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Hybrid nanocomposites based on polystyrene and a reactive organophilic clay

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The preparation of new hybrid nanocomposites, by emulsion polymerization of styrene in the presence of a reactive organophilic clay, and their characterization are described. The reactive organophilic clay is synthesized by exchanging the inorganic cations in the interlayer structure of a natural clay with the quaternary salt of the aminomethylstyrene. This salt is prepared by a Gabriel reaction starting from the (chloromethyl)styrene. The polymeric matrix of the resulting materials was found to be constituted by polystyrene homopolymer and by a blocky copolymer of styrene and quaternary salt of the (aminomethyl)styrene units. The glass transition temperature of the nanocomposites increase as the percentage of organophilic clay increases, although the average molar masses of the polymeric matrix decrease, because of termination and/or chain-transfer reactions caused by the organophilic clay during the polymerization. Accordingly, the inherent reinforcing action due to the presence of the reactive organophilic clay is higher than the observed one.

1. Introduction

The addition of reinforcing fillers, particles or fibres, to polymeric matrices [1] has been extensively employed, to obtain composite materials with increased stiffness and strength. The characteristic structural features of these conventional composites are designed on the micrometre scale.

Recently, a new class of composite materials, with characteristic structural features on the nanometre scale was introduced. These composites were called nanocomposites [2] because of their scale-phase dimensions. On account of their peculiar volume and interface effects, these nanostructured materials can exhibit unusual and unexpected properties compared with the same materials endowed with larger structures. Accordingly, the control and design of the characteristic structural features on the nanometre scale allow materials to be obtained with properties specifically designed for a diversity of advanced structural [3], magnetic [4], catalytic [5] and biomedical applications [6].

A special case of nanocomposites is constituted by those consisting of a polymeric material and laminar inorganic additives belonging to the smectite class, like the montmorillonites. In general, the inorganic fillers such as talc and mica [7] are substantially incompatible with the organic matrix and, accordingly, their reinforcing efficiency is quite low. In contrast, the montmorillonites [8] can be easily modified superficially to obtain favourable interactions between the inorganic component of the filler and the polymeric matrix [9, 10]. In fact, isomorphous replacements of Si^{4+} with Al^{3+} in the tetrahedral lattice and of Al^{3+} with Mg^{2+} in the octahedral arrangement cause an excess of negative charges within the montmorillonite layers. In natural clays, these negative charges are balanced by solvated Ca^{2+} and Na^{+} ions arranged between the clay layers. These cations can be easily exchanged and, when organic cations are employed, modified clays, called organophilic, are obtained. The surface of these clays is highly hydrophobic and favourable interactions can be established between the organophilic clays and the organic matrix, either polymers or polymeric precursors. For example, preformed polymeric materials can be directly melt-intercalated [11–13] between the layers of the clays, thus leading to true nanocomposites. Alternatively, nanocomposites by intercalation of a suitable monomer between the interlayers of the mineral followed by polymerization [14–19], can be obtained. The expected properties of these materials include outstanding gas-barrier characteristics [20], because of the increase of the total path of the diffusing gas, and increased glass transition temperature [21], because the glass transition process should involve a multiple unanchoring of the adsorbed chains from the layer surface. However, in these systems, the organic phase is just reversibly fixed to the inorganic

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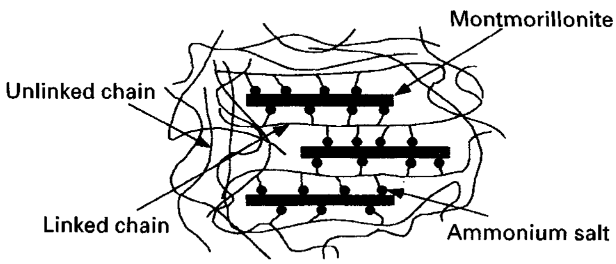

Figure 1 Schematic structure of nanocomposites from reactive organophilic clays.

phase. A most effective method for achieving strong bonding between the filler and the polymeric matrix consists in the use of a reactive one, that is a filler which can actively participate in the polymerization process. This reactive filler can be prepared by exchanging the inorganic cations of the natural montmorillonite with ammonium salts presenting polymerizable groups. In this case, the *in situ* polymerization involves not only the functional groups of the monomer but also those of the ammonium salt linked to the inorganic layers of the montmorillonite, thus leading to a nanocomposite with the schematic structure shown in Fig. 1. In this system, the adherence of the polymer chains to the inorganic layers is ensured by the copolymeric chains linked to the clay by electrostatic interactions [22]. Materials with improved thermo-mechanical properties are expected.

