THERMOGRAVIMETRIC ANALYSIS OF POLYSTYRENE –TiO$_2$ NANOCOMPOSITES

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ABSTRACT

Polymer-based nanocomposites have been prepared by the dispersion of nanometer-sized TiO$_2$ particles within polystyrene. The physical properties of the interface between TiO$_2$ nanoparticles and macromolecular chains have been studied by thermal analysis (thermogravimetric analysis and differential scanning calorimetry). The addition of nanoparticles modifies the temperature at which the maximum mass loss is recorded and the glass transition of the polymeric matrix.

I. INTRODUCTION

The dispersion of nanometer-sized fillers within polymeric matrices can affect significantly their physical properties. The main source of these modifications is due to the interface macromolecular chains-nanofiller and to the huge area of the nanofiller. Technically, in such nanocomposites, the physical properties of the interface become dominant over the bulk properties of the polymeric matrices.

The addition of nanometer-sized fillers to polymeric matrices typically enhances the thermal and thermo-oxidative degradation of the polymer, the Young modulus, and the strength of the polymeric matrix and affects the crystallization process. In most cases, the effect of nanofillers consists in a rather modest increase of the temperature at which the mass loss of the polymer is highest. This parameter, easily obtained by TGA analysis (more frequently done in inert atmosphere) can be considered a fingerprint of the formation of a polymer-nanoparticle interface.

The effect of the nanofiller on the glass transition temperature of the polymeric matrix is rather complex, shifts towards lower and higher temperature being reported. While the actual glass transition temperature is extremely important for the final physical properties and applications of the nanocomposites, the shift of the glass transition temperature is not always a correlated in a simple manner to the existence and the size of polymer-nanofiller composite.

The present study is focused on the thermal features of polystyrene (PS)–TiO$_2$ nanocomposites. The polymeric matrix is completely amorphous –a feature that simplifies the experimental study as melting and crystallization effects are not involved. TiO$_2$ nanoparticles are among the smallest nanoparticles available commercially. This allows for huge areas of contact between the nanofiller and the polymeric matrix.

The thermal degradation of PS is well known. The depolymerization process is well understood; consequently, the effect of the nanometer-sized filler on the thermal stability of the polymeric matrix can be easily assessed. In order to keep the system as simple as possible the research was focused on almost cubic TiO$_2$ nanoparticles (anatase) with an edge of about 15 nm.

METHODOLOGY

PS-TiO$_2$ nanoparticles were obtained by dispersing PS into a theta solvent (cyclohexane), at the theta temperature. TiO$_2$ nanoparticles have been added to this solution. In order to have a homogeneous distribution of nanoparticles, the mixture TiO$_2$ nanoparticles-PS solution has been sonicated using a Hielscher high power sonicator operating at 1 kW (see Fig. 1). Composites loaded with various amounts of nanofiller, ranging from 0 % to 60 % wt. TiO$_2$, have been obtained and measured by
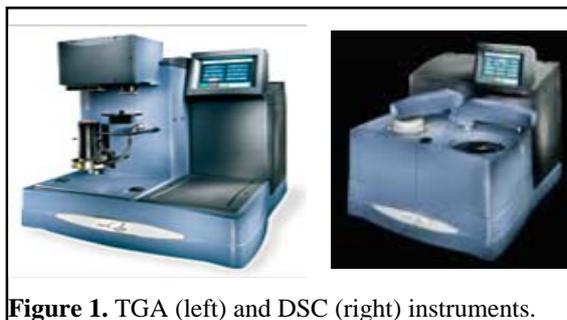

Figure 1. TGA (left) and DSC (right) instruments.

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using thermogravimetric analysis (Q 500 TGA TA Instruments) and Differential Scanning Calorimetry (Q1000 DSC TA Instrument). The TGA measurements have been performed in nitrogen atmosphere in order to avoid the complications due to competing oxidation reactions.

