

# Radiation-induced modification of montmorillonite used as a filler in PP composite

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## Abstract

In order to improve compatibility between inorganic fillers and polymeric matrix, montmorillonite (MMT) particles were modified with maleic anhydride (MA), then irradiated with electron beam, and finally were dispersed in polypropylene (PP). It was found that absorption of MA on the surface of layered clay results in the formation of salt-type bonding. Radiation treatment generates in the organic modifier stable carbon-centered radicals which, upon dispersion of activated particles in PP, induce filler-matrix linkages. Thus, such a process is another approach which has been shown to be an effective way in overcoming organophobic character of inorganic fillers in polymeric composites. © 2006 Elsevier Ltd. All rights reserved.

*Keywords:* Montmorillonite; Composite; Electron beam; Maleic anhydride; Polypropylene

## 1. Introduction

Fillers are a class of particles that are applied to polymeric composites and other materials to improve some of their properties (Bhushan, 2004). Elements, oxides, carbides, simple and composite salts, and other compounds can be used as a dispersed phase. Investigation and manufacturing of the composites obtained from fillers and common polymers, e.g. polypropylene (PP) (Manias et al., 2001), polyethylene (Arroyo et al., 2003), polyurethanes (Pattanayak and Jana, 2005), polyamides (Loo and Gleason, 2004), polystyrene (Yei et al., 2005; Su et al., 2004), copolymers (Stretz et al., 2005) and others, e.g. biodegradable polymers (Ray and

Okamoto, 2003), have recently focused attention of many laboratories in polymer science.

The main problem in obtaining a composite of suitable properties from polymers and fillers rises from incompatibility of the components. Inorganic, hydrophilic compounds or minerals are usually dispersed phase, whereas the main types of polymeric matrices are hydrophobic. In order to achieve good properties of the multiphase mixtures, fillers have to be modified with the purpose of achieving organophilic layer on their surface. The modification is possible in many different ways; the most popular is the impregnation of fillers with bi-functional molecules, containing in one molecule hydrophobic (e.g. long alkyl) and hydrophilic (e.g. ionic or polar) groups. Usually the process is conducted with application of quaternary ammonium salts comprising long alkyl chains (Filho et al., 2005; Zhang et al., 2006; Viville et al., 2004; Dragan et al., 2002). Such a treatment was frequently carried out for bentonites that

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subsequently were mixed with polymers, e.g. PP, polyethylene or polystyrene, in molten state ([www.nanocor.com](http://www.nanocor.com)). Occasionally other methods of the modification were used, e.g. grafting of the compatibilizer particles to polymer matrix (Zheng et al., 2004; Manias et al., 2001).

Polymer composites with bentonites reveal very interesting properties, e.g. better mechanical strength (Manias et al., 2001), higher thermal stability, enhanced resistance against oxidation (Filho et al., 2005), and lower flammability (Zhang et al., 2006). However, it was also found that under specific conditions some nanocomposites degrade faster than the pristine polymer (Qin et al., 2005). A filler might lead to decrease of the material durability. A mechanism of photodegradation of montmorillonite (MMT)/PP composites has not been elucidated yet (Morlat-Therias et al., 2005). Generally, it is accepted that dispersed clay particles reduce diffusion of oxygen in the nanocomposites what is supposed to result in gas barrier enhancement and consequently reduction of oxidizing degradation. On the other hand, it was found that in such a material photodegradation and thermal degradation in the solid state proceed faster in comparison with, e.g. undoped PP (Filho et al., 2005). Some authors suggest that the absorption of antioxidants on the clay significantly diminishes their role as the protective agents. The other factor that must be taken into account is degradation of the alkylammonium cations. It is well known that they can undergo Hoffman reaction resulting in the release of ammonium and corresponding olefin. Another degradation pathway is oxidation of the hydrocarbon fragments of modifiers and eventually production of the additional amount of organic radicals (Filho et al., 2005). The processes induce undesired destruction and loss of compatibility between the components in nanocomposite. In order to avoid such a phenomenon we investigated other approach, i.e. application to fillers the chemical treatment associated with radiation grafting.

In our previous work, such a processing was applied to the commonly used mineral fillers (zinc and magnesium oxide). Selected vinyl monomers were grafted on the inorganic particles via radicals generated by ionizing radiation (Legocka et al., 2000). The main conclusion driven from the studies on the model compounds was that the vinyl monomers could be grafted on inorganic surface as a result of processes induced by electron beam irradiation. Additionally, the range of ionizing radiation doses was found to optimize the filler production.

In the recent work, we have concentrated our efforts on the adaptation of this method to the modification of layered aluminosilicates known as MMT occurring in bentonites. The enhancement of organophilic properties of the mineral fillers by unsaturated compounds was reported earlier by Khalil et al. (2005). The authors used styrene monomers for the modification of layered

aluminosilicates. The aim of our work was to evaluate the absorption efficiency of some vinyl monomers on the surface of MMT and subsequently to determine the interaction between PP and irradiated fillers modified by the compatibilizing agent. Maleic anhydride (MA) was selected as an unsaturated, unable to homopolymerize the modifier. The strongly polar groups of anhydride interact with ionic centers of MMT. On the other hand, due to organophilic segments, MA facilitates dispersion of the modified particles in polymer and prompts formation of covalent bonds between the fillers and matrix. Preliminary results were published earlier (Legocka et al., 2000) and now we are reporting results of further investigations.

We studied MMT occurring in three different bentonites, either without any treatment or modified with MA and irradiated with electron beam. The fillers were dispersed in PP and some properties of the final composite were characterized by several experimental methods.

## 2. Experimental

### 2.1. Materials

Isotactic PP Malen P J601 was purchased from ORLEN. Unmodified bentonite “Tixogel VP” containing >90% MMT in the form of sodium salt was obtained from Riedel-deHaen. Two kinds of unmodified Polish bentonites were received from Mine Zebiec, Starachowice: “Specjal” containing more than 70% of pure MMT and type “SW” containing ca. 50% of pure MMT. Acetone, maleic and phthalic anhydride were obtained from P.O.Ch. (Poland) while succinic anhydride was purchased from Fluka.

### 2.2. Preparation of samples

Anhydrides were absorbed by bentonites from 10% w/w solution of acetone for half an hour. The sediment was washed with acetone (to remove excess of anhydride) and dried for 6 h under low pressure at 50 °C. In order to avoid degradation of PP upon ionizing radiation and loss of mechanical properties, only fillers were radiation modified. Such a procedure enables to form bonding between MMT and anhydride, and simultaneously facilitate functionalization of the clay by introducing organic groups into filler, so increasing compatibility with PP. Additionally, stable radicals created upon irradiation are able to initiate linkages between the organic parts of compatibilizers and polymeric matrix. The samples of MMT/anhydride were irradiated with 10 MeV electron beam to the overall doses of 26, 52, 78 or 104 kGy. All samples, before testing and mixing with polymer, were grinded and

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