

Progress in shape memory epoxy resins

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ABSTRACT

This review analyses the progress in the field of shape memory epoxy resins (SMEPs). Partial crystallisation and vitrification are the basis of shape memory effect in SMEPs. Several synthetic approaches for SMEPs, their composites and foams have been reviewed. Strategically incorporated thermally reversible segments induce the shape memory effect in epoxy resins. By varying the nature and concentration of shape memory segments, wide range of shape memory properties and transition temperatures (shape memory temperatures) can be achieved. Triple shape memory, self-healability and electroactive capability are some of the additional features that can be created in SMEPs. Among the thermoset resins, shape memory epoxies are the most attractive systems because of the ease of processability, composite forming properties and dimensional stability. Shape memory epoxy polymers that can be processed into elastic memory composites are candidate materials in the processing of many smart engineering systems. In this background, a review consolidating the progress in SMEP has contemporary relevance. The present article takes a stock of the trend in SMEP with a view to assess the direction of future initiatives in this area. It is concluded that there is tremendous scope for research leading to technological evolution in the field of SMEP.

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1. Introduction

Polymers with diverse 'smart' properties evince a lot of interest of researchers across the globe due to their versatility and fascinating applications. In 1980s, to the class of smart polymers, a group of polymers *viz*: shape memory polymers (SMPs) emerged with the potential capability to memorise their shape (recover original shape from transient or fixed shapes) with respect to external stimuli such as heat, light, pH, electricity and moisture. Of these, SMPs employ heat as stimulus (thermoreponsive SMPs) gain attention due to easiness in application and hence plenty of temperature sensitive SMPs were developed with a range of transition temperatures.

Physically and chemically cross-linked shape memory polymers (PC-SMPs and CC-SMPs) have been investigated extensively during the last two decades. In PC-SMPs, majority of research is linked to polyurethane chemistry and their development as a shape memory polymer was revolved on the sharp transition temperature of soft domains [1–6]. Other systems like polyhedral oligomeric silsesquioxane–polyethylene glycol (POSS–PEG) [7,8], aramid–polycaprolactone [9], polyethylene terephthalate–polyethylene glycol (PET–PEO) [10,11], nylon 6–polyethylene [12,13], polystyrene–polybutadiene [14,15] are some of the examples in which physically cross-linked structures hold the permanent shape. Chemically

cross-linked systems are developed to achieve excellent mechanical robustness, wide transition temperatures and improved shape memory performance over the thermoplastic based SMPs like polyurethanes. In chemically cross-linked SMPs (CC-SMPs), the shape memory temperature has the origin from T_m (if the reversible phase is semi-crystalline segment) or T_g (if the SMP is a conventional thermoset, e.g. shape memory epoxy resins (SMEPs)). Epoxy resins are widely accepted for use in many areas of coating, sealants, adhesives, etc. due to excellent thermal, adhesive and mechanical properties. Conferring shape memory (SM) properties to these versatile resins has been the subject of many researchers leading to some advances in the development of SMEPs.

Though some reviews on shape memory polymers and associated systems have been reported, a review focusing specifically on chemically cross-linked SMPs, more precisely on shape memory epoxy resin (SMEP) has not been reported [16–20]. This review focuses the shape memory effect in cross-linked polymers, preparation of various SMEPs, their composites, foams and other major developments in SMEP systems.

2. Advances in shape memory epoxy resins (SMEPs)

As was stated above, shape memory epoxy resins (SMEPs) merit a special reference among the diverse shape memory polymers such as polyurethane, polynorbonene, crosslinked polyethylene, styrene rubbers and acrylate systems as they are unique thermoset shape memory polymer systems with excellent thermal,

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thermophysical and mechanical properties along with ease of processability into engineering components. As epoxy polymers find extensive use as adhesives, coating, structural material, etc., additional function of shape memory will be a good aspect for extending their further applications.

