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Polyamide-6 nanocomposites with electron-beam-treated clay

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Abstract

The "in situ" polymerisation principle has been applied in our work to modify the efficiency of montmorillonite (MMT) as a reinforcement in polymer composites. The dry silica powder of MMT has been dispersed in (2-hydroxyethyl)-methacrylate (HEMA) monomer, and it has been treated by electron-beam (EB) and by heat. The treated silica powder has been mixed in polyamide (PA) melt by a Brabender kneader. The solid polymer samples have been tested for mechanical features as well as for dynamic-mechanical properties (DMA), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Surprisingly the thermally initiated "in situ" polymerisation was more efficient than 150 kGy EB dose in improving the composite properties.

Keywords: Electron beam; Montmorillonite; Nanocomposite

1. Introduction

Nano-size lamellar, natural silica additives—such as certain clays—may improve the most important mechanical properties of thermoplastics, at quite low (1–3%) silicate content. In the nanocomposite technologies, montmorillonite (MMT) is preferably applied because of its large specific surface (~700 m^2/g). The interface between the reinforcement and the embedding matrix is the most critical factor in all technical polymer composites (Czvikovszky, 2003). This large specific surface of the MMT is only achieved, if its lamellar surface, connected with strong polar ionic bonds are opened to the cooperation with much less polar polymer chains (Friedrich et al., 2005; Thostenson et al., 2005). This can be solved in different ways. The first way is the high-shear melt mixing, when the silica particles are put into a melted polymer at a high level of shear force (in a kneader or twin-screw extruder) (Cai et al., 2007; Gatos et al., 2007; Ito, 2006). The second way to achieve better nanocomposites is the "in situ" polymerisation. It means that the polymerisation of the monomers takes place between the silica layers (Uthirakumar et al., 2005; Tung et al., 2005). "In situ" polymerisation can be initiated with different radiations (X-ray, UV, electron beam). The advantages of these methods are that they can be handled easily and that they take place at low temperatures, hence no great thermal shock is expected during the process of polymerisation (Benfarhi et al., 2004; Czvikovszky, 2003).

Decker et al. (2005) attempted to produce layered silicate-polymer nanocomposites using UV radiation while Keller et al. (2004) used similar technology to prepare nanocomposites by UV curing of organoclay-acrylic systems.

We considered that the electron beam (EB) radiation may be more suitable since it may result in reactive centres on both the silica reinforcement and the polymer matrix as well. The acrylate monomers may form bridges between them.

In our work we applied MMT, swollen in (2-hydroxyethyl)-methacrylate (HEMA) monomer, treated by EB or heat, then mixed in polyamide (PA) melt in a high-shear (Brabender) mixer. The efficiency of the procedure we evaluated on the mechanical and thermo-mechanical properties of the composites. Possible structural changes have also been tested.

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2. Materials and methods

Quaternary ammonium salt treated MMT (Nanofil 919, from Süd Chemie AG) was applied in our experiments. MMT was first mixed with HEMA (from Merck) in the ratio of 1:3. The suspension was held at room temperature for 12 h for swelling, and then was spread in a 100 μm-thick layer on a glass plate. An electrocurtain type low-energy EB machine was applied to initiate polymerisation in inert atmosphere. The delivered radiation dose was 150 kGy. The irradiated MMT was removed from the glass plate and powdered. For comparison a heat treatment (of 80 °C at 24 h) was applied on the MMT–HEMA system.

The surface treated MMT samples were mixed into the PA 6 matrix (Schulamid 6 MV 13 F of A. Schulman AG) with the help of a 50 ml Brabender mixer chamber at 220 °C, at the speed of 20 rpm in order to achieve higher shear forces in the melt so that the separation possibility of nanoparticles would increase. Composites of 0.5, 1, 1.5, 2 and 3 wt% MMT content were produced with this method, whereas at EB treatment the HEMA content were 1.5, 3, 4.5, 6 and 9%, respectively. At the heat treatment the HEMA content were 0.5, 1, 1.5, 2 and 3 wt% in these composites. For comparison, pure PA has been processed on the same way. From these samples $160 \times 100 \times 1$ mm and $40 \times 40 \times 2$ mm large sheets were pressed with a Collin-type laboratory press at 230 °C and at 150 bar. Specimens for tensile tests corresponding to Standard EN ISO 527-1 were cut out of the larger sheets.

