

Contents lists available at [SciVerse ScienceDirect](http://SciVerse.Sciencedirect.com)

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Effect of the type of organic modifier on the polymerization kinetics and the properties of poly(methyl methacrylate)/organomodified montmorillonite nanocomposites

Alexandros K. Nikolaidis, Dimitris S. Achilias*, George P. Karayannidis

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 541 24, Greece

ARTICLE INFO

Article history:

Received 19 July 2011

Received in revised form 1 November 2011

Accepted 9 November 2011

Available online 18 November 2011

Keywords:

Nanocomposites

Poly(methyl methacrylate)

Organomodified montmorillonite

Polymerization kinetics

ABSTRACT

A series of organomodified montmorillonite clays (OMMTs) such as intercalated modified montmorillonite with alkylammonium or alkylphosphonium salts (AA-MMT or AP-MMT) and double modified MMT with alkylammonium or alkylphosphonium salts and silane coupling agent (SAA-MMT or SAP-MMT) was successfully prepared in this study. The effect of the amount of nanofiller and type of organic modifier of the OMMT on poly(methyl methacrylate) (PMMA)/OMMT nanocomposites synthesized by in situ bulk polymerization was investigated. The structural and morphological characteristics of the obtained nanocomposites were studied by means of X-ray diffraction and transmission electron microscopy, indicating that exfoliation is more likely to occur in case of nanocomposites with small amounts of AA-MMT and SAA-MMT. The kinetic study results showed that the presence of AA-MMT enhances polymerization kinetics, while AP-MMT acts rather as a reaction retarder. The presence of the nanofiller and the augmentation of the OMMT content increased the thermal stability of all nanocomposites, as measured by thermogravimetric analysis, as well as their average molecular weight measured by gel permeation chromatography. Measurements of the tensile properties revealed that the Young's modulus increased for all nanocomposites along with a decrease of the ultimate strain, while the tensile strength varied regardless of the extent of exfoliation.

© 2011 Elsevier Ltd. All rights reserved.

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 small 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 [1–3]. For example, in terms of the mechanical properties, a nylon-6/layered silicate nano-

composite, with a silicate content of only 5 wt.%, exhibit a 40% higher tensile strength, 68% greater tensile modulus, 60% higher flexural strength, and a 126% increased flexural modulus over those for the pure nylon-6 [4].

The main feature that leads to such improved performances is, in the best case scenario, the full dispersion of individual silicate layers in a polymer matrix with nanoscopic dimensions, known as exfoliated structure. However, in many cases, the silicate layers are not completely dispersed throughout the polymer matrix and are instead better described as being intercalated or, in fact having both types of structure present [5,6]. The formation of nanocomposites has been accomplished by several methods: in situ polymerization [7–14], polymer melt [15–18] or solution intercalation/exfoliation [19–21]. By in situ polymerization, the clay is swollen in the monomer for a

* Corresponding author. Tel.: +30 2310 997822; fax: +30 2310 997769.
E-mail address: axilias@chem.auth.gr (D.S. Achilias).

certain time depending on the polarity of the monomer molecules, surface treatment of clay and the swelling temperature, then the reaction is initiated by addition of a curing agent in case of thermosets and by a curing agent or by increasing the temperature in case of thermoplastics [22]. Regardless of the process which is used, there must be good compatibility between the clay and the organic monomer or polymer [10].

The presence of inorganic cations on the basal planar surface of montmorillonite (MMT) layers makes it hydrophilic in nature and hence renders the clay ineffective for adsorption of aliphatic and relatively hydrophobic compounds [23]. Thus, it is very important to improve the organophilicity, so that it can be compatible with organic polymers. The organophilicity of MMT clay is increased by two types of modification as follows [22]: (1) Interlayer galleries modification in which the MMT clay is treated with compatibilizing agents such as amino acids [24,25] or alkyl ammonium ions [26], because they can exchange easily organic with inorganic cations between the silicates layers, hence increasing the distance between the clay layers [22]. Most of the commercially available organoclays are produced by exchange of alkali or alkali earth cations in the interlayer space of clay minerals with alkyl ammonium salts. Other cations, such as phosphonium, pyridinium and imminium have also been used due to their higher thermal stability [27]. (2) Surface and edges modification using silane or titanate coupling agents to generate organophilic surfaces and edges. Although quaternary ammonium salts can be adsorbed on the MMT surface, interlayer galleries modifiers are not enough for MMT surface and edges modification because this adsorption is unstable and the modification by a coupling agent on the surface and edges can form a stable covering [22]. The coupling agent is expected to react with the hydroxyl groups at the clay edges and surfaces [28,29].