2.1. Epoxy-amine based SMEPs

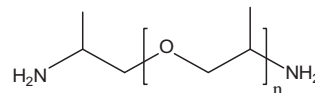
SMEP based on epoxy resin DGEBA (diglycidyl ether bisphenol A) and varying content of curing agent DDM (4,4-diaminodiphenyl methane) were prepared to investigate the effect of different curing degree on transition temperature (T_g) of the SMEP (Scheme 1) [21]. T_g increased from 45 to 145 °C for 50–100% cure degree. However, SMEP with 50% cure was not useful due to its low mechanical property. SMEP of 60% cure (SMEP-60) possessed a T_g of about 64 °C and showed a three order change in storage modulus (from DMA) above and below T_g which is considered as a criterion for any polymer to manifest good shape memory properties. However, 100% cure produced only 1.5 order decrease in storage modulus at T_g . SMEP-60 showed shape retention of 99% in all cases. SMEP-60 started to show shape recovery from 14 °C below T_g but permanent shape was recovered completely in a few minutes. SMEP-60 exhibited a recovery time of 6.5 min at 85 °C and 3.5 min at 100 °C. These results indicate that if the polymer is stable sufficiently, the recovery time is not a matter if use temperature is relatively higher than T_g . The breaking strain was 1.77% at room temperature and 30.5% at about 75 °C. This big difference indicates its potential as SMP. Repeated shape memory cycles (9 times) reduced the tensile strength by about 6%. This work highlights the effect of cure degree on shape memory characteristics of epoxy systems.

A series of SMEP were prepared by using the same epoxy resin, DGEBA by varying the content of curing agents 4,4'-methylenedianiline and *m*-phenylenediamine [22]. The T_g s were 55–83 °C. These SMEPs showed shape fixity of about 97% and shape recovery of above 96%. The transition temperatures were enhanced by increasing the content of curing agent. One important observation is that excess or low quantity of curing agent can turn the material insensitive to shape memory. This ascertains that a definite cross-link density is required for functional realisation of shape memory effect in thermoset systems. Type of curing agents also affects the SM behaviour in epoxy resins. This work reflects the influence of curing agent on the shape memory performance of SMEPs.

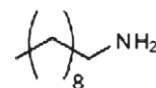
Architecturing SMEP with defined switching temperature is always attractive for designing them for specific applications. A work by Xie et al. described the easy tailoring of transition temperature using various curing agents for epoxy resins (Scheme 2) [23]. They used DGEBA epoxy resin with decylamine as variant and Jeffamine as curing agent. The T_g s ranged from 30–89 °C. When the aromatic epoxide was replaced with more flexible aliphatic diepoxide, T_g



Neopentyl glycol diglycidyl ether (NGDE)



Jeffamine D-230 ($n \sim 2.5$)

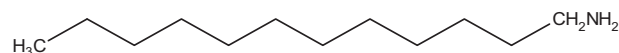


Decylamine

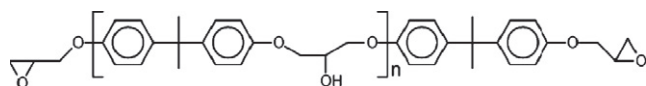
Scheme 2. Structures of epoxy resin and long chain curatives.

decreased to 6 °C and it was very sharp. In all series based on DGEBA and neopentyl glycol glycidyl ether (NGDE), 2–3 order decrease in storage modulus above and below T_g was observed. They showed fast shape recovery in 6 s in one of the compositions with a T_g of 50 °C. The system possessed good shape recovery characteristics even after repeated 18 shape memory cycles.

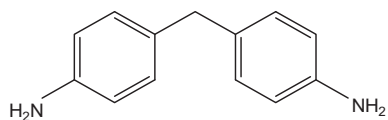
One of the drawbacks of SMP compared to SMA is its low recovery stress. Recovery stress is the stress generated in the SMP when it is allowed to recover original shape under constrained condition. Realisation of an SMP with about 75% deformation and stress recovery of about 3 MPa is a challenge. One of the reports reveals the use of stoichiometric amount of amines DA (aliphatic amine) and MXDA as curing agent for DGEBA resin (Scheme 3) [24]. The amine DA was incorporated for physical cross-links and MXDA for chemical crosslinks. Physical crosslinks will give large strain and chemical crosslinks to high stress recovery. The calculated ratio of physical to chemical crosslinks was 4:1. These polymers showed large strain of 75% and stress recovery of 3 MPa. The SMP exhibited a ductile behaviour with a yield stress of 42 MPa at room temperature and failure strain higher than 25%. In repeated cycles (4 cycles) the shape recovery slightly reduced from 96.8 to 95.5 but shape fixity unchanged, exhibited fast shape recovery in 3 s at 60 °C in immersed water. It is to be remarked that the shape recovery in water and in hot air might be different and the latter is more appropriate for actual application.



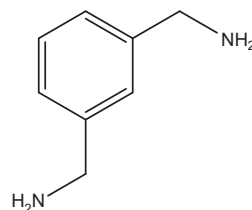
Dodecyl amine (DA)



DGEBA



4,4' diaminodiphenyl methane (DDM)



m-xylylene diamine (MXDA)

Scheme 1. Structure of diglycidyl ether bisphenol A (DGEBA) and 4,4'-diaminodiphenyl methane (DDM).

Scheme 3. Aromatic and aliphatic curing agents.

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