
Mechanical and Thermal Characterization of Shape Memory Polymer Reinforced with Carbon based Fillers

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Abstract

The main objective of this dissertation would have been to create shape memory polymer nanocomposites using epoxy resin and resorcinol diglycidyl ether (RDE). In the creation of shape memory polymer composites, carbon black and carbon nanotubes were utilised singly as well as in combination as a hybrid filler. The mechanical (tensile and impact testing), thermal (DSC analysis), and shape memory characterisation tests were performed on all samples (bending test). As a result, polymers containing 15 weight percent of RDE monomer were discovered to offer excellent qualities. In weight fractions of 0.5, 1.0, 1.5, and 2 %, carbon black and carbon nanotubes were added to the polymer. The ideal filler loading was found to be 1.5 weight % for CB-loaded composites and 1.0 weight % for carbon nanotube-loaded composites. Carbon black content was held constant at 1.5 wt % for all formulations for creating hybrid composites, while carbon nanotube content was changed. A hybrid composite comprising 1.5 % CB and 1.0 % CNT was shown to have improved characteristics for the majority of characterization tests.

Keywords: *Shape Memory Polymers, MWCNT, Epoxy.*

Introduction

Shape memory polymers (SMPs) are a type of smart polymer that respond to environmental stimuli such as heat, light, magnetic fields, electrical fields, pH levels, and moisture to shift from a temporary shape to their original shape. SMPs provide a number of benefits over other shape memory materials, including affordability, light weight, high elastic deformation, biodegradability, and biocompatibility. SMPs have a growing potential for use in a range of industries, including aerospace constructions, functional fabrics, biomedicine, self-healing materials, and pattern transformation because to their benefits. Different triggering techniques can be used to implement shape memory actuation [1-3]. In addition to conventional methods, innovative strategies are essential for creating multifunctional gadgets. The most popular and flexible method of inducing shape memory polymer is thermal triggering. Because of their significant potential for biocompatibility and biodegradability, shape memory thermoplastics are recommended. Additionally, especially for phase separated block copolymers, the ratio of soft to hard domains may be changed to change the shape memory properties. Because of their significant potential for biocompatibility and biodegradability, shape memory thermoplastics are recommended. Additionally, especially for phase separated block copolymers, the ratio of soft to hard domains may be changed to change the shape memory properties [4-5].

A number of ways to activate the shape recovery effect. Even while applying heat is the classic and typical method, different triggering mechanisms have begun to catch the interest of researchers. When non-conductive polymer matrices are filled with conductive particles, such as carbon-based fillers, semi-conductive polymers are produced, and these composites can be triggered by electricity. There are more triggering types as well, such as magnetic field, solution, and infrared triggering techniques [6-7]. Polyethylene, polystyrene, polyurethane, polymethacrylate, and epoxy resin are only a few of the polymers with shape memory capabilities. There are many more polymers as well. Compared to other forms of shape memory polymers, epoxy resin offers better characteristics. Epoxy polymer is a more durable polymer due to its superior mechanical qualities, particularly its high tensile strength and modulus. Additionally, epoxy polymers can have their characteristics adjusted by varying the quantity of curing agent employed or by adding extra monomers to the resin [8-10].

Epoxy matrix is often diluted with monomers to adjust the polymer's mechanical and thermal characteristics. Lower glass transition temperature and increased toughness are results of monomer addition. Monomers also help to positively influence memory characteristics [11]. To increase the conductivity of polymers, conductive particles including carbon nanotubes (CNT), carbon black (CB), graphite, carbon fibres, and metal powders like nickel can be used. Carbon black is a relatively affordable conductive filler that is far less costly than carbon nanotubes. Its low cost makes it the favoured option for applications, but when compared to carbon nanotube-filled polymers, its low aspect ratio, which is near to unity, leads in worse conductivity performance. CNTs have a greater aspect ratio as a fibrous filler, often 10000 or higher, than particle fillers like CB. The two types of CNTs that may be categorised are single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNT). One rolled graphene sheet makes up SWNT, but MWNT is made up of many concentric rolled graphene sheets, which is the difference between the two [12-15].

