Short communication

Viscoelastic properties and long-term stability of polystyrene-carbon nanotube nanocomposites. Effect of the nature of the carbon nanotubes and modification by ionic liquid

C. Espejo, F.J. Carrión-Vilches, M.D. Bermúdez*

Grupo de Ciencia de Materiales e Ingeniería Metalúrgica, Departamento de Ingeniería de Materiales y Fabricación, Universidad Politécnica de Cartagena, Campus de la Muralla del Mar, C/Doctor Fleming, s/n. 30202 Cartagena, Spain

A B S T R A C T

Dynamic mechanical analysis (DMA) measurements have been used for determining the viscoelastic behaviour of polystyrene (PS) nanocomposites containing a 1 wt.% of single- or multi-walled carbon nanotubes, both pristine (SWCNT and MWCNT) and modified by previous treatment with a room-temperature ionic liquid (SWCNTm and MWCNTm). Two sets of multiple frequency tests have been carried out. The Arrhenius relationship has been used to estimate the apparent activation energies for the glass transition. Master curves have been generated using the time–temperature superposition principle. The nanocomposites show an increase of the activation energy up to an 8% with respect to PS, in the order PS + MWCNT > PS + MWCNTm > PS + SWCNTm > PS + SWCNT > PS. The nanophases also induce a displacement of the onset of the storage modulus to longer times following the order PS + SWCNTm > PS + SWCNT > PS + MWCNT > PS + MWCNTm > PS, at 40 °C. At higher temperatures, the storage modulus onset is very similar for all materials. In the case of PS + SWCNTm, the period of time for the onset of the storage modulus is multiplied by a factor of 28 with respect to PS. The surface modification of the SWCNT by the ionic liquid could improve the interfacial compatibility. The results described here show that a very low proportion of carbon nanotubes can effectively improve the long-term stability of PS under service temperature conditions.

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1. Introduction

Polymer nanocomposites containing carbon nanotube fillers are currently attracting increasing attention for their thermal, mechanical and electrical properties [1–6]. There also exists a growing interest in the development of polymer/carbon nanotube nanocomposites with enhanced surface stability and tribological performance [7–9].

Polystyrene (PS) is currently been used in a broad range of domestic and industrial applications, but its brittle nature is responsible for a poor mechanical and tribological performance even in the presence of additives.

PS matrix nanocomposites containing carbon nanotubes have been the object of a growing number of studies [2] reporting increases in tensile strength and stiffness with increasing nanotube content. Jia et al., have recently described [5] the creep resistance of

PS nanocomposites containing MWCNT and surface-modified MWCNT, finding that MWCNT are very effective reinforcing additives.

Room-temperature ionic liquids have shown outstanding lubricating performance for metals, polymers and ceramic materials under severe conditions [10]. The combination of ionic liquids and nanophases has given rise to new nanofluids which are finding some promising applications [11]. The ability of ionic liquids to disperse and functionalize carbon nanotubes has raised a great interest. In some cases, the interfacial strength between carbon nanotubes and a polymer matrix increases dramatically when the carbon-nanotube surface is chemically functionalized or physically modified [6].

ILs have been used as external lubricants to reduce friction and wear in PS/steel sliding contacts and also as lubricating additives in PS + IL dispersions, with lower dry friction and wear when the IL proportion increases from 1 to 3wt.%. A one order of magnitude reduction with respect to PS, is reached for PS + 1wt.%IL (IL = 1-ethyl-3-methylimidazolium tetrafluoroborate) [12].

* Corresponding author. Tel.: +34968325958.
  E-mail address: mdolores.bermudez@upct.es (M.D. Bermúdez).

Imidazolium cation-based room-temperature ILs grounded with pristine single-walled carbon nanotubes form gels by physical cross-linking of the nanotube bundles, mediated by local molecular ordering of the ionic liquids [13]. The combinations of room-temperature IL and single- or multi-walled carbon nanotubes give rise to new nanolubricants which have been recently shown to give ultralow friction and negligible wear in polymer/stainless steel sliding contacts [7–9,14].

We have previously described the preparation, characterization and tribological performance under adhesive and abrasive wear [7,9,14] of PS and its composites containing unmodified carbon nanotubes (PS + SWCNT and PS + MWCNT), and ionic liquid-modified carbon nanotubes (PS + SWCNTm and PS + MWCNTm).

The new nanocomposites show an enhanced tribological performance due to the combination of the good lubricating performance and surface-modification ability of ionic liquids with the reinforcing and self-lubricating effect of carbon nanotubes.

The main reason for adding neat and IL-modified SWCNT or MWCNT to PS was to improve the wear resistance of the polymer, however, under application conditions, polymer materials are frequently subjected to different stresses for a period of time. Therefore, the time-dependent deformation is significant for polymer applications which require dimensional stability.

The purpose of the present study is to assess that there was no degradation of the viscoelastic properties of PS by the presence of the nanophases.

