Polymer 53 (2012) 3230–3237

Contents lists available at SciVerse ScienceDirect

Polymer

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

Impact of large aspect ratio, shear-stiff, mica-like clay on mechanical behaviour of PMMA/clay nanocomposites

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ARTICLE INFO

Article history:
Received 14 March 2012
Received in revised form
27 April 2012
Accepted 28 April 2012
Available online 11 May 2012

Keywords:
Mica-like nanofiller
Large aspect ratio
Poly(methyl methacrylate)

ABSTRACT

For the first time poly(methyl methacrylate) (PMMA) nanocomposites based on a synthetic shear-stiff, mica-like K-fluorohectorite clay were prepared by melt -compounding. Besides stiffness, this new synthetic type of clay offers very high aspect ratios above 600 after exfoliation, whereas a tailored surface modification of the clay yielded a good compatibility to the matrix material. The influence of different clay loadings (0–4 wt.-%) on mechanical behaviour of PMMA/clay nanocomposites were studied for two aspect ratios (≈55 and ≈620), set into correlation with morphology and compared to natural montmorillonite (MMT) clay, which has an aspect ratio of ≈50. It was found, that the use of these novel nanoplatelets leads to a significantly increased fracture toughness of about 25 and 70% in the case of an aspect ratio of 55 and 620, respectively, in comparison to neat PMMA, without sacrificing tensile strength. Scanning electron microscopy (SEM) analysis of the corresponding fracture surfaces and μ-computer tomography (μ-CT) revealed a high dispersion quality of the synthetic organo-clay in PMMA. Different fracture mechanisms could be identified. The presence of the nanofiller varies the local stress state in the matrix and promotes additional energy dissipating mechanisms like crack deflection, crack pinning as well as debonding effects with platelets pull-out leading to enhanced fracture toughness.

1. Introduction

Since the first studies performed by researchers from Toyota in 1985, the rapid development of polymer/clay nanocomposites brings continuous improvement of the overall properties of such materials along [1–8]. Besides the mechanical properties of the filler itself, the key issues that significantly influence the resulting properties are the aspect ratio and the quality of the surface modification of the nanofiller. Commercially available organically modified clays have the drawback that they have limited aspect ratios <100 and a high heterogeneity of surface charge. Furthermore, during melt compounding the delamination of tactoids is hardly ever complete, which reduces the maximal possible aspect ratios and therefore the desired properties. So it is an important step to use synthetic clay, which allows higher dispersion quality in the polymer matrix together with much higher aspect ratios as compared to natural clay.

PMMA is a glassy polymer, which offers excellent properties for the packaging industry [9] and optical [10] or biomedical [11] sector due to its high strength, optical clarity, desirable dimensional stability and weatherability. However, due to its high stiffness, PMMA shows a high brittleness that limits the potential application areas. Therefore it is predominantly of interest to improve the toughness of this material without sacrificing optical or mechanical properties. Blending or copolymerisation with rubber implies the drawback of a decreased stiffness and strength [12]. Due to the high surface area and the small interparticle distances, nanoparticles can alter the local stress state in the matrix polymer and promote additional forms of energy dissipation, e.g. multiple crazing, crack deflection, crack pinning and particle/matrix debonding, leading to a tougher material [13]. Despite melt processing is the relevant method for many industrial applications of nanocomposites, relatively few studies exist on the processing of PMMA/clay nanocomposites. It is reported that the use of commercially available organo-clay for melt -compounding increases the stiffness for PMMA while embrittlement takes place, caused by unsatisfactory dispersion quality of the nanoclay in the PMMA matrix [14]. Therefore, it is very challenging to incorporate synthetic organo-clay with a large platelets diameter to thickness ratio (L/h) and to achieve a high dispersion quality.

In this study, a novel synthetic modified, mica-like, shear-stiff K-fluorohectorite (K-hect) clay is used. In order to improve the

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doi:10.1016/j.polymer.2012.04.055

dispersion of the nanofiller a strategy was applied with no need for exfoliation and intercalation. In addition to the better dispersion, by achieving a high aspect ratio beside an increased E-modulus also an increased fracture toughness of PMMA is expected. The preparation method applied for the clay allowed for adjusting aspect ratios in a controlled way, whereas, a subsequent surface modification should guarantee the compatibility between nanofiller and polymer matrix. This novel synthetic nanofiller is dispersed in the matrix during melt compounding but no further desagglomeration and exfoliation is necessary or intended during compounding. The tailored surface modification is based on anchoring of polymer chains bearing multiple quaternized amino groups on the external basal planes of the synthetic K-hect, which yielded a synthetic organo-clay (O-hect) and assured a high quality of dispersion. A series of PMMA/clay nanocomposites was prepared by melt compounding with various clay concentrations and two different aspect ratios, i.e. 55 and 620. The low aspect ratio of the synthetic clay (55) is roughly the same as in the commercial Bentone, which allows for a commendable comparison and highlights the advantages of the novel synthetic clay. The microstructure and mechanical properties were investigated and the micromechanics of the observed deformation behaviour was analysed in detail.

