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# Synthesis and characterization of novel nanocomposite materials based on poly(styrene-co-butyl methacrylate) copolymers and organomodified clay

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## ABSTRACT

In this research, synthesis of nanocomposites based on poly(styrene-co-butyl methacrylate) copolymer matrix was investigated with different types and amounts of organomodified MMT clays under the trade names Cloisite 15A and 10A. The *in situ* polymerization technique was selected with dispersion of the MMT nanoparticles into the corresponding co-monomer mixture and subsequent bulk radical polymerization. Reaction kinetics was measured gravimetrically and the structural characteristics of the nanocomposites formed were verified with XRD and FTIR analysis. Their glass transition temperature was measured with DSC, while their molecular weight distribution and average molecular weights with GPC. Thermal degradation characteristics of the nano-hybrids formed were measured with TGA. The copolymer composition was verified with <sup>1</sup>H NMR spectroscopy. It was found that, since diffusion-controlled phenomena did not affect much the polymerization kinetics, also the presence of the nano-filler did not influence much the variation of conversion with time. In addition, the average molecular weights and the glass transition temperature of the polymer in the nanocomposites was not changed significantly compared to the neat polymer. However, the thermal stability of the nanocomposites formed was significantly improved with the presence of the nano-filler.

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## 1. Introduction

Over a decade of research has shown that nanostructured materials have the potential to significantly impact growth at every level of the world economy in the 21st century. Compared to conventional filled polymers, polymer/layered silicate nanocomposites have attracted the attention of researchers because of their unique behaviour; the addition of only a very limited amount of clay (usually less than 5 wt.% inorganic) to a polymeric matrix has a significant impact on the mechanical, thermal, fire and barrier properties of the polymer [1–4].

From the structural point of view, two idealized polymer–clay nanocomposites are possible: intercalated and exfoliated. Intercalation results from the penetration of polymer chains into the clay's interlayer region and interlayer expansion. Usually, the ordered layer structure is preserved and can be detected by X-ray diffraction (XRD). By contrast, exfoliation involves extensive polymer penetration and silicate crystallites delamination and the individual nanometer-thick silicate platelets are randomly dispersed in the polymer matrix. Exfoliated nanocomposites usually provide the best property enhancement due to the large aspect ratio and surface area of the clay [5]. Moreover, since clay is naturally hydrophilic and inherently incompatible with most organic polymers, several methods have been studied to make clay compatible with

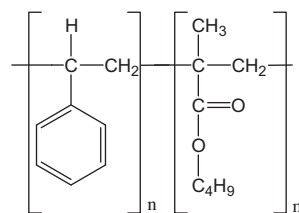
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polymer. The most popular involves surface ion exchange, in which the metal cations on clay's surface are exchanged for organic cationic surfactants typically ammonium compounds with long alkyl chains [6].

The formation of polymer based nanocomposites has been accomplished by several methods including *in situ* polymerization [7–14], and polymer melt [15–18] or solution intercalation/exfoliation [19,20]. Among them, dispersing *in situ* polymerization may be the most desirable method for preparing nanocomposites, because the types of nanoparticles and the nature of polymer precursors can vary in a wide range to meet the requirements. By *in situ* polymerization, the clay is swollen in the monomer for a certain time depending on the polarity of the monomer molecules and the surface treatment of clay. The monomer migrates into the galleries of the layered silicate, so that the polymerization reaction occurs between the intercalated sheets. Long-chain polymers within the clay galleries are thus produced.

Radical polymerization kinetics has been the subject of extensive studies for long time [21–27]. Besides, the chemical reaction mechanism, diffusion-controlled phenomena usually play an important role in the reaction rate and final product properties. Concerning polymer nanocomposites prepared by the *in situ* polymerization technique, though several papers have been published describing the effect of a number of factors on the properties of the nanocomposite prepared, [8–11,13,19,28–30] detailed studies on the radical polymerization kinetics are rather limited. Moreover, from the methacrylates family only methyl methacrylate has been extensively studied [28–30] with a limited number of articles on butyl methacrylate (BMA) [31–34]. Copolymers of the latter with styrene (S) find applications in leather finishing, as emulsions for coatings, etc. [35]. Although a number of papers have been published on the synthesis and characterization of S-BMA copolymers [36–38], a study on the formation of nanocomposites based on this copolymer has not appear so far in literature.

Recently, synthesis of nanocomposites based on poly(-methyl methacrylate) (PMMA) and organically modified montmorillonite (OMMT) using the *in situ* bulk free radical polymerization technique was investigated [39–41]. It was found that the presence of the nano-filler could affect the radical polymerization kinetics either accelerating or retarding it. In the present work we focus on the synthesis of new nanocomposite materials based on poly(styrene-co-butyl methacrylate) with OMMT using the same polymerization method. Two copolymer compositions are investigated with different grades and amounts of commercial organically modified clay. The structural unit of the copolymer formed appears in Scheme 1. Polymerization kinetics was studied gravimetrically having the advantage of providing absolute measurements of conversion versus time while samples at different time intervals are available. Structural and morphological characteristics of the nanocomposites were measured by means of  $^1\text{H}$  NMR, X-ray diffraction (XRD) and FTIR spectroscopy. The average molecular weights and the full molecular weight distribution of the materials formed were measured with Gel Permeation Chromatography (GPC), while their glass



**Scheme 1.** Structural unit of the poly(styrene-co-butyl methacrylate) copolymer.

transition temperature,  $T_g$  with DSC. Finally, their thermal stability and degradation characteristics were investigated using thermogravimetric (TGA) analysis.

## 2. Experimental

### 2.1. Materials

The monomers used i.e. styrene and butyl methacrylate with a purity  $\geq 99\%$  were purchased from Fluka and the hydroquinone inhibitor was removed by passing them, at least twice, through disposable inhibitor-remover packed columns, supplied from Aldrich, before any use. The free radical initiator, benzoyl peroxide (BPO) with a purity  $>97\%$  was provided by Fluka AG, and purified by fractional recrystallization twice from methanol, which was purchased from Merck. All other chemicals used were of reagent grade.

For the preparation of the nanocomposites, commercial organically modified montmorillonite clays (OMMTs), Cloisite 15A and Cloisite 10A, (Southern Clay Products) were used. These are MMT modified with a quaternary ammonium salt, which is dimethyl hydrogenated tallow and dimethyl, benzyl, hydrogenated tallow for Cloisite 15A and 10A, respectively. The chemical structures of the ammonium salts and their cationic exchange capacity (CEC) are illustrated in Table 1.

### 2.2. Preparation of the initial monomer–nanoclay mixtures

Two copolymers with different initial monomer ratios were studied. The first was rich in BMA, while the second in styrene. These were given the code names P(S-BMA) 20:80 and P(S-BMA) 60:40 denoting a 20:80 or 60:40 ratio of S:BMA, respectively. The latter monomer proportion selection was based on preliminary kinetic experiments, where it was observed that a S:BMA 80:20 ratio resulted in a conversion vs time curve similar to that of neat styrene polymerization at the same conditions. Initially, the proper monomer mixture (i.e. S with BMA) was prepared. Following, the appropriate amount of OMMT in 25 g of the monomer mixture was dispersed in a 100 mL conical flask, by adequate magnetic and supersonic agitation. The magnetic agitation lasted for 24 h, while the supersonic agitation was 1 h for all samples. The dispersion of the particles in the monomer mixture was homogeneous, as indicated by the high translucency in the visible region. In the final suspension, the initiator, BPO 0.03 M was added and the mixture was degassed by passing nitrogen and immediately used.

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