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Electrical conduction in thermoplastic elastomer matrix composites containing catalytic chemical vapour deposited carbon whisker

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Electrical conduction in carbon whisker/thermoplastic elastomer (TPE) composites was found to be a thermally activated process. The carbon whiskers used were obtained by a catalytic chemical vapour deposition (CCVD) technique conducted at 500 °C and the TPE was a styrene–ethylene butylene–styrene (S–EB–S) block copolymer. The resistivity, (ρ), versus $1/T$ curves of the composites exhibited two regions with distinct slopes with an inflection at the glass transition temperature, T_g, of the elastomer, EB; Region I $< T_g$ and II $> T_g$. The thermally activated conduction mechanism of these composites is explained on the basis of electron transport in low-mobility solids with a large number of trap sites. Intra- and intermolecular motion of the polymer chains can result in the electron transport from such trap sites and were correlated to the observed activation energies. Intramolecular motion in region I, was related to the thermally assisted hopping with the activation energy, ΔE_A, of 0.067 and 0.030 eV for 33% and 52% whisker volume fraction composites, respectively. Similarly, ΔE_A due to the intermolecular segmental chain motions in region II for 33% and 52% whisker volume fraction composites was related to the equilibrium rate of trapping–detrapping of electrons from 0.240 and 0.138 eV deep traps.

1. Introduction

Electrical conduction in carbon filler-reinforced polymeric composites has attracted much attention [1–3] because of the ability of the fillers to control and modify the electrical property of the polymers. Conductivity mechanisms of carbon filler-reinforced polymeric systems were proposed based on a series of conductor–insulator elements [4–6]. Although these models, based on the percolation theory [7], were able to predict the change in resistivity reasonably well from the filler aspect ratio and volume concentration, the temperature dependence of resistivity cannot be explained completely. Further, according to the percolation threshold theory there is a critical concentration level for the fillers, depending on the geometry of the fillers, above which the composite became a conductor from an insulator (typically around 30 vol % fraction). In the present work, an attempt has been made to explain the conduction behaviour of highly loaded (above the percolation threshold) catalytic chemical vapour deposited (CCVD) carbon whisker-reinforced thermoplastic elastomer (TPE) composites on the basis of electron transport and tunnelling phenomena.

2. Experimental procedure

2.1. Processing of carbon whisker/TPE composites

The CCVD carbon whiskers used in this study were grown by decomposing C_2H_2 gas in the presence of Cu–Ni catalyst at 500 °C [8]. The TPE was supplied by Shell Chemical company under the trade name Kraton G1901X^R. The TPE is a linear tri-block copolymer with 28% terminal polystyrene blocks and elastomeric central blocks. The elastomeric block consists of a copolymer of ethylene and butylene. The chemical structure of styrene–ethylene butylene–styrene (S–EB–S) thermoplastic elastomer is given in Fig. 1. CCVD carbon whisker/TPE composites were prepared by mixing 33% and 52% volume fraction of CCVD carbon whiskers in TPE solution. Prior to mixing, TPE was dissolved in chloroform. The whiskers were well mixed in the TPE solution and then solution cast on to a glass plate. The glass plate was kept in a vacuum oven to remove the solvent. Thin sheets of the composite were peeled off from the glass plate and subsequently used for characterization and electrical conduction measurements.

2.2. Characterization of carbon whisker/TPE composites

The morphology of the composites was characterized by scanning electron microscopy (SEM). Prior to

