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NANOFILLER EFFECT ON THE GLASS TRANSITION OF A POLYURETHANE

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The effect of silica nanofiller on the glass transition of a polyurethane was studied by DSC. The pristine polymer exhibits a single glass transition at about –10°C. Uniform SiO_2 spheres with different average sizes and narrow size distributions were synthesized in solution by the Stöber method [1]. Both the effects of silica content within the polymer and particle size were investigated, as well as two different surface treatments. Scanning electron microscopy (SEM) clearly confirms the presence of the particles within the polymer matrix, showing uniform distribution and no agglomeration. While shifting of the glass transition has been reported by many authors, we have not seen any noticeable shift in this polymer. Surprisingly, we found no relevant effects when either increasing the filler content or changing the particle size. Different amounts of particles with average diameters of 175, 395 and 730 nm did not affect the glass transition temperature of the pristine polymer.

Keywords: *DSC, glass transition temperature, nanocomposite, nanoparticle*

Introduction

The introduction of inorganic nanoparticles within polymers and other organic matrices gives raise to hybrid materials (nanocomposites) which offer a simple way to modify the properties of the pure polymer. The loading of inorganic particles within polymers is usually performed by a wide range of methods, with the common feature of mixing powders with the polymer as a matrix either before or after polymerization. However, this often leads to an inhomogeneous distribution of particles within the nanocomposite, which strongly affects the final properties and which is often not properly considered. It has been found that the thermal stability of some polymers is affected by the type of nanoadditives [2]. Glass transition, T_g, is one of the most important properties in determining the suitability of a polymer in an engineering application. The value of T_g depends on a large number of variables such as the degree of polymerization, chemical structure, solvents, fillers, etc., and on the interactions between them. Some of these properties can change with the introduction of inorganic nanoparticles, changing in turn the glass transition of the final composite. For this reason, studies of the glass transition of nanocomposites can lead to different results depending on the materials involved and the method of mixing. Among these results it is usual to find both very large increases [3] and decreases [4] in T_g with a modest amount of particles. Tendencies have been reported that change depending on the amount of particles [5, 6], but there are also examples of marginal variations of the glass transitions [7–9]. Some authors start accepting as a good result the invariance of T_g upon the incorporation of nanoparticles and therefore study the DSC curves [10]. Considering these difficulties, in the present work, we studied the T_g of a polyester polyurethane which has been modified by the introduction of different types of silica particles depending on their size and surface functionalization.

All the thermal study has been carried out using temperature modulated differential scanning calorimetry, with a fixed test setup that appears to give optimun results with this kind of materials.

Experimental

Materials

Synthesis of silica nanoparticles

The synthesis of colloidal silica spheres was performed by the well-known Stöber method [1], which is based on hydrolysis and condensation of tetraethoxy silane (TEOS) in ethanol/ammonia mixtures. The reaction was performed in a 500 mL beaker by

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mixing NH_3, TEOS, ethanol and water according to the concentrations optimized by Bogush *et al*. [11] for various final particle sizes. TEOS was added under vigorous stirring in a bath at 25°C and the mixture was stirred for at least 4 h. The excess TEOS, NH_3 and H_2O were removed by centrifugation followed by redispersion in ethanol. The average sizes obtained by this method were 175, 395 and 730 nm.

Surface modification

175 nm silica particles were splitted in three aliquots for surface modification. One of the aliquots was left unchanged for comparison of the results. The second was treated by addition of 3-(trimethoxysilyl) propyl methacrylate (TPM) in excess, followed by slow distillation of ethanol [12, 13]. The surface modification of the third aliquot was performed by addition of 10% octadecyltrimethoxy silane [14] (OTMS) in chloroform onto the particle dispersion in ethanol, in the presence of ammonia. In this case vigorous stirring was maintained for 24 h at room temperature. A final centrifugation step, followed by redispersion in dimethyl formamide (DMF), was required in all methods to obtain the desired concentration of silica particles in the composite.

Preparation of nano-silica/PU composites

Once the desired amount of silica particles has been dispersed in DMF, the next step is to process with the polyester polyurethane. In this case the poly[4,4'-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/poly(butylene adipate)] from Aldrich was used without previous treatment. A certain amount of polymer in pellet form was mixed with DMF, stirred and left overnight to ensure complete mixing. The same process was required to mix both components, starting with a short period of vigorous mechanical stirring. The mixture was then kept for about 4 h at room temperature in a closed flask to allow de-gassing of the bubbles originated in the previous step. Films were obtained by placing some drops of the mixture on a glass slide and keeping in an oven at 60°C to evaporate DMF. The nanocomposite films were peeled from the glass, cut into sizes suitable to fit in the DSC pans. Sample mass was about 15 mg.

Methods and results

TEM and SEM characterization

The shape and size of the particles were studied by transmission and scanning electron microscopy. The UTHSCSA ImageTool freeware software was used to measure the particle size distribution.

