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Investigations on d.c. conductivity behaviour of milled carbon fibre reinforced epoxy graded composites

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Abstract. This paper reports the d.c. conductivity behaviour of milled carbon fibre reinforced polysulphide modified epoxy gradient composites. Milled carbon fibre reinforced composites having 3 vol. % of milled carbon fibre and poly sulphide modified epoxy resin have been developed. D.C. conductivity measurements are conducted on the graded composites by using an Electrometer in the temperature range from 26°C to 150°C. D.C. conductivity increases with the increase of distance in the direction of centrifugal force, which shows the formation of graded structure with the composites. D.C. conductivity increases on increase of milled carbon fibre content from 0·45 to 1·66 vol.%. At 50°C, d.c. conductivity values were $1{\cdot}85 \times 10^{-11}$, $1{\cdot}08 \times 10^{-11}$ and $2{\cdot}16 \times 10^{-12}$ for samples 1, 2 and 3, respectively. The activation energy values for different composite samples 1, 2 and 3 are 0·489, 0·565 and 0·654 eV, respectively which shows decrease in activation energy with increase of fibre content.

Keywords. Milled carbon; epoxy; gradient; d.c. conductivity.

1. Introduction

Polymer composites developed with fillers of carbon nature have made it possible to produce a new polymer composite material possessing the shape memory effect accompanied by a considerable volume increase (Beloshenko *et al* 2000). Another investigation on a composite basing on a high-deformable epoxy polymer and thermo expanded graphite has mainly found the mechanism explaining the kinematics of its formation and development of the boundaries of the domain for its existence (Beloshenko *et al* 2002a,b). Conduction process in conductive filler–polymer composite is complicated and depends on the number of parameters such as filler concentration, filler matrix interaction, process techniques, aspect ratio and filler orientation. It is known that the electricity conductive filler gives us a possibility of controlling the electrical properties of the composites by using the filler. At threshold, there is a sudden increase of the electrical resistance, in some critical temperature range, due to thermal expansion of the polymer matrix (Kovalenko and Syrovatskaya 2000). Composites developed by Quivy *et al* (1989) with filler content close to the threshold, the conductor – dielectric transitions resulted in the realization of the effect of heating temperature self-regulation. Kovalenko and Syrovatskaya (1999) investigated the influence of technological parameters on electric conduction of carbon-containing composites. Irving and Thiagarajan (1998) reported the properties of carbon fibres.

Functionally graded composites are one such class of materials, which exhibit a variation in chemical composition over definable distances. Electrical properties of such materials are important along the centrifugation direction. There is no report on the d.c. conductivity characteristics of milled carbon reinforced epoxy graded composites.

In this paper, graded composites of epoxy reinforced with milled carbon fibres have been developed. D.C. conductivity behaviour of milled carbon fibre reinforced graded epoxy composite has been determined and explained.

2. Materials and methods

Polysulphide modified epoxy (PSEP) resin used in this study was obtained from M/s Choksey Chemical, India. The density of epoxy resin cured at room temperature with hardener in the ratio of 2 : 1 was 1·15 g/cc. Panex 33 MX milled carbon fibre added in this study was obtained from M/s Amalgamated Composites (P) Ltd., Mumbai, India. It had 95% carbon content and average fibre diameter was 7·2 μm and fibre length, 150 μm.

Milled carbon fibre reinforced epoxy gradient composites were developed by using centrifugation technique which was developed by Chand and Hashmi (2003). The centrifugal force was applied in the direction of X. Gradient samples were prepared from the milled carbon rein-