Within this frame, in this report the synthesis by emulsion polymerization, and the physico-mechanical properties of a new class of nanocomposites, consisting of a polymeric matrix of polystyrene and a montmorillonite modified by exchanging the inorganic cations with (ammoniummethyl)styrene chloride, are described.

2. Experimental procedure

2.1. Materials

Na^+-type montmorillonite (BH) was supplied by Laviosa Company (Livorno, Italy) and is characterized by a cation exchange capacity (CEC) [8] of 53.4 meq/100 g. No particle size selection was carried out and the clay mineral was used after drying 12 h at 150 °C under vacuum. (Chloromethyl)styrene ($d = 1.074$ g mol^{-1}; a mixture of *meta-para* isomers), potassium phthalimide, trimethyl hexadecylammonium bromide, hydrazine hydrate ($NH_2NH_2 \cdot xH_2O$, $x \simeq 1.5$; $d = 1.024$ g mol^{-1}) were purchased from Aldrich and used without further purification. Styrene was purchased from Aldrich and was washed with 3 × 100 ml 2.0 M sodium hydroxide, 3 × 100 ml water, dried with anhydrous sodium sulphate and stored at 5 °C. Immediately before use, the monomer was distilled under vacuum.

2.2. Synthesis of (amino)methylstyrene

100 ml DMF and 20.0 g potassium phthalimide (0.108 mol) were stirred at 50 °C in a 250 ml three-necked round bottom flask. 0.2 g NaI were added to this solution and 11.0 ml (chloromethyl)styrene (0.078 mol) were dropped in 15 min. After 4 h, the solvent was eliminated under vacuum. 150 ml chloroform were added to the resulting brown liquid and the solution was washed twice with 100 ml 0.2 M NaOH solution and twice with 100 ml NaCl saturated solution. The organic layer was dried over Na_2SO_4, filtered and the methylstyrene phthalimide (PIMS) was crystallized upon cooling at 5 °C and then recrystallized in methanol ($T_m = 79$ °C; yield 70% mol mol^{-1}).

9.26 g PIMS (0.035 mol) and 50 ml ethanol were placed in a 250 ml three-necked round flask. The solution was refluxed and 3.2 ml hydrazine (0.053 mol) diluted in 10 ml ethanol were dropped in 15 min. After 90 min, the reaction mixture was cooled to room temperature and 100 ml 3.0 M KOH solution were added to the reaction mixture which was extracted twice by ethyl ether and then was washed twice using a 6% K_2CO_3 solution. The organic phase was dried over Na_2SO_4 and the solvent was evaporated under vacuum. The resulting product was distilled under vacuum (2.0 mm Hg) at 46 °C (yield 65% mol mol^{-1}).

2.3. Preparation of the organophilic clay

3.3 g aminomethylstyrene, 2.4 ml concentrated hydrochloric acid and 5 ml deionized water were placed in a 500 ml beaker and the solution was heated to 50 °C. At the same time, 7.8 g dried BH were stirred at 50 °C in 400 ml deionized water for 20 min and the resulting suspension was added to the solution containing the ammonium salt. The white precipitate was isolated by filtration, placed in a 500 ml beaker with 400 ml deionized water, stirred for 1 h at 50 °C and then filtered. This washing procedure was repeated five times. The resulting product was dried at 45 °C under vacuum for three days. This organophilic montmorillonite was marked BHAMS.

2.4. Preparation of the nanocomposites

The mixture of styrene and BHAMS, to a total weight of 6.0 g, was placed in a schlenk tube equipped with a three-way stop cock for high vacuum, degassed by three freeze–thaw cycles, sealed and stirred in the dark for 24 h at ambient temperature. After that, 25 ml deionized water, 0.5 g potassium persulphate and 0.2 g sodium laurylsulphate were added, the mixture degassed by two freeze–thaw cycles and placed in a bath at 82 ± 1 °C. After 1 h, the obtained lattice was treated with a 5% solution of aluminium sulphate, the solid product was separated by filtration, washed with water and dried at 50 °C for 3 h. The same procedure was repeated for all the nanocomposites prepared from different percentages of BHAMS in the initial mixture styrene–BHAMS.