This dissertation's primary goal was to create shape memory polymers utilising epoxy resin with a thermoset basis. RDE monomers with aliphatic and aromatic structures were used to modify epoxy resin, and the effects on mechanical, thermal, and shape memory characteristics were noted. In a different way, two distinct fillers were combined in order to see whether there was any synergistic impact and if the specified characteristics of the polymer improved. After choosing the ideal filler concentrations, the final desired composites were created by combining the advantages of both additives into a single composite.

Experimental

Preparation of Epoxy Shape memory composite

Epoxy resin and a curing agent are the two components that react to form epoxy polymers. Depending on the stoichiometry of the reaction, these components are combined in a certain ratio. Epoxy polymer mixes are finally moulded and demoulded for shape when the curing process is finished. Resorcinol diglycidyl ether (RDE), the monomer, was acquired from Sigma Aldrich. We employed two distinct kinds of conductive fillers. Quantum Materials Corporation supplied the multi-walled carbon nanotubes (MWCNT), while Nanografi provided the carbon black (CB).

The following steps should be followed to create a shape memory polymer composite. In a beaker, three times as much acetone as epoxy was used to combine the carbon fillers. This combination was subjected to ultrasonic treatment for an hour. After adding epoxy glue to the slurry, the ultrasonic treatment was once more performed for another 30 minutes. The mixture was simultaneously stirred with a mechanical stirrer at a speed of 40 rpm while being heated in a water bath at 60 °C. They were combined using a mechanical stirrer at 40 revolutions per minute for 25 minutes after being at room temperature for 30 minutes. The hardener was then combined with the mixture, and the combination was then mechanically stirred in a beaker at 40 rpm for 15 minutes. As required by ASTM requirements for shape memory specimens, the slurry was then poured into rectangular aluminium moulds with dimensions appropriate for the samples. The moulded polymer was allowed to cure for one hour at room temperature.

The table 1 lists the sample compositions that were created and described for this study.

Table 1 **Composition of the Samples**

| Sample Code | Epoxy (%) | RDE (%) | CB (%) | CNT (%) |
|-----------------|-----------|---------|--------|---------|
| Neat Epoxy (NE) | 100 | 0 | 0 | 0 |
| E-RDE5 | 95 | 5 | | |
| E-RDE10 | 90 | 10 | | |
| E-RDE15 | 85 | 15 | | |
| E-RDE20 | 80 | 20 | | |
| SECB0.5 | 84.5 | 15 | 0.5 | |

| | | | | |
|-----------------|------|----|-----|-----|
| SECB1.0 | 84 | 15 | 1.0 | |
| SECB1.5 | 83.5 | 15 | 1.5 | |
| SECB2.0 | 83 | 15 | 2.0 | |
| SECNT0.5 | 84.5 | 15 | | 0.5 |
| SECNT.0 | 84 | 15 | | 1.0 |
| SECNT1.5 | 83.5 | 15 | | 1.5 |
| SECNT2.0 | 83 | 15 | | 2.0 |
| SECBCNT 1.5/0.5 | 83 | 15 | 1.5 | 0.5 |
| SECBCNT 1.5/1.0 | 82.5 | 15 | 1.5 | 1.0 |
| SECBCNT 1.5/1.5 | 82 | 15 | 1.5 | 1.5 |

Characterization Methods

Tensile samples were made in accordance with ASTM D638-10 (Standard Test Method for Tensile Properties of Plastics). Using a WDW-50E mechanical testing equipment, the tensile characteristics were evaluated at a rate of 10 mm/min while the test was conducted at room temperature. An aggregate impact tester was used to conduct an impact test to assess the impact resistance of both neat and composite specimens (SICMAIT-01 6967). The samples were thermally characterized using a Shimadzu DSC-60 equipment. The glass transition temperature was also calculated using DSC. The samples were heated to 250 °C from room temperature by using a heating rate of 10°C/min. It was calculated how much heat the specimen absorbed. Using this information, the average of three independent observations was used to calculate the glass transition temperature (T_g).

