, a broad range of application temperatures which can be tailored, easy processing, potential biocompatibility and biodegradability. SMPs have found wide applications in self-deployable structures in spacecraft, orthodontic applications, intelligent medical devices, smart textiles and apparels.^(1, 2, 3)

Recently, Xie and Rousseau⁽⁴⁾ developed methods to tailor epoxy SMP's transition temperature and shape recovery properties by using aromatic epoxy as hard segment, aliphatic epoxy as soft segment and aliphatic amine as curing agent. The authors found that, the T_g of epoxy SMPs ranged from room temperature to 89°C and their shape memory properties, with shape fixity above 90% and shape recovery around 100%. However, curing agent of epoxies have more disadvantages such as toxic to the user, corrosion to the processing apparatus and high viscosity.⁽⁵⁾

Benzoxazine resins (BA-a) are a novel class of thermosetting phenolic resins that can be easily synthesized from phenol, formaldehyde and amine group. The curing process of a benzoxazine resin into a polybenzoxazine occurs via a ring-opening polymerization by thermal cure without a

catalyst or curing agent and does not produce by-products during cure which results in no void in the products. Polybenzoxazines have been reported to possess outstanding properties such as near-zero volumetric shrinkage upon polymerization, ease of processing or compounding due to low melt viscosity before, high glass-transition temperature, high thermal stability and low water absorption.⁽⁶⁾ Interestingly, the resin has also been reported to be a curing agent of epoxy, thus avoiding the use of toxicity epoxy curing agents and to yield synergism in some properties of resulting copolymers with epoxy.⁽⁷⁾

In the recent study by Rimdusit *et al.*⁽⁸⁾, benzoxazine resin was selected for alloying with shape memory epoxy using both aliphatic and aromatic epoxies also with amine curing agent. The obtained SMPs also showed excellent shape fixity values of about 98-99% and all of samples needed only a few minutes to fully recover to their original shape, including easily tailored glass transition temperatures ranging up to 120°C. However, the obtained SMPs consisted of many substances and toxic to the user.

In this study, we aim to develop BA-a/aliphatic epoxy based SMPs with improved thermal stability in order to use at elevated service temperature, and for greater load-bearing applications. The characteristics of BA-a/aliphatic epoxy SMPs such as glass transition temperature, shape fixity and recovery stress are evaluated.

Materials and Methods

Materials

The materials used in this research are benzoxazine resin and aliphatic epoxy. BA-a type benzoxazine resin based on bisphenol-A, aniline and formaldehyde was synthesized according to the patented solventless technology.⁽⁹⁾ The bisphenol-A (polycarbonate grade) was provided by Thai Polycarbonate Co.,Ltd. (TPCC). Paraformaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was contributed by Panreac Quimica S.A. Company. The neopentyl glycol diglycidyl ether (NGDE) was available from Aditya Birla Chemical (Thailand). All chemicals were used as received. The chemical structures of NGDE is shown in Figure 1.



Structure of neopentyl glycol diglycidyl ether (NGDE)

Figure 1. Chemical structures of aliphatic epoxy.

Preparation of Benzoxazine Resin

BA-a resin was synthesized from bisphenol-A, paraformaldehyde and aniline at a 1:4:2 molar ratio as illustrated in Figure 2. The mixture was heated to 110°C and was mixed until a homogeneous mixture was obtained for approximately 30 minutes to yield a light yellow liquid monomer. The BA-a resin was solid at room temperature and was crushed to powder before use.

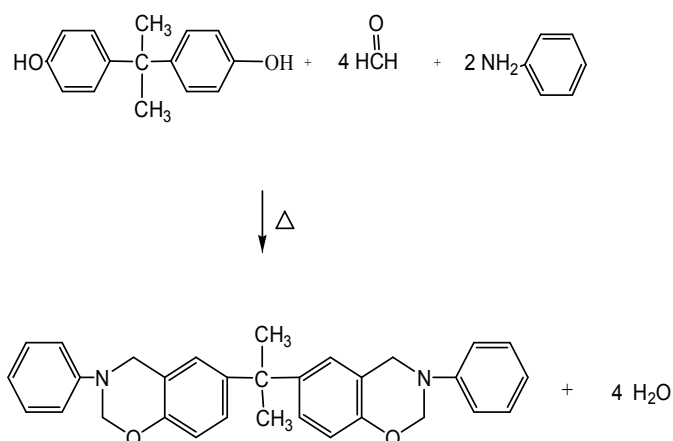


Figure 2. Synthesis of BA-a resin.