2.5. Separation of PS from PS–PAMS

All the nanocomposites were extracted with boiling chloroform in a Soxhlet extractor for 6 h to remove the polystyrene homopolymer (PS). Then, 0.25 g of the solid residue of the extraction, 25 ml chloroform and

5 g trimethylhexadecylammonium bromide were stirred in a 50 ml flask at 50 °C for 1 h. After separating the clay by centrifugation, a second fraction of polymeric material, marked PS–PAMS, was recovered by precipitation in methanol.

2.6. Characterization

Fourier transform–infrared (FT–IR) spectra were collected using a Perkin–Elmer 1750 with a nominal resolution of $4\,cm^{-1}$. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA7 thermobalance at a scanning rate of $10\,°C\ min^{-1}$ from 50–850 °C under an air flow. X-ray diffraction measurements on powder samples were performed using the INEL CPS 120 powder diffractometer, equipped with a position sensitive detector covering 120° in the scattering angle 2θ, with an angular resolution of 0.018° in θ. Ge(1 1 1) monochromatized CuK_α radiation was used. The mechanical characteristics of the nanocomposites were studied by dynamic mechanical analysis (DMA) using a Perkin–Elmer DMA-7 with the three-point bending geometry at the frequency of 1 Hz, from − 50 to 150 °C, at the rate of $4\,°C\ min^{-1}$. The sample for the dynamic mechanical measurements were prepared as follows. The powder nanocomposites were introduced into a regular mould. The entire assembly was placed between press plates with a nominal pressure of 7.0×10^7 Pa. The temperature was raised to 170 °C and the pressure released to a contact pressure. After 20 min the sample was recovered as rectangular 18 mm × 5mm × 2 mm sheets. Average molar masses were determined by SEC of chloroform solution with a 590 Waters chromatograph equipped with a Shodex KF-804 column. An ultraviolet (UV) spectrophotometer at 260 nm was used as a detector.

3. Results and discussion

3.1. Preparation of the reactive organophilic clay

The reactive organophilic clay BHAMS was prepared according to Fig. 2 by exchanging the interlayer inorganic cations of the natural clay BH by a large excess of (ammoniummethyl)styrene chloride (AMS). The AMS was prepared starting from the (chloromethyl)-styrene by a Gabriel reaction followed by a reaction with hydrochloric acid. The exchange yield was evaluated by TGA. Fig. 3 reports the TGA curves of BH and BHAMS. Before the analysis, the BH sample was dried at 150 °C under vacuum for 24 h, whereas the BHAMS sample was placed in a drier at only 50 °C under vacuum for 24 h to avoid the thermal polymerization of AMS. The water adsorbed in the interlayer space of BH, after the above thermal treatment, was only 5% (wt/wt) of the sample, as can be evaluated from the weight loss occurring between 50 and 150 °C. Another weight loss was observed from 460–700 °C, corresponding to the loss of the OH groups belonging to the crystalline structure [20]. The TGA curve of BHAMS was more complex because, in addition to the weight losses of the BH, there is a loss due to the degradation of AMS in the interlayers at temperature between 600 and 850 °C. The observed weight loss of BHAMS due to AMS is 7.50%. As the estimated value, calculated on the basis of the CEC and of the molecular weight of the cation under the assumption that the cation exchange yield was 100%, is 7.16% we can conclude that the exchange reaction is almost quantitative.

The X-ray diffraction pattern of BH (Fig. 4) shows a small-angle peak, centred at $2\theta = 7.6°$ and corresponding to 1.16 nm, characteristic of the succession of inorganic and water layers of the montmorillonite structure. The X-ray diffraction pattern of BHAMS shows a sharp small-angle peak, at 1.53 nm, corresponding to the distance between the inorganic layers separated by the insertion of AMS molecules. The