The bending test was used to conduct shape memory tests using thermal actuation. To assess the resilience of form memory features including recovery, fixity, and recovery time against additional shape memory cycles, shape memory polymers were put through ten cycles of the procedure. Heat is delivered to the sample, which elevates its temperature over the transition point and gives the sample an externally positive distortion. After the sample's temperature recovers to room temperature, the heat is removed and the strain is measured as L_i . When the sample is cooled, more physical crosslinks are created as a result of the solidification of switching domains. Depending on the form-fixity property of the material, stress is now visible. An innovative strain is known as L_f . L_i/L_f , the ratio of the aforementioned two strain values, is used to calculate shape fixity. The symbol θ_f stands in for the deformation angle. The final angle of the sample is indicated by the symbol θ_r , and the ratio $(\theta_f - \theta_r)/\theta_f$ may be used to calculate the shape recovery ratio.

Results and Discussion

Mechanical Characterization

Figures 1a and 1b, respectively, show the calculated and depicted tensile strength values and Young's modulus. It has been determined that neat epoxy has a tensile strength of 63 MPa, and a rise in tensile strength is anticipated when the RDE concentration is increased. When compared to plain epoxy, sample E-RDE15 exhibits the maximum tensile strength, measuring 69 MPa, or around a 10% increase in value. Due to its aromatic composition, RDE enhances the strength of epoxy when added, and it does not reduce the crosslink density of the epoxy molecular chains. Young's modulus values did not significantly alter, but they did slightly rise, which could be related to potential interactions between the epoxy resin, monomer and curing agent functional groups.

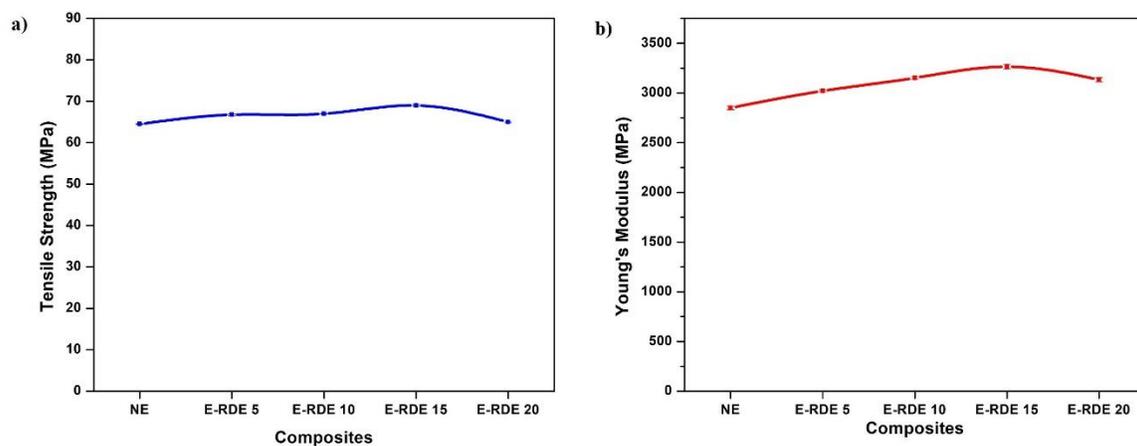


Figure 1 Tensile strength and Young's modulus of Epoxy with different percentage of addition of RDE monomer