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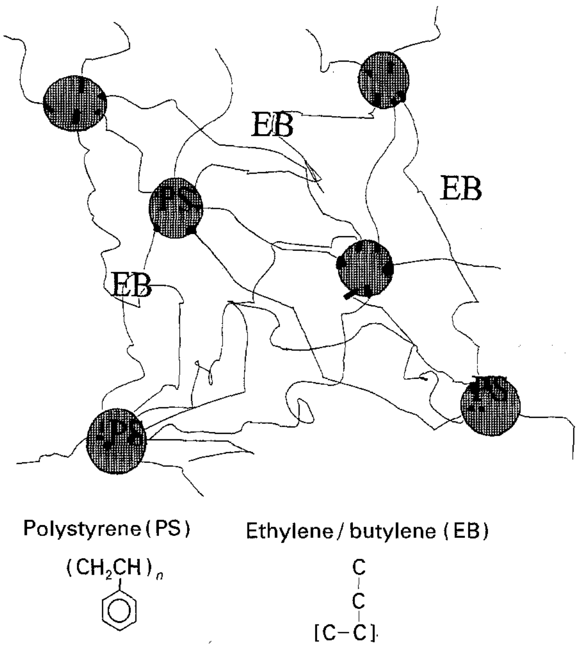

Figure 1 Chemical structure of thermoplastic elastomer.

observation, the samples were slightly etched on the surface by chloroform and gold sputtered. Dynamic mechanical thermal analysis (DMTA) was performed on the TPE and the composites. The loss tangent, tanδ, of the samples was monitored as a function of temperature from -100 to $-20\,^{\circ}\mathrm{C}$. Attenuated total internal reflection infrared spectroscopy (ATIR) was performed in the near infrared region for the TPE and the composite. ATIR samples were prepared by pressing the material against the KRS-5 crystal. A d.c. power source (up to 100 V) was used to measure the electrical resistance as a function of temperature.

3. Results

3.1. Morphology of CCVD carbon whisker/TPE composites

The microstructure of the composites containing 33% and 52% volume fractions of whisker is shown in Fig. 2. The carbon whiskers tend to form agglomerates. The thin polymeric coating on the whiskers prevented the whiskers or agglomerates from coming into contact with each other. This was possible, because the whiskers were mixed in a polymer solution. Thus the conduction or electron transport between carbon whiskers has to go through the polymer barrier, i.e. a carbon–polymer–carbon junction (C–P–C). The volume fraction of whiskers and their dispersion will determine the effective polymer gap through which the electrons have to tunnel.

3.2. DMTA analysis

Dynamic loss tanδ values of the elastomer and the composites are shown as a function of temperature in Fig. 3. A maxima peak at $-52\,^{\circ}\mathrm{C}$ of the TPE corresponds to the glass transition temperature, T_g, of the amorphous ethylene butylene copolymer. The T_g data of the composites agreed well with the TPE indicating that CCVD whiskers did not have any influence on the T_g of the elastomer. As such, the CCVD carbon whiskers were physically embedded in the polymer. Because rigid PS domains (28%) act as the physical tie points for the EB copolymer, the TPE exhibits two T_g, one corresponding to the EB segments and the other corresponding to PS at $110\,^{\circ}\mathrm{C}$ [9]. When the TPE is below $-52\,^{\circ}\mathrm{C}$, all the segments are in the glassy (frozen) state, i.e. only intramolecular chain motions are possible, whereas above $-52\,^{\circ}\mathrm{C}$, the EB segments are in the rubbery region. Though PS is still in the glassy state the EB segments will now have segmental intermolecular chain motions.