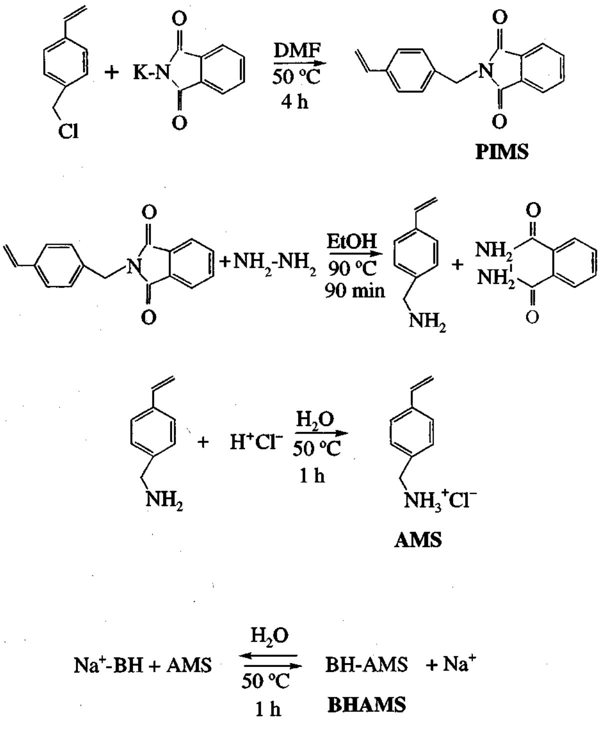

Figure 2 Synthesis of the quaternary salt of the (aminomethyl)-styrene and its cation exchange with the Na^+ of the natural clay to obtain the reactive organophilic clay.

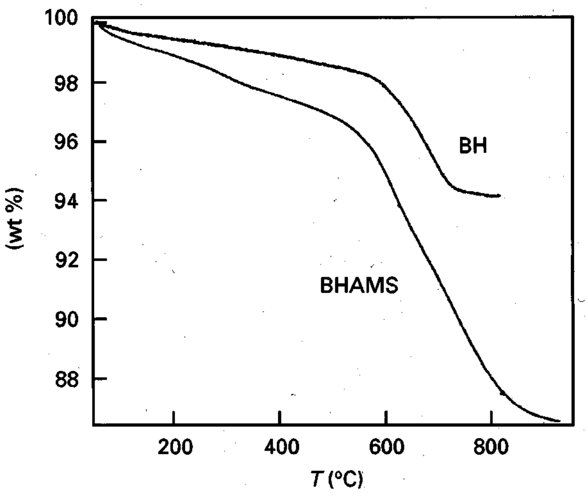

Figure 3 TGA profiles of BH and BHAMS.

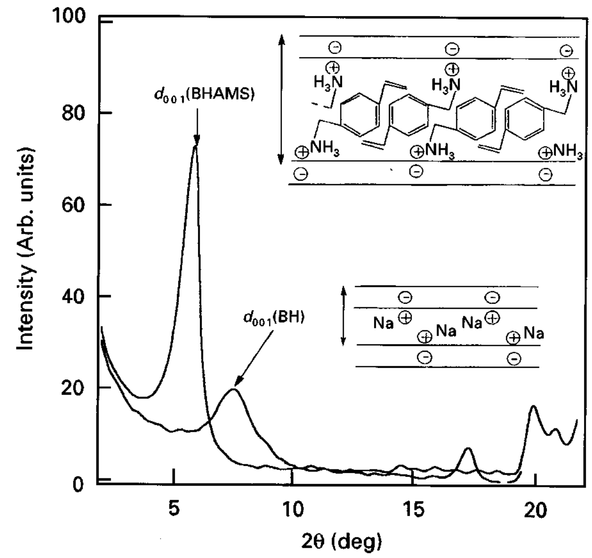

Figure 4 X-ray powder diffraction spectra of BH and BHAMS.

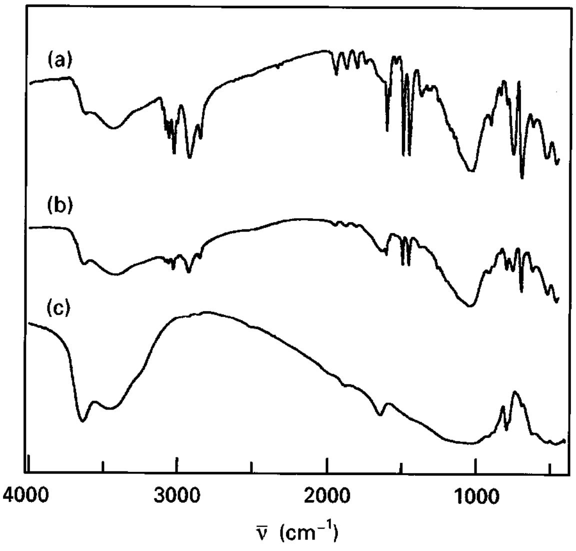

Figure 5 FT–IR spectra of (a) PS13, (b) PS13 after the chloroform extraction, and (c) PS13 after the chloroform extraction and the substitution with the ammonium salt.

observed interlayer distance is lower than the value (2.10 nm) calculated supposing that the AMS molecules are disposed perpendicularly to the clay layers. Accordingly, on the basis of purely geometric considerations, it is possible to estimate a tilt angle between the AMS molecules and the clay layers of 22° thus indicating that the AMS molecules lie completely on the clay surface.