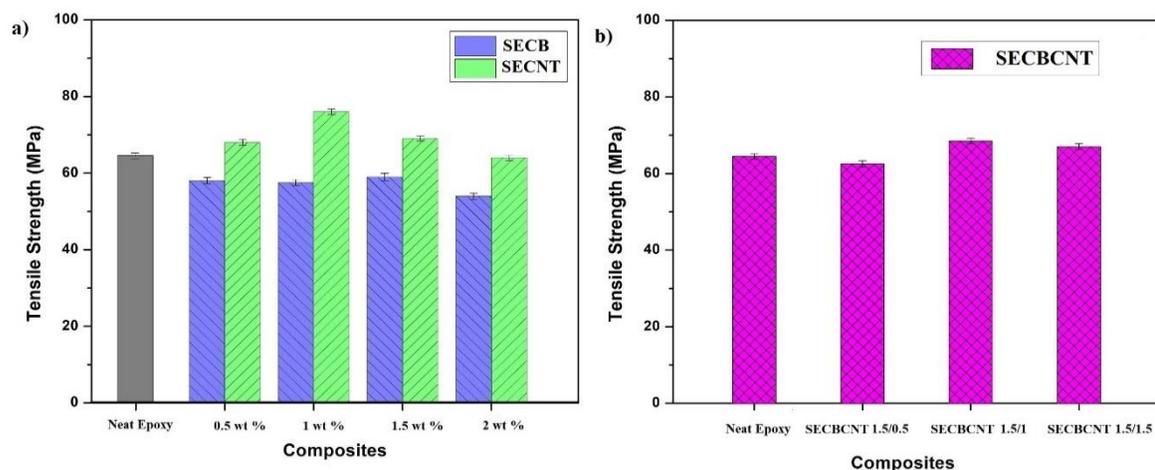


Figure 2 Tensile strength of Shape memory Epoxy polymer with addition of two different carbon based fillers

Figure 2a depicts the tensile characteristics of all shape memory polymer composites. The sample containing 1.0 wt. % carbon nanotubes had the maximum tensile strength, according to the test findings. Tensile strength dropped when the fraction of carbon nanotubes increased over 1.0 wt. %, which might be described by stress concentrated areas created by the matrix's heavily agglomerated particles. Similarly, at 1.5 wt.% carbon black, tensile strength decreased. This may be explained by growing viscosity, which caused difficulty in the resin mixture mixing operation, perhaps resulting in agglomerates and a large amount of air bubbles in the polymer. Tensile strength was reduced because stress was focussed directly on these inhomogeneous locations. The hybrid composite effect of two fillers is seen in Figure 2b. Among the other hybrid composites, the sample SECBCNT 1.5/1.0 has the best tensile strength, which was associated to lower agglomerations and stress avoidance.

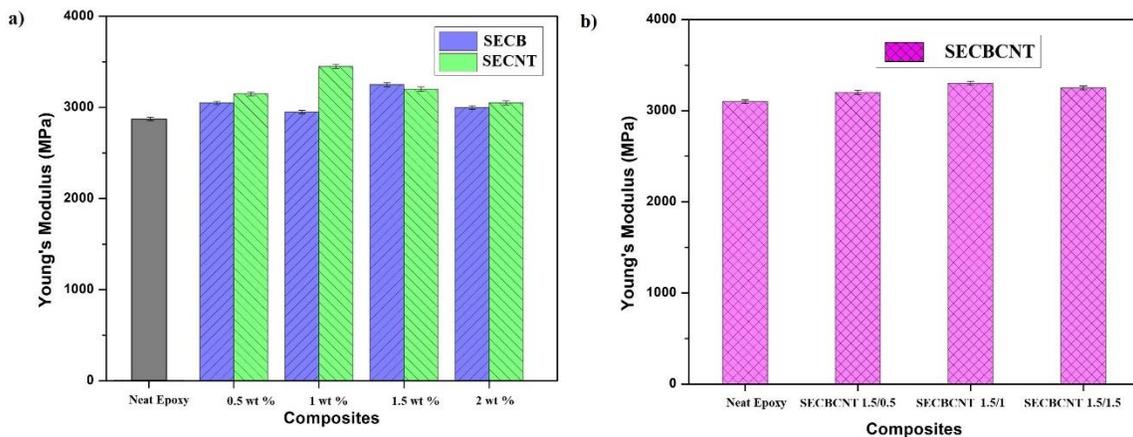


Figure 3 Young's Modulus of Shape memory Epoxy polymer with addition of two different carbon based fillers

Figure 3a depicts the modulus characteristics of all shape memory composite materials. The carbon nanotube fillers' large aspect ratio contributed to the polymer's hardness, resulting in high elastic modulus values for carbon nanotube filled composites, particularly at 1.0 wt.% loading. In the instance of carbon black, a high elastic modulus was found for a carbon black filled composite with a loading of 1.5 wt.%. The epoxy mix became very viscous at concentrations more than 1.0 wt.% CNT and 1.5 wt.% CB, preventing further growth of the elastic modulus values of these specimens. Figure 3b depicts the hybrid composite effect of two fillers. For hybrid compositions and carbon black materials, elastic modulus rose due to stiffness rise when more carbon based filling was added to the mixture.

