

MULTI-PERFORMANCE SHAPE MEMORY EPOXY RESINS AND THEIR COMPOSITES WITH NARROW TRANSITION TEMPERATURE RANGE

Lan Luo¹, Fenghua Zhang² Yanju Liu³ and Jinsong Leng⁴

¹ Centre for Composite Materials and Structures, Harbin Institute of Technology (HIT), Harbin, 150080, People's Republic of China, luolan27@126.com

² Centre for Composite Materials and Structures, Harbin Institute of Technology (HIT), Harbin, 150080, People's Republic of China, <u>fhzhang_hit@163.com</u>

³ Department of Astronautical Science and Mechanics, Harbin Institute of Technology (HIT), Harbin, 150001, People's Republic of China, yj liu@hit.edu.cn

⁴ Centre for Composite Materials and Structures, Harbin Institute of Technology (HIT), Harbin, 150080, People's Republic of China, <u>lengis@hit.edu.cn</u>

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ABSTRACT

Shape memory epoxy resins are one of the most widely used engineering intelligent polymers, mainly used in aerospace, intelligent bionics, and other fields of active deformation structures. A series of shape memory epoxy resins with a narrow transition temperature range, showing strong intersegment forces and regular uniform cross-linked networks are designed and synthesized. By adjusting the stoichiometry and cross-linking density, the length of the segments is uniformly controlled. The glass transition temperature range can reach 14-23°C, which improves the efficiency of shape memory action. Besides, the multi-amines crosslinking agents were used to adjust the distribution of the chain segment to achieve the effect of adjusting Tg. Moreover, the addition of epoxy-terminated liquid nitrile rubber (ETBN) composites can toughen the system. The elongation at break can be increased up to 4 times. Furthermore, combing the two-stage curing method, and add the nano-particle high-temperature latent curing agent based on the ETBN toughening system, the super curing effect is achieved, Tg, modulus and strength of composites are improved. The resulting composites are appropriate for shape fixation and recovery temperature with more precision and closer distance between, which can meet the higher requirements of the aerospace field.

1 INTRODUCTION

In nature, the response of organisms to environmental stimuli is extremely common. For example, chameleon changes color to adapt to the environment, mimosa leaves slowly close when they encounter rain. In external stimuli such as heat, light, magnetism, electricity, and chemical solvents, the deformable polymer that is memorized temporary shapes returning to the original shape in response to stimuli is called shape memory polymers (SMP)[1]. Owing to the characteristics of variable stiffness, variable shape, self-driven, and self-adaption. SMPs has shown wide application prospects of biomedical, intelligent manufacturing, bionics, engineering, etc, and they have attracted more and more attention[2,3]. The folding unfold structures had great favors compared with the traditional space structure, with smaller storage space, lighter weight, and easier deployment. These can eliminate the shortcomings of the aerospace deployment structure. Epoxy resins have excellent mechanical properties and radiation resistanc, and most of the components used are made of shape memory epoxy resins (SMEPs)[4]. On the other hand, to overcome the weakness of insufficient shape restoring force, composite materials are made by combined with reinforcing materials such as continuous fibers, short fibers for space deployment structures. Ordinary epoxy resin with a random cross-linked network structure, shows a side-chain space effect. When the shape fixed or restored, obtaining sufficient thermal energy in the glass transition interval can provide coordinated molecular motion and configuration changes[5,6]. The glass transition temperature range of ordinary epoxy resins exceeds 60° C and the rigidity will be lost at a higher temperature. However, it is particularly required to maintain the rigidity of the material around the Tg temperature (Tg-10°C). The temporary shape needs to be completely fixed at Tg-10°C, and the original shape must be completely restored at Tg[7]. However, most epoxy resins are basically unable to quickly complete the entire fixed-recovery process within a narrow temperature range. At present, only shape memory alloys can be realized in a narrow temperature range, such as NiTi alloys.