3.2. Preparation and properties of the nanocomposites

The nanocomposites were prepared by emulsion polymerization of styrene in water in the presence of BHAMS, employing the potassium persulphate as the free radical initiator and the sodium laurylsulphate as the surfactant agent. Variable amounts of BHAMS were employed ranging from 4%–25% by weight. Accordingly, the nanocomposites were marked by the letters PS followed by a number which indicates the percentage of BHAMS. The reaction temperature was fixed at 82 °C and the reaction time was 1 h. At the end of the reaction, the lattices were treated with a solution of aluminium sulphate, the solid products were separated by filtration, washed with water and dried. In all cases, the yield was practically quantitative. The FT–IR spectra of the resulting nanocomposites show no signals associated with the styrene double bond. The average molar masses of all the nanocomposites were evaluated by SEC analysis after separating the polymeric matrices from the filler. The non-grafted fraction of the polymer was removed by continuous extraction with boiling chloroform. To recover the fraction of the polymer grafted to the clay layers, it was necessary to substitute the grafted units derived from the quaternary salt of the (aminomethyl)styrene by an organic ammonium salt. Accordingly, the materials resulting from the extraction were treated with an organic ammonium salt, namely the trimethyl hexadecylammonium bromide. After separating the clay by centrifugation, the grafted-polymer fraction was precipitated in methanol. The FT–IR spectra of the starting nanocomposite PS13, the nanocomposite fraction recovered after extraction in chloroform and the nanocomposite fraction recovered after extraction in chloroform and ion exchange are reported in Fig. 5. It is clear that the extraction with chloroform allows only the fraction of the polymeric matrix non-bonded to the clay surface by electrostatic interactions, to be recovered, whereas the ion exchange procedure allows the fraction of the polymeric matrix bonded to the clay surface to be recovered. In this respect, we can conclude that the polymer fraction soluble in chloroform is constituted by polystyrene, whereas the polymer fraction recovered using the ion exchange procedure is a copolymer consisting of styrene and a quaternary salt of the (aminomethyl)styrene units.

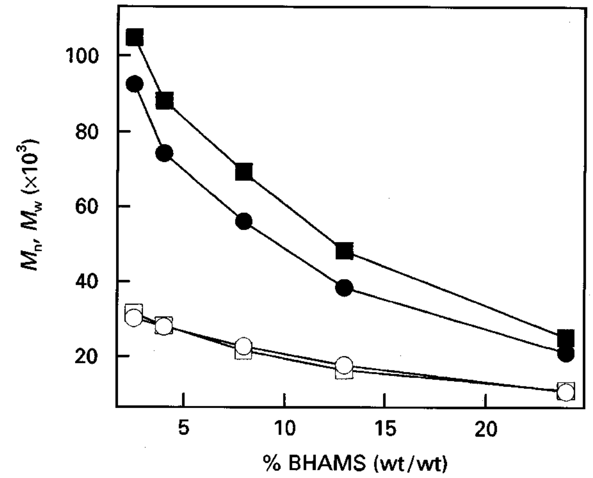

Figure 6 Trend of (○, □) M_n and (●, ■) M_w for the (○, ●) polystyrene homopolymer and (□, ■) the blocky copolymer of styrene and quaternary salt of the (aminometyl)styrene units, as a function of the BHAMS percentage.

Fig. 6 shows the trends of the number average and weight average molar masses for the two types of polymers as a function of the BHAMS percentage.

TABLE I M_n, M_w and T_g data for all the nanocomposites prepared

Sample	M_n PS	M_n PS-PAMS	M_w PS	M_w PS-PAMS	T_g (°C)
PS2.5	30 000	31 000	99 000	93 000	72
PS4	28 000	27 000	84 000	72 900	73
PS8	25 000	23 000	70 000	57 500	80
PS13	13 000	18 000	32 500	37 800	82
PS25	12 000	10 500	25 200	21 000	83

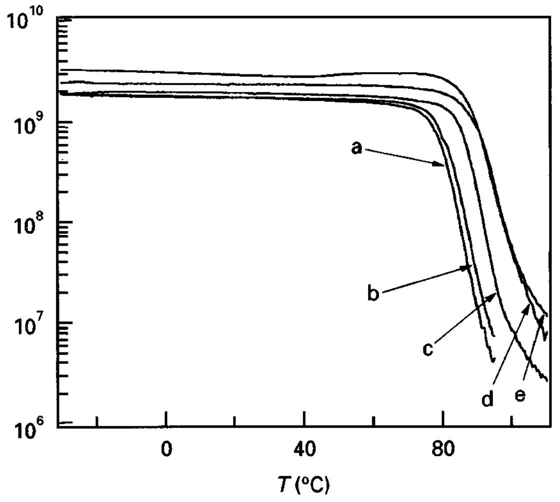

Figure 7 Storage modulus E' of (a) PS2.5, (b) PS4, (c) PS8, (d) PS13 and (e) PS25 as a function of temperature at 1 Hz (scanning rate 4 °C min^{-1}).