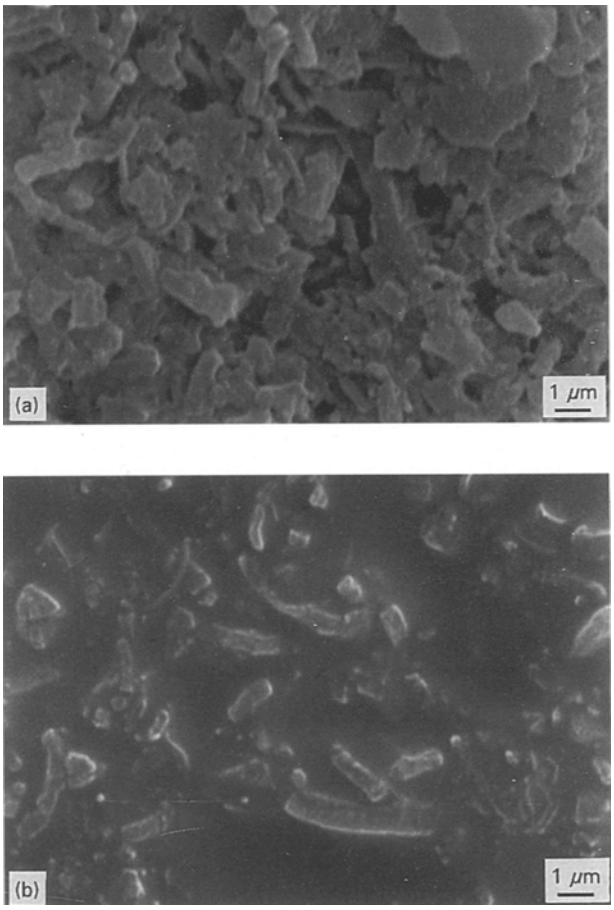

Figure 2 Scanning electron micrographs of (a) 33% and (b) 52% whisker volume fraction composites.

3.3. ATIR spectroscopy

The IR spectra of the TPE and composites are given in Fig. 4. The spectra obtained were entirely independent of specimen geometry. The spectra of the composites matched the TPE spectrum indicating that there was no chemical reaction between CCVD whiskers and TPE. Hence from SEM, DMTA and ATIR it can be inferred that carbon whiskers were embedded in the TPE matrix and the contact between the whisker and TPE is purely a physical one.

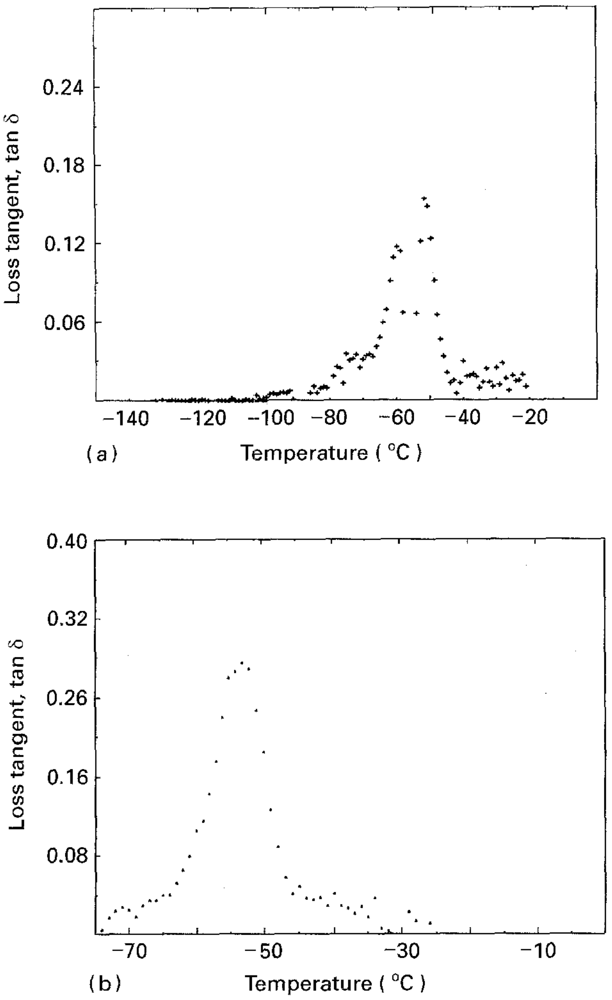

Figure 3 Dynamic loss, tanδ, as a function of temperature for (a) TPE and (b) 33% whisker volume fraction composites.

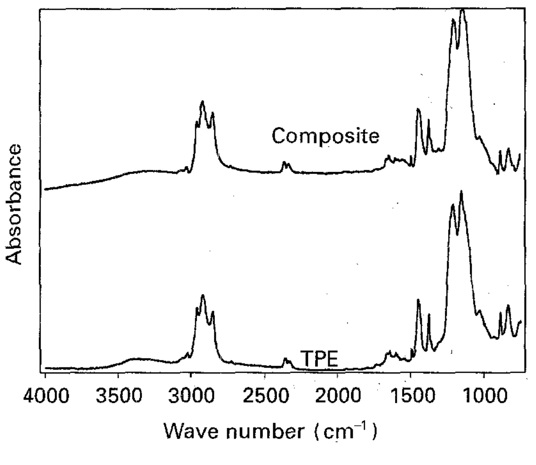

Figure 4 ATIR spectroscopy of TPE and composites.