EXPERIMENTAL RESULTS AND DISCUSSIONS

The dependence of mass loss versus temperature for some PS-TiO$_2$ nanocomposites containing various amounts of TiO$_2$ is shown in Fig. 2. The actual thermograms are represented by single sigmoids. It is noticed that the temperature at which the mass loss reaches the highest value (i.e. the inflection point, or T$_M$) increases by more than 25 ^{o}C as the concentration of the filler is increased
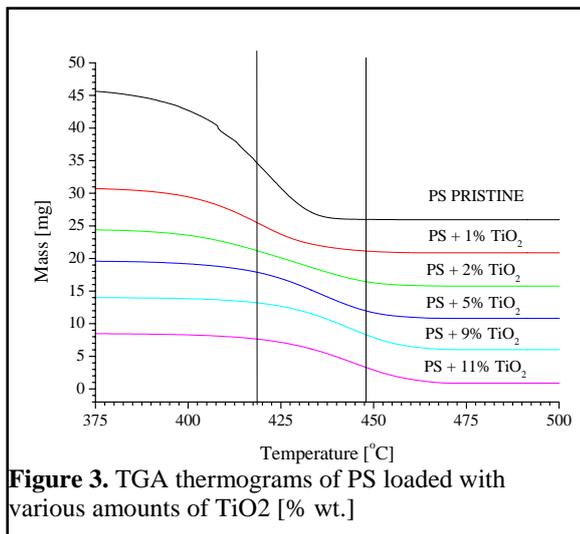
Figure 3. TGA thermograms of PS loaded with various amounts of TiO2 [% wt.]

up to 11 %. Further increase of the filler concentration does not resulted in a further enhancement of this temperature. This demonstrates the formation of an interface between the nanofiller and the nanocomposites.

In order to determine accurately T$_M$ and the width of the thermal degradation process the as recorded thermograms have been fitted by a modified Breit-Wigner lineshape.

$$ M(T) = M_0 \frac{1 + p(\frac{T - T_0}{d})}{[1 + (\frac{T - T_0}{d})^2]} $$

Where M$_0$ is the mass of the sample, at the inflection temperature T$_M$, d describes the width of the thermal degradation process, and p is a parameter associated with the departure from a symmetric Lorentz line.
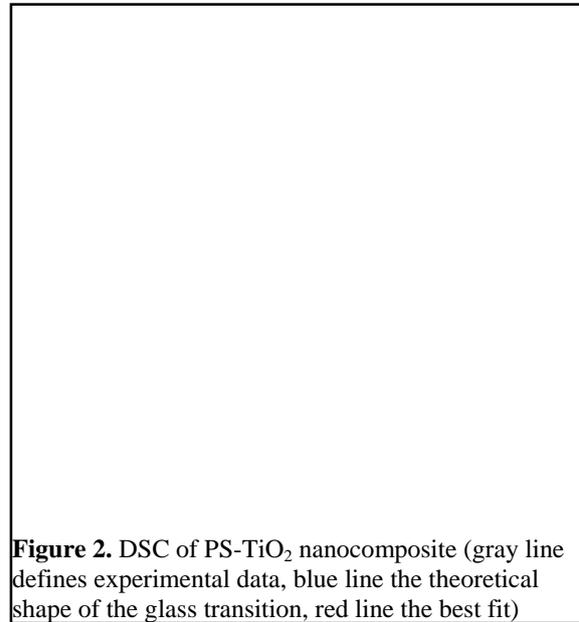
Figure 2. DSC of PS-TiO$_2$ nanocomposite (gray line defines experimental data, blue line the theoretical shape of the glass transition, red line the best fit)

DSC data revealed the decrease of the glass transition temperature as the concentration of TiO$_2$ has been increased as well as the stretching of the macromolecular network. To deconvolute these contributions and to estimate accurately the glass transition temperature a convolution between a sigmoid and a symmetric Lorentzian has been used. The fitting of experimental data, represented by the red line in Fig. 3 is excellent.

CONCLUSIONS

Thermal investigations revealed the formation of the interface PS-TiO$_2$ and the mechanical stretching of macromolecular chains due to the loading with nanoparticles.