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EFFECTS OF INCORPORATION OF MODIFIED SILICA NANOPARTICLES ON THE MECHANICAL AND THERMAL PROPERTIES OF PMMA

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Silica nanoparticles of various sizes have been incorporated by melt compounding in a poly(methyl methacrylate) (PMMA) matrix to enhance its thermal and mechanical properties. In order to improve nanoparticles dispersion, PMMA grafted particles have been prepared by atom transfer radical polymerization (ATRP) from well-defined silica nanoparticles. This strategy was expected to ensure compatibility between both components of the PMMA nanocomposites. TEM analysis have been performed to evaluate the nanosilica dispersion whereas modified and non-modified silica/PMMA nanocomposites thermal stability and mechanical properties have been investigated by both thermogravimetric and dynamical mechanical analysis.

Keywords: *Atom Transfer Radical Polymerization (ATRP), mechanical properties, poly(methyl methacrylate), silica nanoparticles, thermal properties*

Introduction

In recent years, there is a great interest in organic polymer-inorganic particles nanocomposites, since they often exhibit unique properties, as improved mechanical and thermal properties, gas permeability and fire resistance compared to the pristine polymer [1–3]. These enhanced performances are achieved by a fine dispersion of selected inorganic nanoparticles within the polymer matrix. As a rule, the establishment of a strong interaction between the polymer matrix and the nanosize dispersed filler is of key importance. It has been demonstrated that appropriate surface modification of inorganic nanoparticles improves the compatibility and the adhesion between filler particles and organic matrix [4, 5].

Poly(methyl methacrylate) (PMMA) is an important thermoplastic material with excellent transparency. One of its limitations, which has severely restricted its use, is its thermal instability. In order to delay its degradation, several strategies can be employed, such as incorporation of nanoparticles in the polymer matrix [6].

In this study, we report the synthesis of PMMA nanocomposites from modified silica particles, which have been prepared by atom transfer radical polymerization (ATRP) from well-defined silica nanoparticles. ATRP initiators were grafted on the silica particle surface in order to ensure a covalent binding of all the growing polymer chains to the nanoparticles [7–9]. Then, these modified nanoparticles were mechanically mixed with polymer to prepare PMMA–SiO_2 nanocomposites in a twin-screw micro-compounder. The nature of molecular interactions between the nanoparticles and the polymer chains, the concentration, the distribution and the diameter of the nanoparticles are expected to play a crucial role on the mechanical and thermal properties of the resulting material, which are investigated by the following techniques: TG, TEM and DMA.

Experimental

Materials

PMMA was supplied by Scientific Polymer Products, Inc. and presents a molecular mass 70000 g mol^{-1}.

Silica nanoparticles (Ludox TM-40, 40 mass% suspension in water, 140 m^2 g^{-1}, diameter from 15 to 20 nm, pH about 10), copper(I) bromide, hexamethyltriethylene tetramine (HMTETA), (3-glycidyloxypropyl)triethoxysilane (GPM), N-methylmorpholine and 2-bromoisobutyryl bromide were purchased from Sigma Aldrich.

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Copper bromide was recrystallized in anhydrous acetic acid and dried overnight at 40°C. Methyl methacrylate monomer (MMA, Sigma Aldrich) was dried two hours over CaH_2 and distilled under vacuum before use and toluene (Sigma Aldrich) was purified by distillation at low pressure.

Sample preparation

Modification of silica nanoparticles by GPM

GPM (50 mL, 20 eq/Si–OH) was added dropwise to a solution of Silica Ludox (100 g water suspension, 4.5Si–OH/nm^2) under nitrogen. The reaction mixture was stirred for 30 h at 100°C. Silica nanoparticles were dispersed in 200 mL of methanol and centrifugated at 18000 rpm for 20 min. The supernatant solution containing ungrafted polymer was removed and the precipitate was dispersed again in MeOH. These procedures were repeated four times. The last cycle was performed in anhydrous toluene.

Grafting of 2-bromoisobutyryl bromide (ATRP initiator) onto silica nanoparticles

N-methylmorpholine (60 mL) and anhydrous toluene (500 mL) were added to a suspension of SiO_2 nanoparticles (24 g) modified by GPM in anhydrous toluene (400 mL). Bromoisobutyryl bromide (66.5 mL; 10 eq/OH) was then added dropwise at 0°C over a period of 2 h. Reaction mixture was then stirred for 70 h at room temperature. After reaction, silica nanoparticles were purified by four centrifugation/redispersion in MeOH cycles for 30 min.

