SELF-ASSEMBLED NANOCOMPOSITES BASED ON BLOCK COPOLYMERS CONTAINING MAGNETIC NANOPARTICLES

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During the last years nanocomposites containing nanoparticles have received increasing interest as potential candidates to replace traditional materials. One of the most important problems is the difficulty of controlling the dispersion of inorganic materials inside an organic medium as a homopolymer or block copolymer. To overcome this problem, it is often necessary to functionalise the nanoparticles, hence ensuring an effective control of dispersion.
In this work, following previous attempts to functionalise magnetic nanoparticles with acrylic polymers[1,2], we have functionalised iron oxide nanoparticles (Fe_3O_4) with polystyrene (PS) brushes via atom transfer radical polymerisation (ATRP) 'grafting from' technique.
Block copolymers offer distinct intriguing possibilities to prepare novel nanostructured materials mainly due to their unique property to self-assemble. This ability is explored in this study with the but to obtain new nanostructured nanocomposites.
Magnetic nanoparticles (MN) modified with PS have been mixed with polystyrene-b-polybutadiene-b-polystyrene (SBS) block copolymer, to develop nanocomposites in which the nanoparticles are selectively segregated in one of the matrix self-assembled phases.
The nanoparticles used, magnetic iron oxide nanoparticles (Fe_3O_4), MN, were kindly supplied by Integran Technologies Inc. Polystyrene-b-polybutadiene-b-polystyrene block copolymer was purchased from Dynasol.
Techniques such as Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and atomic force microscopy (AFM) were used to characterize the functionalised particles. SBS copolymer and its composites have been characterised by DSC, rheological and AFM measurements.
Magnetic nanoparticles (MN) were modified first with an initiator (2-(4-chlorosulfonylphenyl) ethyl trichlorosilane) (CTCS)[1,2] that allows the initiation of the polymerisation. The second step was the polymerisation of polystyrene by ATRP. The reaction of hydroxyl groups of MN and CTCS was confirmed by FTIR (Fig. 1). Two new peaks were observed in the magnetic nanoparticles spectrum modified with the initiator (MN-CTCS) with respect to neat CTCS spectrum (not shown here); one of them was attributed to the appearance of the formed Si-O-Si bond (ν Si-O-Si 1039 cm^{-1}) that indicates that trichlorosilane groups have self-condensed to form a polysiloxane film on the iron oxide surface. The other peak (ν Si-O 1129 cm^{-1}) was attributed to formed MN-O-Si bonds that were created between MN and CTCS. Other peaks were observed in both spectra, one of them was assigned to the symmetric stretching of S=O (ν S=O 1377 cm^{-1}) of CTCS, another peak was attributed to asymmetric stretching of S=O (ν S-O 1178 cm^{-1}) of CTCS. These results confirm that there was CTCS anchored on surface of MN.
The modification of MN-CTCS with PS[3,4] was confirmed by FTIR (Fig. 1), where three new peaks attributed to PS appeared at 1600 cm^{-1}, 1500 cm^{-1}, 1450 cm^{-1}. A relative shift of the S=O peak due to the influence of neighbour groups was also observed. The position for this group Ar-SO_2-Cl (ν S=O 1377 cm^{-1}) was different to the position of Ar-SO_2-R (ν S=O 1318 cm^{-1}). There was a new peak at 730 cm^{-1}, which can be attributed to stretching of the S-C bond (ν S-C 730 cm^{-1}). A high increase of the characteristic stretching bands of aryl and alkyl groups at 3200-2800 cm^{-1} was observed in MN-PS.
MN modified with PS were mixed with SBS block copolymer. Preliminary results seem to indicate that the modified MN could be segregated[5,6] in one of the phases (PS), thus opening up the possibility of creating novel nanocomposites.

A corona of brushes of PS were grown onto surface of commercial magnetite MN powders using "graft from" technique by ATRP. Those MN were characterized using FTIR, confirming that brushes of PS were anchored onto surface of MN.
Novel nanocomposites can be created by mixing PS-modified MN with SBS block copolymer by selective functionalization of the magnetic particles.

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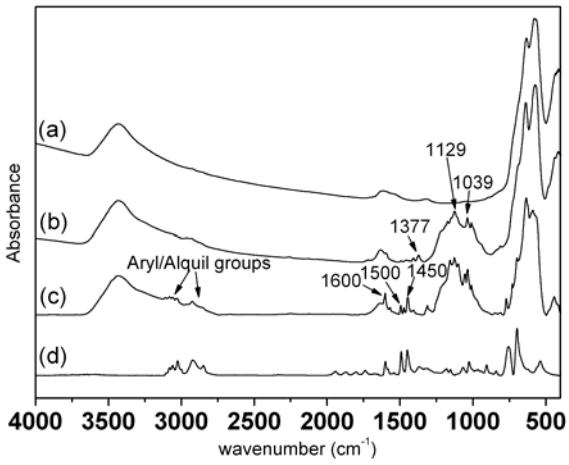

Fig.1. FTIR spectra for: (a) MN, (b) MN-CTCS and (c) MN-PS brushes, (d) PS homopolymer.