3.4. Resistivity measurements

A plot of resistivity as a function of temperature (ρ versus $1/T$) is given in Fig. 5. The resistivity decreased with increasing temperature, exhibiting two distinct slopes which were separated near the T_g of the EB copolymer. The activation energies, ΔE_A, associated with these slopes were determined from the following relation

$$\rho = \rho_0 \exp(\Delta E_A / kT) \tag{1}$$

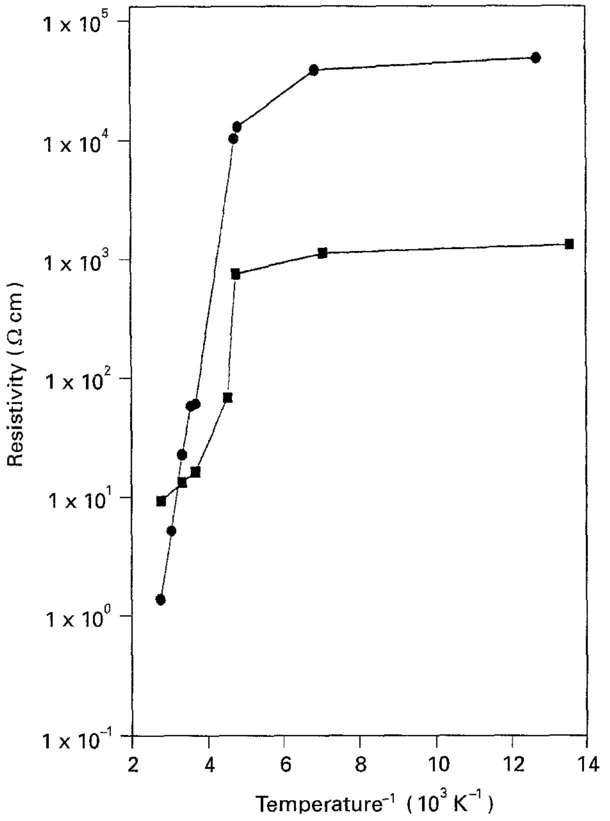

Figure 5 Resistivity as a function of temperature: (●) 33% and (■) 52% whisker volume fraction composites.

It can be seen from Fig. 5, that the slope of region I ($T < T_g$) is smaller than that of region II ($T > T_g$). The activation energy values, ΔE_A, for the 33% whisker composite are 0.067 and 0.240 eV in regions I and II, respectively. The corresponding values for the 52% whisker composites are 0.03 and 0.138 eV, respectively.

4. Discussion

In order to examine the effect of the contact between carbon whiskers and TPE on the conduction behaviour of the composites, metal–polymer–metal (M–P–M) sandwich samples with well-known electrical properties were processed. The M–P–M sandwich was made from two materials, namely aluminium and graphite. The TPE dissolved in chloroform was coated on a circular aluminium foil with the solvent subsequently evaporated. Another aluminium foil with the same geometry was tightly held on top of the polymer layer. Graphite samples were also processed in a similar fashion. The resistance of these sandwich structures as a function of temperature is shown in Fig. 6. The R versus $(1/T)$ curves of these two samples exhibited two distinct slopes similar to the effect of Fig. 5.