In this work, we have proposed a series of shape memory epoxy resins and their composite materials with a narrow transition temperature range. The network structure with strong inter-chain forces and regular cross-linking, and the ratio between reagents is controlled to increase the degree of uniformity of the chain segment distribution. Different cross-linking agents can adjust the length of the segment, to adjust the Tg. Secondly, liquid epoxy-terminated nitrile rubber (ETBN) is added. Compared with other rubbers, the epoxy groups at both ends of ETBN also participate in the crosslinking network to form a tough composite. Finally, based on ETBN/EP composite materials, we chose a nanoparticle high-temperature latent curing agent for two-stage curing to improve the internal cross-linking density, mechanical strength and heat resistance.

2 3.RESULT AND DISCUSSION

The DSC curves of all different mixtures are shown in Figure 1(a). It can be seen from the curves (a)-(c) that as the amount of active hydrogen in the multi-amines curing agent increases, the Tg of the multi-amine system gradually decreases. As a result, the length of the molecular chain segment is shortened and the movement ability of the chain end is high, so the network cross-linking and Tg reduction are shown in Figure 1(b). With the increase of the content of ETBN, the Tg of the ETBN/EP composites moves to the low temperature directly from the curve (d)-(g). Especially when the content reaches 20 phr, the Tg drops to 80°C, a decrease of nearly 20°C. The more flexible chains in the molecular chain, the more obvious the movement of the chain, and the more the Tg of the sample decreases. It can be seen from the curves (h) and (i) that the difference before and after the second thermal curing is about 30°C. The tighter the cross-linked network, the smaller the free volume and the more difficult the chain movement. The thermal stability of multi-amine epoxy and its composites under nitrogen are shown in Figure 1(c). Each sample has a significant degradation stage, which is the weight loss caused by the decomposition of the main carbon chain. After adding ETBN, the ETBN/EP composites appeared a step at 200°C-300°C and the weight loss reached 9.8% as shown in the upper right corner of Figure 1(d). It has been verified that prepared all samples can be safely handled and used within their Tg range. Besides, the results show that the thermal stability of the EP-ETBN10** composites was slightly improved after two-stage curing, and the decomposition temperature is significantly higher than before high-temperature curing.



Figure 1: (a) DSC thermograms of systems. (b) thermogravimetry curves of systems.

The characterization of mechanical properties can be used as an indicator of material toughness. As the amount of active hydrogen in the multi-amine crosslinking agent increases, the number of chain segments increases with the same degree of cross-linking. The mobility of the molecular chain end increases, the strength gradually decreases, and the elongation gradually increases as shown in Figure 2(a). When the ETBN content was added from 0 phr to 20 phr, the greater the precipitation density of the rubber phase, the lower the strength. It is worth mentioning that the strength of ETBN-EP5 reached 70 MPa, which is about 7 MPa higher than that before toughening. When the content was 10 phr, the strength was not sacrificed and the elongation at break reached 11.7 %, which is increased by more than 4 times as shown in Figure 2(b). After the two-stage curing, the modulus also increased significantly as shown in Figure 2(c). In particular, in the absence of high-temperature initiation, since the curing modulus of the nano-sized particles is 3.5 GPa, it is reduced by 0.8 GPa after high-temperature initiation. The results show that high temperature curing effectively improves the mechanical properties of ETBN/EP composites. The toughness of the material was indirectly evaluated by the area of the strain-stress curve, as shown in Figure 2(d).





Compared with pure SMEP, the toughness of ETBN/EP composites at room temperature can be greatly improved. After two-stage curing, the toughness of ETBN/EP composites has decreased, but it is better than that of SMEP. The fracture morphology of pure epoxy resins were smooth planes, as shown in Figure 3(a). It indicated that there are no bubbles in the curing process of the system, the fracture was relatively neat, and there was no gap, which belongs to the brittle fracture mechanism. After adding ETBN, the rubber phase gradually precipitated to form small spheres dispersed in the resin matrix to form a "sea-island structure" as shown in Figure 3(b)-(d). When the content was 5 phr to 15 phr, the size of the rubber particles was smaller. The size of rubber particles in the composites become larger and agglomerates, resulting in a decrease in strength when increased to 20 phr. The crack stopped when it met the rubber particles, and micropores were formed around the rubber particles[8]. The micropores reduce the stress at the crack tip and toughen the resin and become ductile fracture as shown in Figure 3(c). The tensile fracture sections of EP-ETBN10** are shown in Figure 3(d). The cross-section was staggered, and the silver fringe appeared at the break of the stress fringe. It is indirectly indicated that the energy absorbed by the cracks were part of the tensile energy, and composites were ductile fracture after two-stage curing.