Preparation of PMMA grafted nanoparticles

SiO_2 nanoparticles bearing bromoisobutyryle (5 mL of methanol suspension, $5.26 \cdot 10^{-3}$ mol of grafted initiator) were added to ethyl bromoisobutyrate (0.31 g, $1.58 \cdot 10^{-3}$ mol), CuBr (0.98 g, $6.38 \cdot 10^{-3}$ mol) and HMTETA (1.57 g, $6.84 \cdot 10^{-3}$ mol). Reaction mixture is degassed by three consecutive vacuum/nitrogen cycles. Methyl methacrylate monomer (220 mL) was then added under nitrogen. The reaction mixture was stirred at 80°C for 24 h and dissolved in toluene. Silica nanoparticles were purified by dispersion/centrifugation cycles in toluene as previously described.

Preparation of PMMA/SiO_2–gPMMA nanocomposites

PMMA/SiO_2–gPMMA nanocomposites were prepared by melt compounding of PMMA-grafted silica nanoparticles (1.1 g; 3 mass% of silica) and PMMA (2.9 g). Mixture was realized in a twin-screw extruder (DSM Xplore 3/7/15 Microcompounder), at 210°C for 5 min, with a rotation speed of 200 rpm.

Preparation of PMMA/non-modified silica nanocomposites

PMMA/non-modified silica nanocomposites were prepared using the same procedure than previously described, by blending SiO_2 nanoparticles (0.12 g; 3 mass%) and PMMA.

Grafting efficiency

The grafting efficiency has been investigated by thermogravimetric analysis of the polymer-grafted nanoparticles. According to the recorded mass losses (Table 1) and the measured molecular mass of the grafted polymer chains, the grafting yield and grafting density may be calculated.

Molecular mass of the grafted polymer (77000 g mol^{-1} with a polydispersity of 1.4) has been determined by size exclusion chromatography.

Instrumentation

Morphology of nanocomposites was analyzed by transmission electron microscopy (TEM). TEM observations were performed with a Phillips CM100 apparatus using an acceleration voltage of 100 kV. Ultrathin sections of composites (ca. 80 nm thick) were prepared at –130°C with a Reichert-Jung Ultracut 3E, FC4E ultra-cryomicrotome equipped with a diamond knife.

Thermogravimetric analysis (TG) was performed under a nitrogen flow (50 cm^3 min^{-1}) at a heating rate of 10 K min^{-1} from 30 to 800°C with a STA 409 PC from Netzsch. The STA measurements were coupled with a mass spectrometer (MS) Aëolos 403C from Netzsch and a Fourier transform infrared spectrophotometer (FTIR) TENSOR 27 from Bruker to identify the species evolved from the sample during the thermogravimetric experiments.

Mechanical properties of the composites were evaluated according to dynamic mechanical analysis (DMA) with a DMA 242C from Netzsch.

Table 1 Grafting density and grafting yield, based on thermogravimetric analysis

Grafted moiety	Mass loss/%	Grafting density/molecules nm^{-2}	Grafting yield
GPM	13.7	4.5	quantitative
2-bromoisobutyryl bromide	29.5	4.5	quantitative

Results and discussion

Nanocomposites morphology

Figure 1 presents TEM micrographs of PMMA nanocomposites containing modified or non-modified silica nanoparticles.

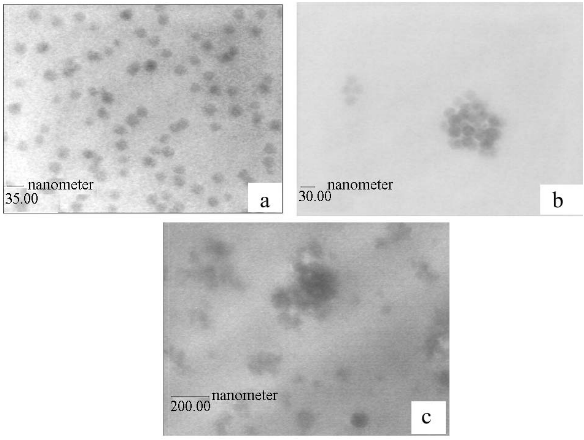

Fig. 1 TEM micrographs of a – PMMA/SiO_2–gPMMA nanocomposites, b – PMMA/SiO_2 (15–20 nm) nanocomposites, c – PMMA/SiO_2 (40–80 nm) nanocomposites

When nanocomposites are prepared from non-modified SiO_2 nanoparticles, these latters tend to aggregate. It is especially the case for the 15–20 nm SiO_2 nanoparticles. On the opposite, a spherical morphology and a good silica nanoparticles monodispersity is observed when PMMA is grafted on silica nanoparticles by ATRP. Functionalization of silica particles surface induces a better compatibilization between both constituents and thus enhances the nanoparticles dispersion.