SMP Sample Preparation

The BA-a resin was mixed with aliphatic epoxy (NGDE) at various mole percent of BA-a as listed in Table 1. The mixture was heated at 70-80°C in an aluminum pan and stirred for about 10-20 minutes to yield a homogeneous mixture. The molten resin was poured into an aluminum mold and was thermally cured at 80°C for 2 hours in vacuum oven and 130°C/ 12 hours, 140°C/ 4 hours, 150°C/ 4 hours and 160°C/ 2 hours, respectively in an air circulated oven. The fully cured specimens were then cut into various shapes for each specific test.

Table 1. Compositions of BA-a/aliphatic epoxy SMPs.

Sample	BA-a (mol%)	Aliphatic epoxy (mol%)
BA-a 30 mol%	30	70
BA-a 40 mol%	40	60
BA-a 50 mol%	50	50

Specimen Characterization

Thermomechanical properties of the BA-a/aliphatic epoxy SMPs were characterized by dynamic mechanical analysis (NATZSH, model DMA242). The specimen, with a dimension of 10 mm × 50 mm × 3 mm, was tested using a three point bending mode at the a frequency of 1 Hz and a heating rate of 2°C /min from 30°C to 200°C. The crosslink density of the obtained polymer network was calculated from the storage modulus (E') at a rubbery plateau, and T_g of the polymeric specimens were obtained from the maximum peak on the Tan δ.

The shape fixity and shape recovery properties of BA-a/aliphatic epoxy SMPs were investigated by Universal testing machine under three point bending mode. The experimental procedure for the shape fixity and recovery stress is schematically shown in Figure 3. Firstly, a fixed shape was formed by applying the force to a specimen (10 mm × 50 mm × 2 mm) at T_g+20°C and left to cool down to room temperature. The force was then removed perfectly to obtain a temporary shape. The deflection after unloading was measured, and rate of shape fixity (R_f) was determined. The specimen was heated up to T_g+20°C by keeping the fixed deflection content afterwards. Force during heating was measured and the recovery stress was obtained.

Results and Discussion

Thermomechanical Properties

The storage modulus of BA-a/aliphatic epoxy SMPs are presented in Figure 4. At room temperature, the storage modulus of the BA-a/aliphatic epoxy SMPs in its glassy state (35°C) were 2.82, 3.85 and 4.5 GPa at BA-a contents of 30, 40, and 50 mol%, respectively. The storage modulus of the SMPs tended to increase with an increase in BA-a content in the alloys. As a result, the addition of the more rigid molecular segment of the poly(BA-a) tended to increase the stiffness of the BA-a/aliphatic epoxy SMPs.

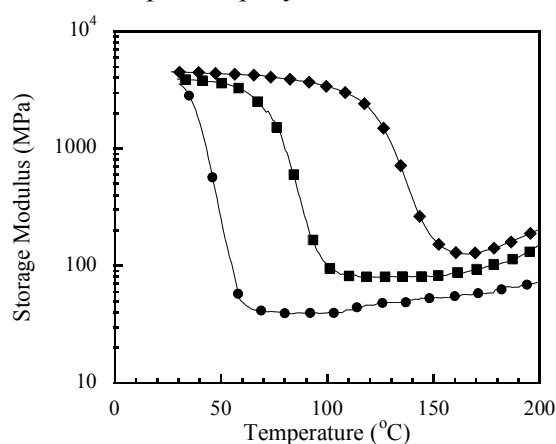


Figure 4. Storage modulus versus temperature of BA-a/aliphatic epoxy SMP at various mole percent of BA-a : (●) 30 mol%, (■) 40 mol%, (◆) 50 mol%.

The addition of BA-a resin also resulted in a systematic increase of the modulus in rubbery plateau region from 39.9 to 175 MPa with an increase in BA-a from 30 to 50 mol%. This result suggested that the presence of the BA-a resulted in a substantial enhancement in crosslink density of BA-a/aliphatic epoxy SMPs. The crosslink density can be estimated from rubbery plateau modulus of the specimen using equation from the statistical theory of rubber elasticity i.e. Nielsen's equation⁽¹¹⁾ as shown in Table 2.

Table 2. Properties of BA-a/aliphatic epoxy SMPs.