2. Experimental

2.1. Materials

A commercial PMMA (Plexiglas POQ62 supplied by Evonik Industries) has been used as matrix material. To detect possible degradation during processing the molecular weight and polydispersity index were determined before and after processing of the material via gel permeation chromatography. Before and after processing a molecular weight (M_w) of 73 kg/mol and a polydispersity index of 1.63 were determined. The commercial clay Bentone 38 modified with alkyl-ammonium chains was supplied by Elementis Specialties, which has a CEC of 70 mequiv./100 g. The starting material for the preparation of the novel nanofiller is a synthetic Na-fluorohectorite with the chemical formula $Na_{0.5}[Mg_{2.5}Li_{0.5}]Si_4O_{10}F_2$ and a CEC of 110 mequiv./100 g [15].

2.2. Tuning of large aspect ratio and functionalization of the filler

The synthetic Na-fluorohectorite (Na-hect) was suspended in deionized water and then processed in a stirred media mill in order to exfoliate the tactoid stacks by applying shear forces. The degree of exfoliation was controlled by the number of milling passages [16]. This was done using a highly hydrated 'shear-labile' state, represented by the presence of Mg^{2+} cations (Mg-hect) in the interlayer space (Fig. 1). Subsequent to the exfoliation process the clay samples were exchanged with K^+ cations which transformed the clay to a non-swollen 'shear-stiff', mica-like state with no intracrystalline reactivity [17].

Due to the inertness of the interlayer space, this mica-like material allows for a selective cation exchange limited to the external basal planes of the clay. Consequently, the hydrophilic nanoplatelets can be converted to hydrophobic fillers compatible with the organic matrix by applying polycations in the cation exchange. The surface modifier chosen by us was a polycationic statistical copolymer, poly(2-(2-bromoisobutyryloxy)ethyl methacrylate)-stat-(2-dimethyl-aminoethyl methacrylate) (PBD, Fig. 1). Moreover, the surface modification concomitantly triggered flocculation of K-hect. PBD (1 g L^{-1}) was quaternized and dissolved in water by adding equimolar amounts of concentrated acetic acid and this solution was added to the aqueous dispersions of K-hect obtained after milling until the clay was fully flocculated. Subsequently, the surface modified shear-stiff, mica-like O-hect was washed several times with deionized water and finally freeze-dried.

2.3. Preparation of the PMMA/clay nanocomposites

The commercial Bentone and the synthetic O-hect with two different aspect ratios were melt -compounded at various concentrations with PMMA in a discontinuous counter-rotating

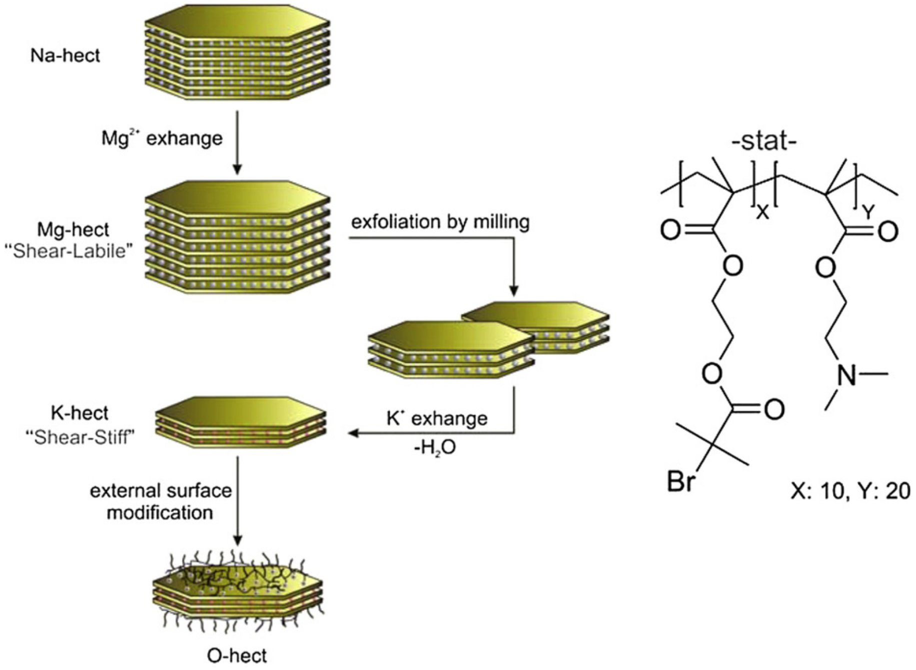

Fig. 1. (Left) synthetic pathway of O-hect; (Right) chemical structure of the polycationic modifier.