Nanocomposites thermal properties

Thermogravimetric curves of PMMA and PMMA/SiO_2 nanocomposites are presented on Fig. 2.

PMMA reveals a single-step degradation from 300 to 450°C involving polymer chain scission. The highest improvement of PMMA thermal stability has been obtained with grafted silica nanoparticles. In this case, the minima DTG curve, corresponding to the maximum of nanocomposites degradation temperature $T_{dg,max}$, is delayed by 15°C (Table 2). According to the thermogravimetric curves incorporation of silica nanoparticles into PMMA always results in a lower thermal degradation kinetic. The $T_{dg,max}$ values highlight that both size nanoparticles and compatibility of constituents play a role in improvement of thermal stability.

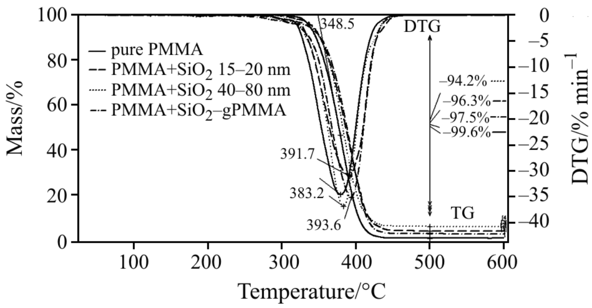

Fig. 2 Thermogravimetric curves of pure PMMA and PMMA nanocomposites under nitrogen at a heating rate of 10°C min^{-1} and a gas flow of 20 mL min^{-1}

Table 2 Value of maximum thermal degradation temperature

Composites	$T_{dg,max}$/°C
PMMA	379.0
PMMA/SiO_2 (15–20 nm)	391.7
PMMA/SiO_2 (40–80 nm)	383.2
PMMA/SiO_2–gPMMA	393.6

Dynamical mechanical properties

Figure 3 shows the variation of storage modulus with temperature for pure PMMA and PMMA/silica nanocomposites.

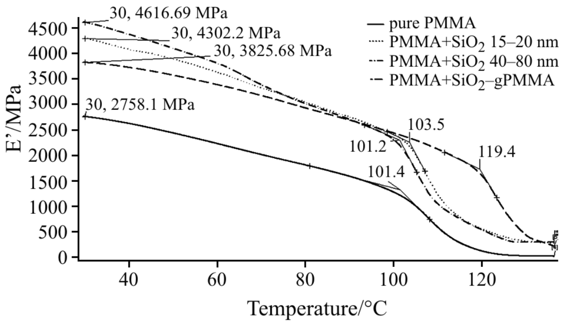

Fig. 3 Variation of storage modulus with temperature for pure PMMA and PMMA/SiO_2 nanocomposites

In all cases, incorporation of silica nanoparticles improves storage modulus of PMMA nanocomposite. Addition of pristine nanoparticles enhances storage modulus by about 65% at 30°C. At the same temperature, incorporation of grafted silica nanoparticles leads to an increase of 40% for the storage modulus of PMMA, probably due to a lower silica content in this sample (Fig. 2). However, the loss of mechanical properties with temperature shows a 20°C delay indicating better interactions between nanoparticles and polymer.

Conclusions

Both thermal and mechanical properties of PMMA have been improved by incorporation of PMMA-grafted nanoparticles in PMMA matrix. A homogeneous dispersion of individual, small and spherical particles has been evidenced by TEM for this sample. By comparison, particle aggregation is observed when PMMA is filled with non modified silica.

Moreover, incorporation of grafted silica nanoparticles leads to a maximum degradation temperature delayed by 15°C. Concerning mechanical properties, a 40% increase of PMMA storage modulus and a 20°C delay of storage modulus decrease have been recorded, indicating better interactions between nanoparticles and polymer.

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