The impact strength characteristics of all shape memory polymer composites are depicted in Figure 4a. Binary composites comprising carbon black and carbon nanotubes have their impact strength lowered. This was mostly due to composites' enhanced brittleness, which reduced the material's resistance to impact fracture. Additionally, the formation of air bubbles in the highly viscous epoxy matrix reduced the actual cross sectional area of the impact samples, resulting in lower impact strength values for the binary composites. Figure 4b demonstrates that the inclusion of both types of fillers in the polymer increased impact strength significantly, which was attributable to reduced agglomerations of fillers reducing crack propagation during impact fracturing. The specimen SECBCNT 1.5/1.0 had the maximum impact strength of the various hybrid formulations.

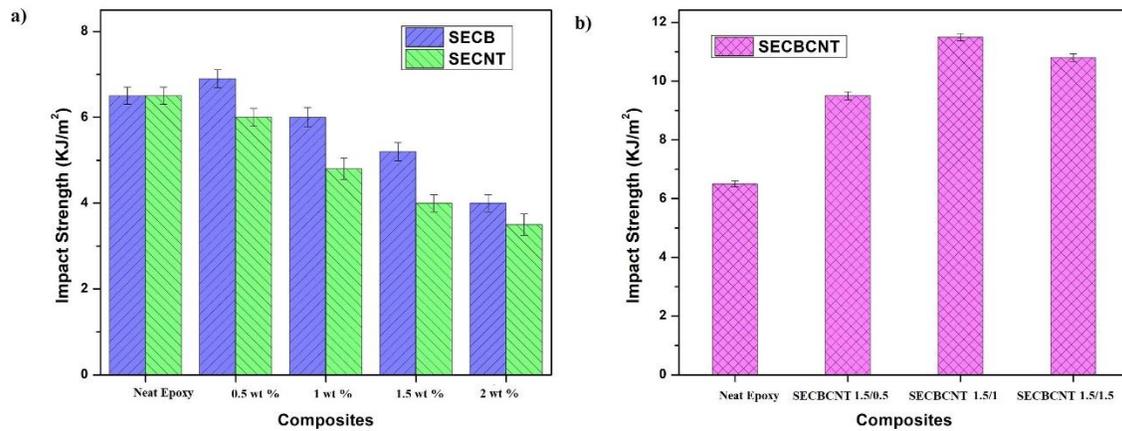


Figure 4 Impact Strength of Shape memory Epoxy polymer with addition of two different carbon based fillers

Differential Scanning Calorimetry

Figure 5 shows the change in glass transition temperature values with loading of two carbon based fillers.

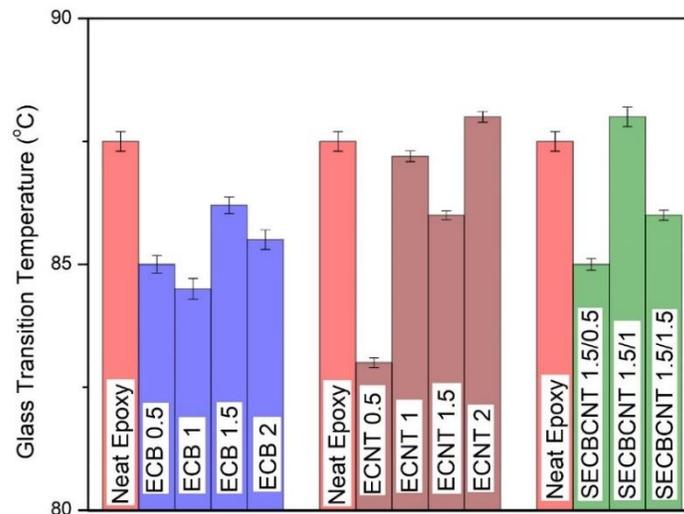


Figure 5 Glass Transition Temperature of Shape memory Epoxy polymer with addition of two different carbon based fillers