Figure 3: SEM micrographs of the fracture surface for systems: (a) pure ESMP,(b) EP-ETBN5, (c) EP-ETBN10 and (d) EP-ETBN10**

As the active hydrogen content in the multi-amine curing agents increases, the Tg of the system decreases. The modulus was reduced by 3 orders of magnitude, which proved the excellent shape memory performance. Figure 4(a) can be observed that the glass transition temperature range was relatively narrow around $20 \,^{\circ}$ C. The main reason is that the benzene ring in the chain makes the molecular chain have interaction, which makes the force between the segments strong. On the other hand, different chain segments require different movement temperature, which shows the glass transition range. When the content of ETBN increases step by step, Tg decreases gradually. The peak width of ETBN was slightly increased by 2-3°C as shown in Figure 4(b). Compared with ETBN-EP10, the Tg of composites increased by more than 30°C and the magnitude difference of modulus after two-stage curing is reduced as shown in Figure 4(c).

The relative displacement of the molecular segment motion is reduced, and the reduced resistance bears so that the internal friction becomes smaller[9]. It is worth mentioning that all the samples were shaped by applying external forces when they were heated to Tg, and the external forces were removed when they did not need to be cooled to room temperature. After leaving the heating table for a few seconds, the shape can be fixed, thus improving the action efficiency of shape memory. Boltzmann Fit was used for S-curve fitting of the tested data, and the recovery rate curve after fitting as shown in Figure 4(d). After two-stage curing, the recovery rate of EP-ETBN10** decreased slightly, which was due to the deepening of the cross-linking degree caused by two-stage curing. Besides, dicyandiamide hindered the movement of the chain segment in the system, leading to a decrease of shape recovery rate.



Figure 4: (a), (b), and (c) The DMA curves of systems. (d) The shape recovery rate of system 3.

Both System 1 and System 2 showed excellent shape memory performance. As shown in Figure 5(a), the multi-amine epoxy resin samples were simultaneously recovered at Tg + 20 °C. The decrease in the degree of crosslink of the system results in a relatively small resistance to the movement of the segments. The deformation recovery ability is improved as the amount of active hydrogen increases. When the recovery rate was increased, the recovery time was shorter. After adding the rubber phase, the higher the ETBN content, the faster the recovery rate as shown in Figure 5(b). This means that ETBN increases the number of internal motion chain segments in the system. To conduct a comparative study on each sample at the same load level. The multi-section folding and unfolding simulation through the space capsule unfolding experiment is shown in Figure 5(c). EP-ETBN10 and SMEP-1 samples were selected for the indentation test as shown in Figure 5(d). The module "HIT's 100th Anniversary" was applied to the sample at a pressure of 0.3 MPa and Tg. The measurement results indicate that the rate of change of the drop height of the sample before and after toughening reaches 30.53% and 20.17% respectively, and the sideshows excellent elasticity after toughening.



Figure 5:Characterization of the shape-memory behavior of systems: (a) and (b) Shape recovery process, (c) Simulation process of space capsule, (d) Engrave "the 100th Anniversary".

3 CONCLUSIONS

A series of shape memory epoxy resins and their composites with multi-performance and narrow transition temperature range were prepared. By adjusting the network structure, chain segment distribution, adding different contents of ETBN, and combing the two-stage curing method. Different multi-amine curing agents can adjust the crosslink density to change the Tg and keep the narrow transition temperature range at 14-23 °C, which can still maintain rigidity at higher temperatures. The SEM results show that the micro-phase separation of the composites after the addition of rubber occurred during the curing process, forming a "sea-island" structure. When the content reaches 10 phr, the elongation at break of the composites can be increased by 4 times, and the strength is improved. But as the ETBN content increases, Tg will gradually decrease. Subsequently, two-stage curing was performed on the toughened system by adding a nano-scale curing agent. After two stages of curing, the tensile strength and heat resistance of the composites were increased by 30 °C and 15 MPa, respectively. The addition of a nano-particle high-temperature curing agent improves the mechanical properties of the composites, and both the strength and modulus are improved.

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