Samples	E' at rubbery state (MPa)	Crosslink density (mol/cm ³)	T _g (°C)	Shape fixity R _f (%)
BA-a 30 mol%	39.04	3.837 × 10 ⁻³	51	99.08
BA-a 40 mol%	80.76	4.884 × 10 ⁻³	88	99.35
BA-a 50 mol%	171.97	6.001 × 10 ⁻³	140	99.55

Figure 5 illustrates the Tan δ curves of BA-a/aliphatic epoxy SMPs at various compositions. Glass transition temperatures (T_g) of BA-a/aliphatic epoxy SMPs were more clearly observed in the DMA thermograms based on the maximum peak of Tan δ . The T_g values of the alloys were 51°C in BA-a 30 mol%, 88°C in BA-a 40 mol% and 140°C in BA-a 50 mol%. An incorporation of BA-a resin in BA-a/aliphatic epoxy SMPs resulted in an increase in the T_g with increasing BA-a fraction. This may be due to the more rigid molecular structure and possibly much higher intramolecular and intermolecular forces in the polybenzoxazine compared with the epoxy.⁽¹²⁾

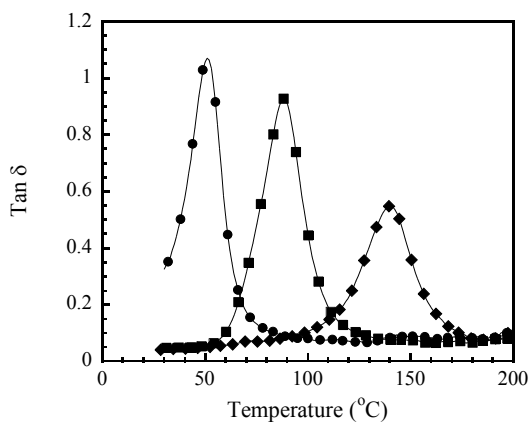


Figure 5. Loss tangent versus temperature of BA-a/aliphatic epoxy SMP at various mole percent of BA-a: (●) 30 mol%, (■) 40 mol%, (◆) 50 mol%.

Shape Fixity and Recovery Stress

The rate of shape fixity (R_f) is defined by the following equation (1)

$$R_f = \frac{y_u}{y_{max}} \quad (1)$$

where y_u is the deflection after unloading at room temperature and y_{max} is the maximum deflection at 10 mm.⁽¹¹⁾

The shape fixity values of BA-a/aliphatic epoxy SMPs were shown in Table 2. The samples showed excellent shape fixity values of about 99%. This range of values corresponds to those reported by Rimdusit et al.⁽⁸⁾

The recovery stress versus time of BA-a/aliphatic epoxy SMPs were shown in Figure 6. The maximum recovery stress of each samples were observed to be 0.25, 0.62 and 1.59 MPa at

BA-a contents 30, 40 and 50 mol%, respectively. As the result, it could be seen that the BA-a resin help improve recovery stress of BA-a /aliphatic epoxy SMPs. Especially, the recovery stress did not reduce with time in all SMP samples. The recovery stress curve remained almost flat over a period time.

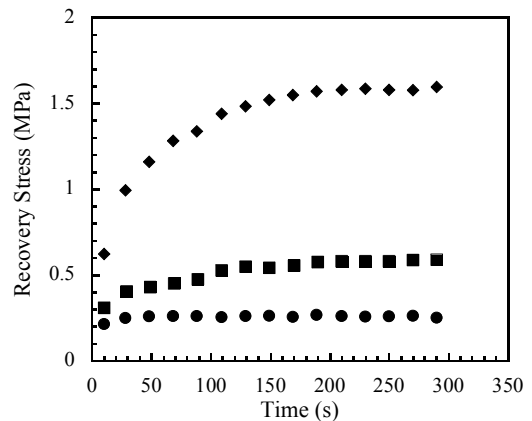


Figure 6. Recovery stress versus Time of BA-a/aliphatic epoxy SMP at various mole percent of BA-a: (●) 30 mol%, (■) 40 mol%, (◆) 50 mol%.

Conclusions

The incorporation between benzoxazine resin and aliphatic epoxy at various BA-a mole percent (30-50 mol%) contributed to significant enhancement in thermo-mechanical and shape memory properties of BA-a/aliphatic epoxy SMPs. The storage modulus of the SMP was found to increase with an addition of benzoxazine content. The T_g value of the SMPs were also increased with an addition of BA-a content which was attributed to the higher crosslink density in the more BA-a content in the SMPs. Shape fixity of all sample was as high as 99%. With an increasing in BA-a content, the shape recovery stress increased and remained constant over a period of time.

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