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forced mix having 3 vol. % milled carbon fibres. Milled carbon fibre was added to a mix of epoxy resin and hardener. Total mix was thoroughly stirred with the help of a glass rod. Details of set up and of the process of making gradient composites are as reported in an earlier patent (Chand and Hashmi 2003). The total mix was filled in the mould to make the sample. The sample was rotated at 800 ± 50 RPM at a radius of 130 mm. Samples were removed from the mould after post curing at room temperature for 24 h. The density of poly sulphide epoxy used in this study obtained was 1·15 g/cc. The density of milled carbon fibres used was 1·81 g/cc. Rectangular section of length, 18 mm, was cut from the circular block and sliced into 3 pieces of 6 mm length and these were polished on both sides to reduce the thickness to nearly 2 mm. Samples were numbered 1, 2 and 3 from the outermost side where maximum carbon fibres were present. These samples were coated by air drying type silver paint before the measurements. The slices contained 1·66, 0·60 and 0·454 vol.% of milled carbon fibre in resin system and density of samples was 1·6, 1·54, 1·53 g/cc, respectively. The density also increases on addition of milled carbon fibre in the PSEP milled carbon composite.

2.1 *Resistivity measurements*

Resistance (R) values of milled carbon fibre reinforced PSEP gradient samples were measured by using a Keithley electrometer model 610C in the temperature range 26–150°C. Heating rate was kept constant at 1°C/min. Resistivity (ρ) and d.c. conductivity ($\sigma_{\text{d.c.}}$) values were calculated by using the following relation

$$\rho = R^*A/l,$$

where R is the resistance value of the sample, A (cm^2) the area of the electrodes and l (cm) the thickness of the sample.

Conductivity was calculated by using the following formula

$$\sigma_{\text{d.c.}} = 1/\rho.$$

3. Results and discussion

Figure 1 shows the schematic view of the gradient sample prepared by using milled carbon fibres and poly sulphide epoxy composites. This schematic shows the distribution of milled carbon fibres in the composite.

Figure 2 shows the variation of d.c. conductivity vs temperature for milled carbon fibre reinforced PSEP epoxy sample 3 having 0·4545 vol% of milled carbon fibres. This plot shows a sharp increase in the d.c. conductivity from 58°C. In this case there is an increase of d.c. conductivity up to 100°C, after that there is a decrease up to 120°C and then there is a further increase of d.c. conductivity up to 150°C. This plot shows a peak around 100°C.

Figure 3 shows the variation of d.c. conductivity vs temperature for milled carbon fibre reinforced PSEP sample 2 having 0·6 vol% milled carbon fibres. This plot shows that up to 88°C there is no increase in d.c. conductivity. After 88°C, there is a sudden increase in d.c. conductivity with increase of temperature and a peak was found at 130°C temperature. After that there is a decrease in d.c. conductivity. This plot shows that there is an increase in d.c. conductivity on increase of milled carbon fibre content at all temperatures. Another important observation is that there is a peak shift towards the higher temperature side on increase of milled fibre content.

Figure 4 shows the variation of d.c. conductivity vs temperature for milled carbon fibre reinforced PSEP epoxy sample 1 having 1·66 vol% of milled carbon fibres and its density was 1·6 g/cc. This plot shows that there is no change in d.c. conductivity up to nearly 108°C, after that there is a sudden increase in d.c. conductivity value. At 108°C, the d.c. conductivity value was found to be $4{\cdot}42 \times 10^{-9}$. It goes on increasing on further increase of temperature to 148°C and a peak was found at 148°C. This shows that the sudden increase of d.c. conductivity at 108°C is dominated by the PSEP resin. There is an increase in d.c. conductivity values at all the temperatures as compared to sample 2. The figure shows that there is no continuous linear increase with temperature.

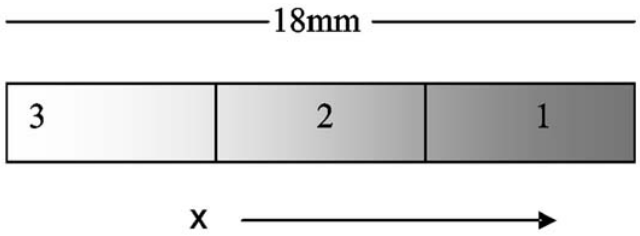

Figure 1. Schematic diagram of milled carbon distribution in three sections.