In 2002, Yeh et al. [30] used both quaternary alkylphosphonium and alkylammonium salts as intercalating agents for the synthesis of poly(methyl methacrylate) (PMMA)/clay nanocomposites via in situ bulk polymerization. The resulting materials showed improved anticorrosion properties, compared to neat PMMA, based on a series of electrochemical measurements of corrosion, as well as an increase in thermal stability and a reduction of water and oxygen permeability [30]. In a similar way, comparative studies of the properties of PMMA/clay nanocomposites prepared by in situ emulsion polymerization and solution dispersion were conducted [31]. Su et al. prepared PMMA and polystyrene (PS) nanocomposites by in situ bulk polymerization in the presence of organically modified clays containing specific ammonium salts. Either exfoliated [9] or exfoliated and intercalated structures [10] were revealed, while nanocomposites showed improved thermal stability and increased Young's modulus in each case. In 2007, Wang et al. synthesized PMMA/MMT nanocomposite materials through in situ intercalative polymerization. A cationic surfactant, (2-Dimethylaminoethyl)triphenylphosphonium bromide, was used as an intercalating agent with MMT. Compared to pure PMMA, the nanocomposites exhibited higher thermal degradation temperatures (T_d) and glass transition temperatures (T_g). A significant

decrease of the dielectric constant and loss for the aforementioned materials was observed [32].

Moreover, Xie et al. studied the influence of silane coupling agent, on the structure and properties of PMMA/MMT nanocomposites prepared by in situ bulk polymerization. In each case, MMT was modified with the coupling agent and converted into organophilic with an alkylammonium salt. XRD analysis showed that the dispersion of clay in nanocomposites with silane-modified organophilic MMT was more ordered than that in nanocomposites with unmodified organophilic MMT. The T_g and the T_d of the resulting nanocomposites was 6–15 °C and 100–120 °C higher than those of pure PMMA [33]. Şen et al. synthesized poly(4-vinylpyridine) nanocomposites using modified MMT with quaternary salt of cocoamine, as well as double modified MMT with cocoamine salt and silane coupling agent. The stiffness and thermal stability of the nanocomposites were improved compared to neat poly(4-vinylpyridine), while the materials containing double modified MMT, having the most effective exfoliated structure, showed the highest thermal stability and the best dynamic mechanical properties [34]. In 2009, Effenberger et al. synthesized and characterized polyacrylate/MMT nanocomposites by in situ emulsion polymerization. Double modified MMT, produced by surface modification of MMT with silane coupling agent followed by intercalated modification with leucine, was used for this purpose. XRD investigation showed that exfoliated structures were formed, as well as TGA results revealed that all weight loss temperatures for the nanocomposites were higher than that of pure polymer, while the increasing in the clay content played an effective role in the increasing of thermal stability of the nanocomposites [22].

The present work focuses on the synthesis of PMMA/clay nanocomposites by in situ bulk free radical polymerization. For this purpose, sodium containing natural MMT was made organophilic by intercalation with quaternary alkylammonium or alkylphosphonium ions, as well as by combining intercalation and surface modification with a silane coupling agent (double modification). An effort was undertaken to understand the effect of the organic modifier on the structure of the nanocomposites by means of wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). Polymerization kinetics of the nanocomposites was studied gravimetrically, their molecular weight distribution was measured with gel permeation chromatography (GPC), thermal stability was estimated with thermogravimetric analysis (TGA) and the mechanical behavior (tensile properties) with an Instron dynamometer.

2. Experimental

2.1. Materials

The methyl methacrylate (MMA) monomer with a purity $\geq 99\%$ was purchased from Fluka and the hydroquinone inhibitor was removed by passing it, at least twice, through a disposable inhibitor-remover packed column, supplied from Aldrich, before any use. The free radical initiator

Download English Version:

<https://daneshyari.com/en/article/1399809>

Download Persian Version:

<https://daneshyari.com/article/1399809>

[Daneshyari.com](https://daneshyari.com)