Glass transition was shown to be lower in 0.5% CNT-containing composites (SECNT 0.5) as compared to clean epoxy. The diminishing impact of composites might be explained by the poor dispersion of nanotubes in the matrix, resulting in the formation of free spaces. When carbon black filler

was used, the glass transition temperature decreased with respect to the clean epoxy for all CB loadings ranging from 0.5 to 2 wt.%. One probable explanation is that carbon black particles with bigger diameters than carbon nanotubes prevent polymer chains from being tightly interlocked to each other, lowering the glass transition temperature. Also, when hybrid composites are considered, the specimen SECBCNT 1.5/1.0 showed an increasing in glass transition temperature comparing with neat epoxy and this may be due to the combined effect of two carbon loadings which facilitates the good dispersion of the fillers in the epoxy polymer matrix.

Shape Memory

Figures 6–8 depict the modifications in the normal shape memory qualities as a result of the addition of carbon-based filler to the matrix. Shape recovery experiments were performed on the finished epoxy composites at 120°C using a thermal stimulus.

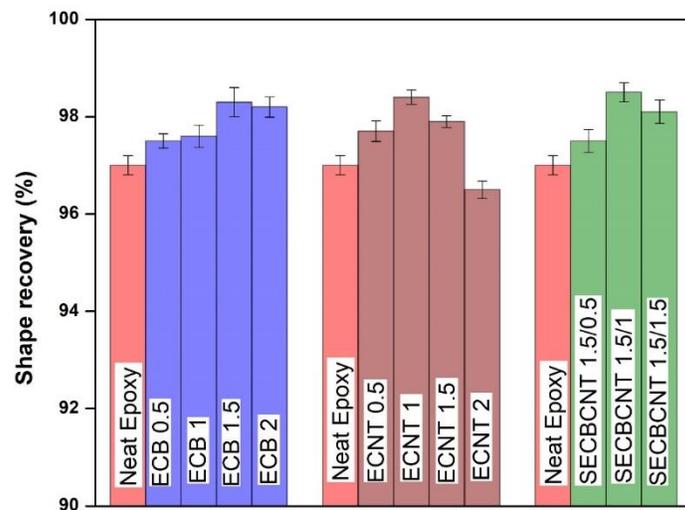


Figure 6 Shape Recovery of Shape memory Epoxy polymer with addition of two different carbon based fillers

All samples recovered at 95% or above. The best recovery rate was around 99% for SECB 1.5, SECNT 1, and SECBCNT 1.5/1.0 specimens. The addition of both carbon-based fillers to the matrix did not result in a significant change in form recovery% as compared to ordinary epoxy. Shape recovery happens when the modulus of epoxy-based polymers changes dramatically during the glass transition.

The Shape Fixity values of a Shape memory Epoxy polymer with two separate carbon-based fillers are shown in Figure 7. The soft region of the polymer has an effect on form fixity. Carbon-based chemicals frequently contribute to the polymer matrix's hard region, making the soft domain less dominant. Only composites containing carbon black and carbon nanotubes demonstrated a slight decrease in this regard. Hybrid composites, on the other hand, showed a slight improvement in form fixity, indicating that the hard segment of these samples was not as effective as composites containing only carbon nanotubes.