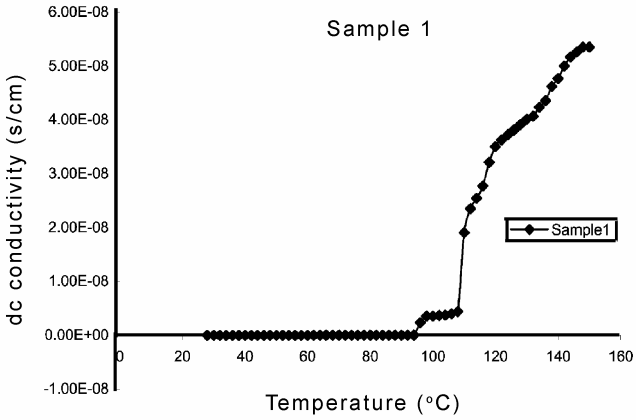

Figure 2. Variation of d.c. conductivity vs temperature for milled carbon fibre reinforced PSEP epoxy sample 3.

It has been observed that d.c. conductivity suddenly increases after 60°C in all the cases. This is because T_g epoxy is around 60°C, obtained earlier for PSEP resin, by using DSC 822e. Below T_g d.c. conductivity does not increase much, after T_g where epoxy comes in amorphous phase and sudden change in conductivity occurs. This is because after T_g free volume increases and chains start moving, which makes the movement of charge carriers easy and hence they take place in conduction process after release from traps. This observation is very similar to the earlier reported work of Rimska *et al* (2002).

Table 1 shows the d.c. conductivity values of samples 1, 2 and 3 at different temperatures. This shows that the sample 1 has maximum d.c. conductivity value due to the presence of maximum milled carbon fibres and sample 3 has minimum value due to presence of minimum fibres in this region.

In polymers at 0 K all the trapped electrons are in deep traps. But at a particular temperature and on application of the applied field some of the electrons can excite into shallow traps or to conduction level. It has been reported in the literature that these electrons can take part in conduction. The increase in temperature does not alter the total amount of space charge but increases the portion of this space charge in the conduction band which increases exponentially on increase of temperature.

In the process, electron occupying an isolated donor had a wave function near the impurity and energy slightly below the conduction band minimum. There is a little overlap of wave function of an electron of donor with those near to the donors. Due to this a conduction process becomes possible in some circumstances in which electrons may move between the centres by tunneling effect without activation. Defect conduction in the case of polypropylene is reported by Singh and Gupta (1986). They reported that the thermal agitation gives rise to defects in the material and conduction takes place by movement of ions from an occupied position to an unoccupied position.

Lnσ vs T^{-1} plot between 26°C and 90°C has been analysed by using the following Arrhenius equation (Singh and Gupta 1986)

$$\sigma = A\exp^{-W_E/kT},$$

where W_E is the activation energy of conduction, k the Boltzmann's constant and A is a constant. T is the temperature in °K.

Activation energy (W_E) of carbon milled composites is listed in table 1 and is always < 1 which shows that there is the predominance of electronic conduction according to Brown and Aftergut (1963).

This decrease of activation energy with increase of carbon fibre content is similar to the activation energy calculated for filled blends (Anatoly *et al* 1998), which has been explained by the formation of border layer at the interface of the filled polymer.

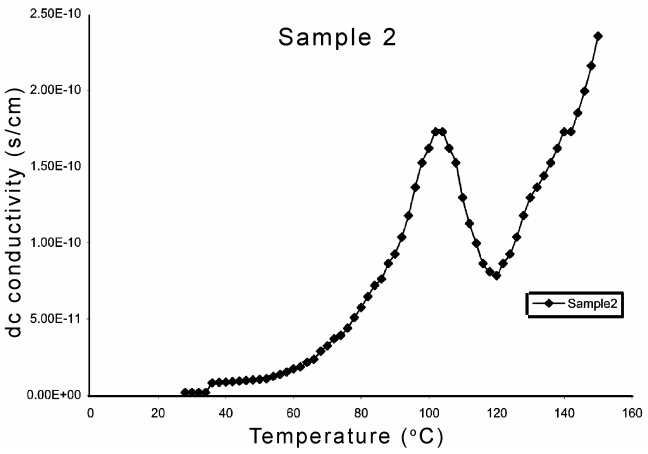

Figure 3. Variation of d.c. conductivity vs temperature for milled carbon fibre reinforced PSEP epoxy sample 2.