The molar masses decrease in both cases as the BHAMS percentage increases. For comparison purposes, a sample without BHAMS, was prepared under the same emulsion polymerization conditions. This sample displayed a number average and weight average molar masses of $M_n = 40\,000$ and $M_w = 150\,000$. These values are substantially higher than those obtained for the nanocomposites. We can conclude that during the emulsion polymerization, BHAMS causes termination and/or chain-transfer reactions thus depressing the molar mass characteristics of the materials.

The degree of insertion of the polymeric matrix within the inorganic layers was monitored by X-ray diffraction analysis. All the nanocomposites have very similar X-ray diffraction patterns consisting of a small-angle reflection at about 1.53–1.55 nm. These interlayer distances are very similar to those of BHAMS and indicate that minor, if any, delamination occurred and only AMS polymerizes between the inorganic layers of the clay. This latter finding suggests that the polymer fraction recovered using the ion exchange procedure is a copolymer with blocky characteristics.

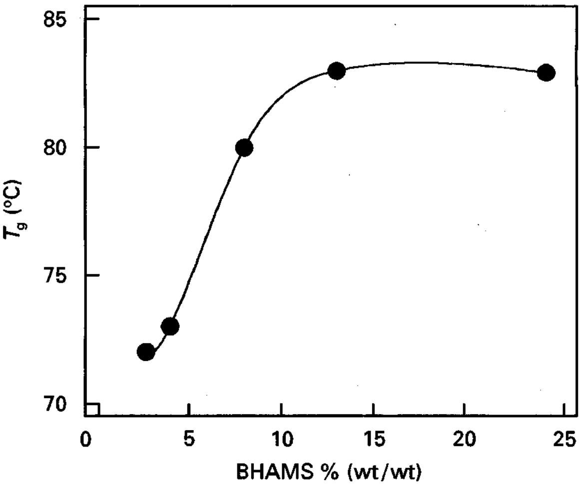

Figure 8 Trends of the glass transition temperature of the nanocomposites as a function of the BHAMS percentage.

The dynamic-mechanical behaviour of the nanocomposites was studied in the linear viscoelasticity region at the frequency of 1 Hz between − 50 and 150 °C with a scanning rate of 4 °C min^{-1}. Fig. 7 illustrates the trends of the storage modulus E', as a function of the temperature, for the prepared nanocomposites. The main relaxation process is observed between 70 and 100 °C and is associated to the glass transition of the polymeric matrix. The glass transition temperatures, T_g, were determined from the onset of the relaxation in the E' curves. Fig. 8 shows the trend of T_g as a function of the BHAMS percentage. The glass transition temperature increases as the BHAMS percentage increases, steeply at first and then more gradually until a limiting value is reached corresponding to a content of BHAMS of 15%. The overall increase of the glass transition temperature can be estimated to be about 12 °C. It should be observed that the T_g increase due to the fixation of the polystyrene chains on to the clay layers is contrasted by the natural tendency of the glass transition temperature to decrease as the molar mass of polymer decreases. Accordingly, the inherent reinforcing action due to the presence of the reactive organophilic clay should be higher than the observed one.

4. Conclusion

This report describes the preparation and the properties of new hybrid organic–inorganic nanocomposites prepared by emulsion polymerization of styrene in the presence of a reactive organophilic clay. After the polymerization reaction, the polymeric matrix was found to be constituted by polystyrene homopolymer and a blocky copolymer of styrene and quaternary salt of the (aminomethyl)styrene units. The glass transititon temperature of the nanocomposites increases as the percentage of organophilic clay increases until a limiting value is reached corresponding to about 15% by weight of the clay. However, the average molar mass of the polymeric matrix decreases as the clay content increases, thus indicating that the inherent reinforcing action due to the presence of the reactive organophilic clay is higher than the observed one. From these data, we can conclude that it is possible partially to improve the mechanical properties and widen the application temperature window of the polystyrene through the preparation of suitable nanocomposites.

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