In the present study, the viscoelastic properties and long-term stability of polystyrene and its nanocomposites containing both pristine and IL-modified single- and multi-walled carbon nanotubes has been determined from dynamic mechanical analysis and by applying the Time–Temperature Superposition Principle (TTSP) [15–17].

2. Experimental

PS (Aldrich; Germany) with an average molecular weight 280,000 (density 1.047 g/cm^3 (25 °C)) was used.

Single-walled carbon nanotubes (CNTs) (1–2 nm diameter; 5–30 μm length) (96.30% C; 0.08% Al; 0.41% Cl; 2.91% Co; 0.29% S) and multi-walled carbon nanotubes (MWCNT) (97.46% C; 0.19%Al; 1.02% Cl; 1.09%Co; 0.24%S) were supplied by (NanoAmor Inc.).

1-Octyl, 3-methylimidazolium tetrafluoroborate ([OMIM]BF4) (Fluka, Germany)(>98% purity) was the ionic liquid used for surface modification of the nanotubes [7,9], following the method described by Fukushima [13].

The materials and preparation procedure followed to obtain the nanocomposites PS + SWCNT; PS + MWCNT; PS + SWCNTm and PS + MWCNTm have been previously described [7,9].

Prismatic test specimens with dimensions 17 × 3.8 × 3.3 mm were obtained from the central part of injection moulded test specimens, obtained as previously described [7].

Dynamic mechanical analysis (DMA) under the single-cantilever clamping mode was carried out with a TA Q800 DMA analyzer equipped with a TA Universal Analysis 2000 software. Glass transition temperature (T_g) values were determined at an oscillatory frequency of 1 Hz, under a 1% strain, for a temperature range from 30 °C to 120 °C at a heating rate of 3 °C/min. All tests were carried out in air. Activation energies were determined in the 90–130 °C temperature range, under seven different frequency values (0.1; 0.2; 0.5; 1.0; 2.2; 4.6 and 10.0 Hz) for oscillatory load application. Master curves have been built from tests at 11 different frequency values, from 0.1 to 10 Hz (0.1; 0.16; 0.25; 0.40; 0.63; 1.0; 1.6; 2.5; 3.0; 6.3 and 10 Hz) in the temperature range from 30 to 120 °C, using the TTSP software 'Rheology Advantage Data Analysis' from TA Instruments.

After determining the storage modulus values vs frequency as a function of temperature, the software automatically shifts each isothermal curve results in a much larger, smooth continuous curve, the master curve. This procedure results in a dramatic increase in the range of the time scale. The shift factor, a_T, represents the magnitude of shifting along the x-axis, necessary for a specific isotherm to superimpose on its neighbour in the final master curve with respect to a given reference temperature (in this case, four references temperatures have been taken, 40, 60, 80 and 100 °C). All adjacent curves should overlap over a reasonable number of data points. The log a_T versus temperature plot is a smooth monotonic curve. The R^2 value at 100 °C shows the reliability of the fit curve for PS.

3. Results and discussion

The time–temperature principle consists of the use of shift factors on plots of polymer properties so that changes in properties which takes place very quickly at high temperature can be displaced at longer times or lower frequencies by shifting the data with respect to time (1/frequency) [15–19].

The temperature-dependent shift factor (a_T) multiplies a frequency or divides a time. Master curves are built from data obtained at several temperatures. The time–temperature superposition method will allow the prediction of the viscoelastic performance of the polymer or composite material over a period of time much longer than that which could be determined experimentally.

In the range of temperatures close to the glass transition temperature (T_g), Williams, Landel and Ferry (WLF model) [15,16] developed Eq. (1) for the frequency–temperature dependence factor a_T:

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \tag{1}$$

where a_T is the shift factor; T_0 is the temperature at which data are determined (in this case, 100 °C); and C_1 and C_2 are constants.

The WLF model assumes that the fractional free volume increases linearly with temperature in the transition region.

3.1. Activation energy

Tan δ is defined as the ratio between loss modulus and storage modulus. In order to determine the value of the activation energy for polymer flow in the glass transition region, glass transition temperature was measured from tan δ maximum values as a function of frequency, as shown in Fig. 1.

T_g from maximum tan δ values for all materials at a frequency of 1 Hz is shown in Table 1. It can be seen that the addition of the nanophases does not alter the glass transition temperature of PS. This result can be explained by the low proportion of nanophases added to the polymer matrix.

The activation energy in the transition region was determined from the tan δ values under variable frequency (0.1; 0.2; 0.5; 1.0; 2.2; 4.6 and 10.0 Hz) (Fig. 2). As the frequency increases, the T_g value increases. This behaviour could be explained by considering that at low frequencies, the maximum modulus value is reached at lower temperature, while at high frequencies the deformation of long polymer chains is restricted, giving rise to high modulus at higher temperatures, thus delaying its decrease, which determines T_g values.

Fig. 2 shows the frequency–temperature dependence for PS and the four nanocomposite materials.