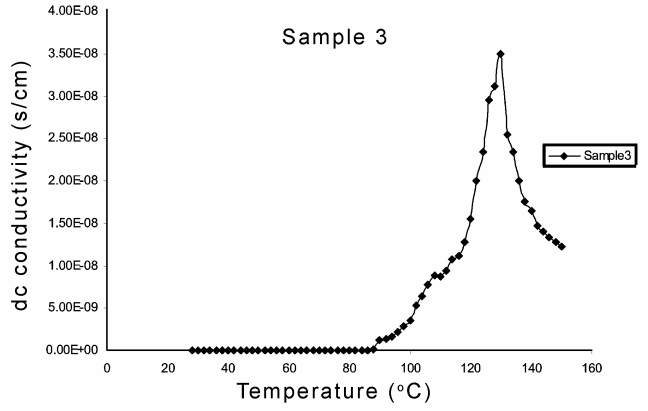

Figure 4. Variation of d.c. conductivity vs temperature for milled carbon fibre reinforced PSEP epoxy sample 1.

Table 1. D.C. conductivity values of samples 1, 2 and 3 at different temperatures.

Temperature	Sample 1	Sample 2	Sample 3
30	$2{\cdot}35 \times 10^{-12}$	$1{\cdot}70 \times 10^{-12}$	$1{\cdot}40 \times 10^{-11}$
40	$2{\cdot}18 \times 10^{-12}$	$8{\cdot}63 \times 10^{-12}$	$1{\cdot}75 \times 10^{-12}$
50	$1{\cdot}35 \times 10^{-11}$	$1{\cdot}08 \times 10^{-11}$	$2{\cdot}16 \times 10^{-12}$
60	$1{\cdot}97 \times 10^{-11}$	$1{\cdot}73 \times 10^{-11}$	$3{\cdot}14 \times 10^{-12}$

Table 2. Activation energy (eV) of samples 1, 2 and 3.

Sl. no.	Activation energy (eV)
Sample 1	0·489
Sample 2	0·565
Sample 3	0·654

4. Conclusions

(I) Increase of d.c. conductivity value from sample 3 to sample 1 shows the existence of graded structure.
(II) Increase of milled carbon fibre content increases the d.c. conductivity value.
(III) D.C. conductivity of reinforced milled carbon fibre increased with increase of temperature. After 60°C there is a sudden increase in d.c. conductivity due to T_g.
(IV) Activation energy decreases with increase of fibre content.

References

Anatoly E, Nester O V, Lipatov Yury S, Horichko Vitaly V and Ignatora Taisa D 1998 *Macromol. Chem. Phys.* **199** 2609

Beloshenko V A, Borzenko A P, Varyukhin V N and Shapranov V V 2000 Polymer composite material and a method to produce articles with shape memory effect. Patent No. 43593 A, Ukraine

Beloshenko V A, Borzenko A P and Varyukhin V N 2002a *High Press. Res.* **22** 589

Beloshenko V A, Beygelzimer Y E, Borzenko A P and Varyukhin V N 2002b *Composites Part A* **33** 1001

Brown G P and Aftergut S 1963 *J. Chem. Phys.* (*USA*) **38** 1356

Chand N and Hashmi S A R 2003 Indian Patents NF438/03

Irving P E and Thiagarajan C 1998 *Smart Mater. Struct.* **7** 456

Kovalenko N A and Syrovatskaya I K 2000 *Plastic Masses* **10** 7

Kovalenko N A and Syrovatskaya I K 1999 *Plastic Masses* **8** 11

Rimska Z, Kresalek V and Spacek J 2002 *J. Polym. Comp.* **23** 95

Singh H P and Gupta D 1986 *Indian J. Pure & Appl. Phys.* **24** 444

Quivy A, Deltour R, Jansen A G M and Wyder P 1989 *Phys. Rev.* **B9** 1026