Striking effect of temperature on conductivity of polyurethane/CNT nanocomposites

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Electrically conducting adhesive nanocomposites are obtained dispersing different amounts of Multiwall carbon nanotubes (MWCNT) in a thermoplastic hot-melt polyurethane (TPU) by a melt mixing method.

The electrical conductivity of the obtained composites can be described in terms of percolation behaviour [1-3] At low filler concentrations, the conductivity remains very close to the conductivity of the pure, electrically insulating polymer matrix since the fillers are dispersed individually or are present as small clusters in the matrix. Above the percolation threshold concentration, close to 2% MWNT, the independent fillers tend to link together to form conductive networks. This leads to a significant increase in the electrical conductivity of the composite.

Frequency dependent conductivity experiments have been performed in the melt and during crystallization with the aim to study temperature effects on the conductive network in an attempt to understand i) the relationship between the dynamics of percolation and the processing conditions and ii) the solidification behaviour, that is, how the actual structure of the filler network is frozen during crystallization. Although it is well known that carbon nanotubes can act as specific nucleating agents in semi-crystalline polymers, the influence of the crystalline phase on the structure of the MWNT-polymer composite is a topic which has not received much attention in the framework of the electrical conductivity.

The effect of melting and crystallization on the conductive network is shown in Figure 1. In a first step, conductivity has been measured during the heating of the melt from 70ºC to 150ºC, after certain resting time at the higher temperature, during a second step the melt is cooled to room temperature.

The conductivity of the sample increases with temperature during the heating step and at the rest period the conductivity experiments an abrupt jump. The result reflects the effect of previous melt mixing process when the shearing applied to facilitate CNT dispersion can disturb conductive network formation [4,6] Annealing at high temperature produces network re-formation as the CNT are easy to re-agglomerate by Van der Waals force and brownian motion at high temperatures beyond the Tm.

During cooling of the melt a significant increase in the conductivity is detected at the crystallization temperature. This is consistently expressed in the conductivity spectra of the Figure 1 and can be explained by the structural changes during crystallization process. The thermal contraction and the reduction of amorphous phase on expense of the crystalline phase reduce the local contact distance and increase the number of conducting paths between tubes, if we assume that the filler is predominantly located out of crystallites. The effect is similar to that obtained in segregated network systems [7] like polymer blends for which the conductive filler is forced to occupy only one of the two dissimilar polymers or the interface between the two polymers.

The conductive filler network alters the rheological behaviour. The contact between polymer chains and carbon nanotubes gives rise to a chain mobility restriction which may be investigated from both dynamic viscoelastic functions, elastic modulus G´ and loss modulus G´´. The network reformation in the melt state has been also investigated from the evolution of viscoelastic functions with temperature. The effect of temperature on moduli is similar to that found for electrical conductivity and can be used as a way to evaluate the effect of percolation dynamic on mechanic and rheological behaviour.

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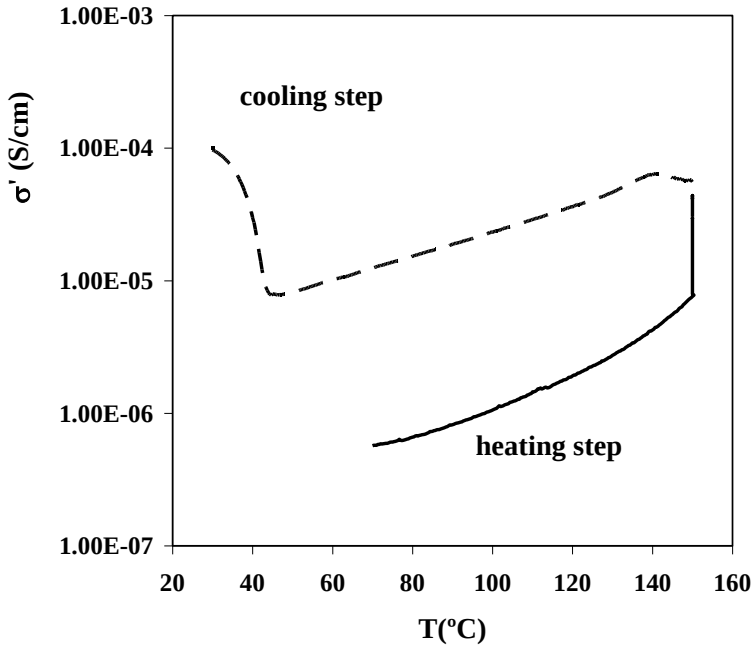
Figure 1:



Real part of the electrical conductivity measured at 1Hz for the composite TPU-4% MWNT. Heating and cooling step are carried out at 2ºC/min.

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