An energy-band diagram is shown in Fig. 7, to explain the electron transport in a model system such as a metal–polymer junction. The energy-band diagram is based on the electron transport in low mobility solids and liquids [10]. When a metal comes into contact with an insulating polymer such as the case

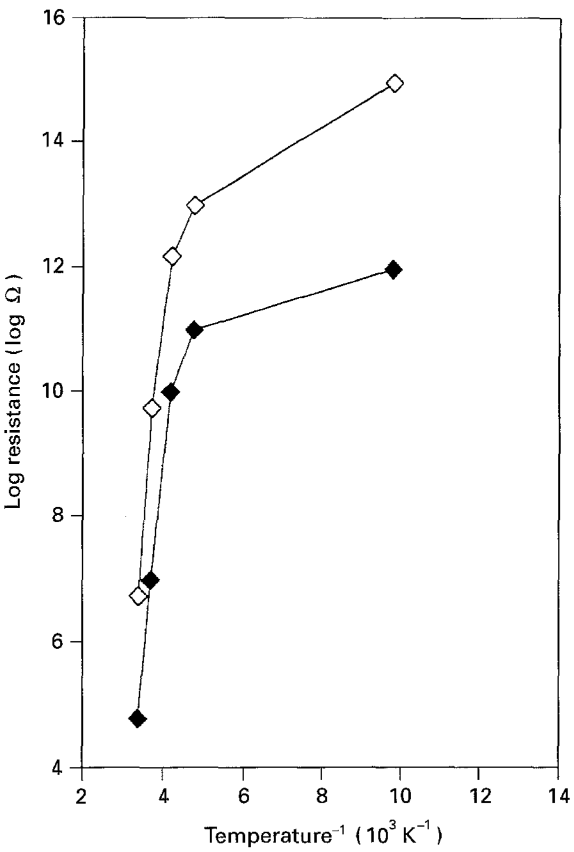

Figure 6 Resistance as a function of temperature for (◇) Al–P–Al and (◆) Gr–P–Gr samples (Gr = graphite).

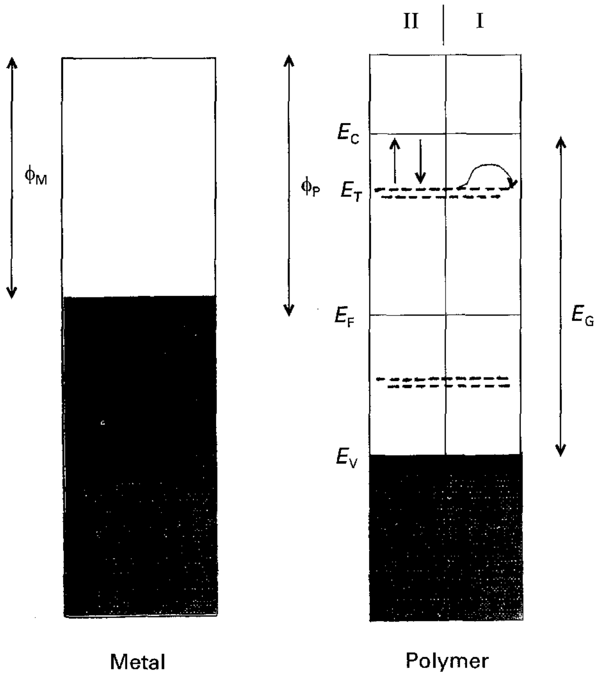

Figure 7 Typical energy band diagram for a metal–polymer junction.

shown in Fig. 7, electrons may flow from the metal to the empty states in the insulator. The nature of such a contact depends on the work function of the metal, ϕ_M, and that of the polymer, ϕ_P. This type of metal – insulator contact will result in the coincidence of the Fermi-level of the metal and the insulator. The work functions of aluminium is 4.28 eV [11], that of graphite is 3.8 eV [12], and that of polymers is around 4.5–5 eV [13]. Depending on the work function, the resulting contact could form a Schottky barrier or an ohmic contact. As such, $\phi_M < \phi_P$, the resulting contact is an ohmic one [14].