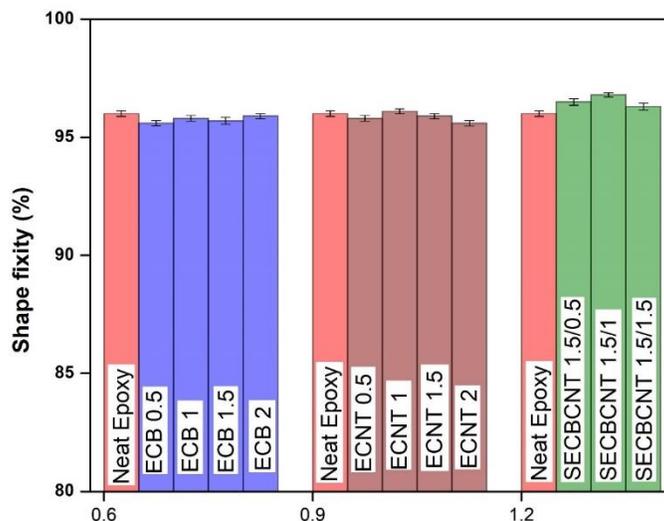


Figure 7 Shape Fixity values of Shape memory Epoxy polymer with addition of two different carbon based fillers

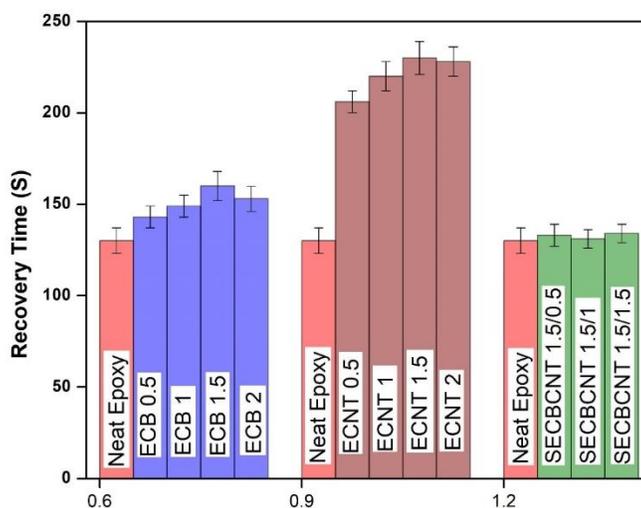


Figure 8 Recovery Time of Shape memory Epoxy polymer with addition of two different carbon based fillers

The recovery period of form memory samples is depicted in Figure 8. The samples containing more carbon nanotubes clearly recovered more slowly. Carbon black composites recovered faster than carbon nanotube composites because to their weaker hard portions. The hard part of the matrix was supported by carbon-based components, and recovery time was related to the hard segment's stability. Carbon nanotube composites with highly developed hard domains produced a decrease in soft segment activity, resulting in an increase in shape recovery time. On the other hand, the samples with the greatest loading levels, such as SECB 2 and SECNT 2, showed structural inhomogeneity induced by air bubbles, which shortened the recovery time. The reason for observing low recovery time values for

samples could be during heating of the sample, it started to recover at lower temperature or the recovery had started earlier for those samples.

Conclusions

The polymer matrix was modified by RDE monomer and Carbon nanotube, carbon black were used to reinforce the epoxy polymer. Mechanical, thermal and shape memory properties were investigated. The summary of this work is concluded as follows:

- Samples were produced containing 5, 10, 15 and 20% of RDE monomer and the results revealed that the sample with loading of 15% RDE exhibited the maximum strength and modulus.
- Carbon black and carbon nanotubes were added to the polymer in 0.5, 1.0, 1.5 and 2 % by weight fractions.
- The sample containing 1.0 wt% carbon nanotubes had the maximum tensile strength, according to the findings of the test. A decrease in the impact strength was observed for binary composites of carbon black and carbon nanotubes, whereas for the hybrid composites the increase in impact strength was observed.
- Glass transition was observed to decrease more for 0.5 % CNT containing composite (SECNT 0.5) in comparing with the neat epoxy and this could be due to the imperfect dispersion of nanotubes and thereby generation of free voids in the matrix.
- Among all the hybrid formulations, the RDE modified epoxy (SECBCNT 1.5/1.0) with 1.5 wt. % carbon black and 1.0 wt. % fillers exhibited the best mechanical, thermal and shape memory properties.

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