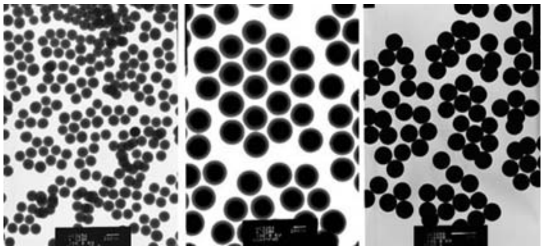

Fig. 1 TEM images of 175, 395 and 730 nm particles. Note that the magnification is the same for the two leftmost images (200 nm scale bar), while lower magnification was used for the sample with bigger particles (1000 nm scale bar)

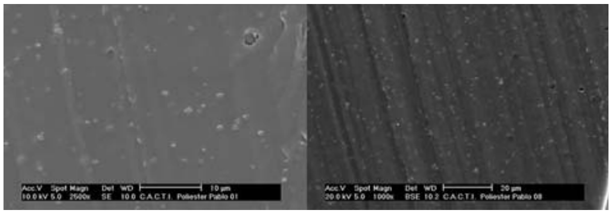

Fig. 2 SEM images of the final nanocomposite sample showing the uniform particle distribution

Figures 1 and 2 show a representative TEM and SEM image from each of the silica samples, in which the uniform shape and size distributions can be observed.

DSC study

DSC tests were performed in a TA Instruments DSC Q 1000, using aluminium crimped pans and a N_2 flow at 50 mL min^{-1}. In order to erase the thermal history effects from the samples, the temperature was equilibrated at 150°C at the beginning of each experiment. The experiments consisted of a modulated heating ramp from –90 to 175°C. The average heating rate was 2°C min^{-1}. An amplitude of ±0.21°C and a period of 40 s were used.

Figure 3 shows that the content of 395 nm particles did not affect the glass transition temperature of the pris-

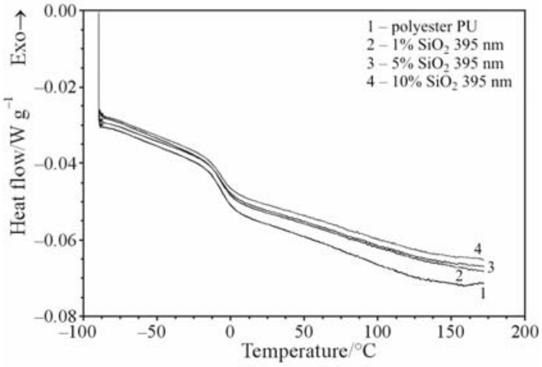

Fig. 3 Reversing heat flow plots obtained from PU samples with different contents of 395 nm silica nanoparticles

tine polymer. The same glass transition was obtained with various contents of 175 and 730 nm particles.

Figure 4 shows that in the case of 175 nm particles the glass transition temperature was not affected by the surface treatment and is the same as that of the pristine polymer. The same behaviour was observed in the case of 1 and 10% nanocomposites.

Figure 5 shows how the particle size did not affect the glass transition temperature in the case of 5% of silica nanocomposites. The same behaviour was observed in the case of 1 and 10% nanocomposites.

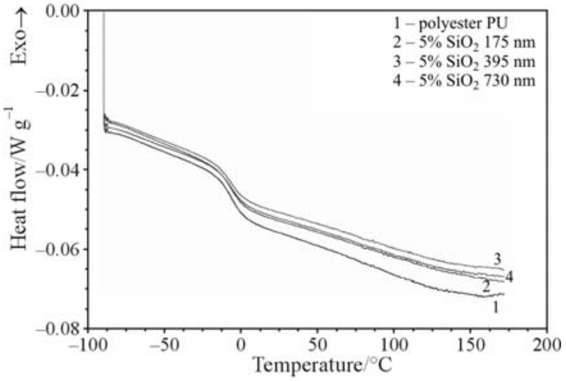

Fig. 4 Reversing heat flow plots obtained from PU samples containing 5% of 175 nm silica particles with different surface treatment along with the pristine polymer

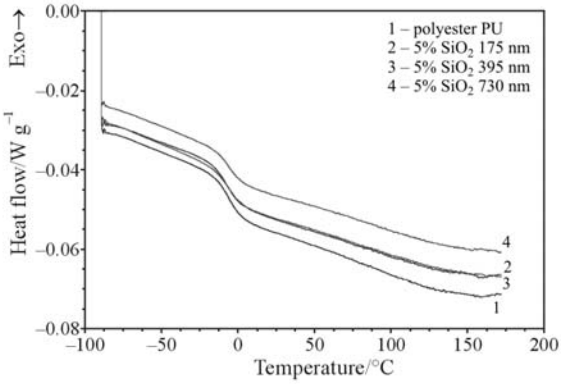

Fig. 5 Reversing heat flow plots obtained from PU samples containing 5% of untreated silica particles of different sizes

Conclusions

Spherical silica nanoparticles with varying average particle size and surface functionalization were obtained and characterized. These silica nanoparticles were incorporated with a good dispersion and distribution in the polymeric matrix. Samples with different size and coating were tested by MDSC to study variations in the glass transition temperature. This temperature was not significantly affected by different fillers applied to the polymer, even for different amounts of silica particles, size and surface treatment. One of the reasons of T_g variation in a composite is the interactions between nanoparticles and the polymeric matrix. Different types of introduction of particles into polymeric matrices reveals to produce the desired interactions modifying the glass transition. It is clear to think about the method used in the present communication does not produce the desired level of particle polymer interaction.

Acknowledgements

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