Polymers contain trap sites as high as 10^{19} cm^{-3}, which have an important role in the conduction and breakdown process. These electron traps can occur from defects, chain folding, branching, entanglements, etc. It has been suggested [15] that electron transport in polymers can be explained on the basis of intramolecular and intermolecular chain motion. When the electrons injected from the electrodes (aluminium, graphite or CCVD carbon whiskers) try to cross the insulating barrier, they are trapped by the polymer at the trap sites, as shown in Fig. 7. When the temperature is lower than the T_g of the EB segments, the entire polymer is in the glassy state and thereby electron transfer is only possible by intramolecular jumps. This is similar to the thermally assisted hopping of electrons in low-mobility solids [16]. When the trap density is large enough the potential wells between trap sites will overlap each other and the energy barrier for hopping will now be lower than the ionization energy of the electrons from the trap site (Fig. 7). The intramolecular jumps can be compared to the hopping distance in the classical sense (several atomic units). The activation energy values in region I (0.067 and 0.030 eV) can be compared to the thermally assisted hopping energy values [17].

When the temperature is increased above T_g, intermolecular interactions become more effective. As the amplitude of the EB segmental motion increases above T_g, more electrons can be released. Detrapping of electrons from the trap sites is thus possible by the intermolecular chain oscillations. The activation energy associated with the trapping–detrapping process can be developed from the kinetics of such a process based on the works of Shockley and Read [18].

Assuming, for simplicity, a single trap level, the rate of capture of electrons $(\mathrm{d}n/\mathrm{d}t)_{\mathrm{trap}}$ can be written as follows

$$(\mathrm{d}n/\mathrm{d}t)_{\mathrm{trap}} = P_{\mathrm{et}}(n)N_{\mathrm{T}}C(n) \qquad (2)$$

where $P_{\mathrm{et}}(n)$ is the probability that the traps are empty and can capture electrons, N_{T} the total number of trap sites, and $C(n)$ the rate constant of capture or trapping of electrons. The rate of detrapping $(\mathrm{d}n_t/\mathrm{d}t)_{\mathrm{detrap}}$ can be written similar to Equation 1, as follows

$$(\mathrm{d}n_t/\mathrm{d}t)_{\mathrm{detrap}} = P_{\mathrm{ft}}(n)N_{\mathrm{T}}R(n) \qquad (3)$$

where $P_{\mathrm{ft}}(n)$ is the probability that the traps are occupied and can release electrons, and $R(n)$ is the rate constant for the releasing or detrapping of electrons.

For a limiting case (e.g. in the steady state) when $(\mathrm{d}n/\mathrm{d}t)_{\mathrm{trap}} = (\mathrm{d}n_t/\mathrm{d}t)_{\mathrm{detrap}}$, then

$$R(n)/C(n) = P_{\mathrm{et}}(n)/P_{\mathrm{ft}}(n) \qquad (4)$$

The probability $P(n)$, of an energy level being occupied can be written in the form of a Fermi–Dirac distribution function, as follows

$$P(n) = 1/\{1 + \exp[(E - E_{\mathrm{F}})/kT]\} \qquad (5)$$

where E is the electron energy level, E_F the Fermi energy level and k the Boltzmann constant. Similarly, $P_{ft}(n)$ can be written as follows (Fig. 7)

$$P_{ft}(n) = 1/\{1 + \exp[(E_C - E_T)/kT]\} \qquad (6)$$

where E_C and E_T correspond to the energy levels for conduction and trap sites, respectively. Because $P_{ft}(n) + P_{et}(n) = 1$, Equation 4 can be rewritten as

$$R(n)/C(n) = \exp[(E_C - E_T)/kT]\} \qquad (7)$$

The activation energy, ΔE_A, in region II based on trapping–detrapping events can be correlated to $(E_C - E_T)$. Hence, the activation energy in region II corresponds to a localized energy state a few electron volts deep. The trap depths in the range of 0.5–0.8 eV have been identified for polymers from thermally stimulated conductivity (TSC) and thermally stimulated luminescence (TSL) studies [19, 20]. Similar energy values have been reported for non-crystalline solids from mobility experiments [21].

5. Conclusions

1. Electron transport in CCVD carbon whisker/TPE composites depends on the state of the TPE and is governed by a thermally activated process.

2. Electron transport in these composites can be explained as an intramolecular (below T_g) and an intermolecular (above T_g) process. The intramolecular process can be shown to be similar to a thermally activated hopping process, and the intermolecular process as a rate process approaching equilibrium between trapping and detrapping of electrons.

Acknowledgements

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