The specimens were kept at 50% humidity for 24 h before the tests on a Zwick Z020-type universal tensile tester and the elongation was recorded with a video-extensiometer. The rate of deformation was 2 mm/min.

The X-ray diffraction (XRD) measurements were made by a Philips-type diffractometer with PW 1730-type generator. The scan range was: $2\Theta = 3$–$30°$, the wavelength $\lambda = 1.54186$ Å. The distance between the crystal planes was calculated with the Bragg's law (Kasai and Kakudo, 2005)

$$2d \sin \Theta = \lambda.$$

The change of the enthalpy was measured by Perkin-Elmer DSC-2 type device. The heating speed was 20 °C/min. The heat of fusion of 100% crystalline polymer is 190 J/g (Chen et al., 2006). PA nanocomposites at 1 m/m% MMT content have been measured comparing them with pristine PA.

3. Results and discussion

To get some information concerning the structure of composites XRD measurements have been made on composites containing 1% MMT as well as on PA. Studying the XRD measurements in Fig. 1, we can observe that the presence of MMT and EB treated MMT causes new peaks on the curve of pure PA. The "A" peaks show another crystallisation form of PA, the "B" peaks indicate

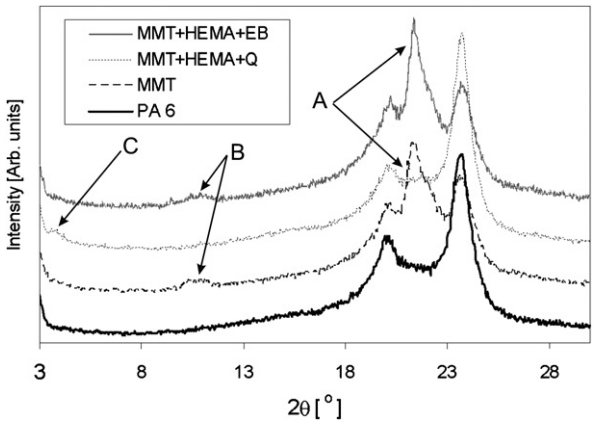

Fig. 1. XRD of PA 6 and PA nanocomposites at 1 wt% particle content. PA 6: polyamide matrix without reinforcement; MMT: montmorillonite as received; MMT + HEMA + Q: montmorillonite modified with (2-hydroxyethyl)-methacrylate and thermal treatment; MMT + HEMA + EB: montmorillonite, modified with (2-hydroxyethyl)-methacrylate and electron beam treatment.

the distance between two MMT layers, being approximately $\Theta = 5.44°$, $d = 8.1$ Å (0.81 nm). In case of using MMT + HEMA + Q there is a new peak (C) around $\Theta = 3.8°$ and there is no peak at the "B" place. The distance between layers increased to 23.3 Å (2.33 nm). This is the first indication that thermal treatment was more efficient in delamination, than the EB.

Fig. 2 presents the main mechanical property of the nanocomposites obtained, comparing with the original PA. The typical nanocomposite behaviour is obtained: only 1–2 wt% of reinforcement is required to achieve significant improvement in mechanical properties, if proper bond is achieved on well-dispersed nanoparticles. To our surprise again the better results we obtained not only on the EB-treated samples, but also on the thermally treated ones.

The thermally treated MMT–HEMA–PA composite is showing a substantial improvement. Close to 30% increase is achieved in the yield strength value at only 1% MMT content.

Similar improvement was observed in the tensile modulus (results not shown), but the improvement is even higher.

Fig. 3 shows the changes in the glass transition temperature (T_g) identified as the maximum place of the $\tan\delta$ curve in the Dynamic Mechanical Analysis. Polyamide plastics are used mostly below their T_g as their mechanical strength and stiffness is optimal in this field. The values seem to decrease at 0.5% particle content, then increase again, in the case of thermally treated MMT–HEMA to the highest, from 69 °C (virgin PA 6) to 90 °C. This can be related to the improved toughness, to the energy-absorbing capability of the nanocomposite of the PA 6 reinforced with 1% lamellar silicate.

Fig. 4 shows the storage modulus of the virgin PA 6 and its nanocomposites, as measured on DMA. The data shows, that the modulus increased by approximately 30% (by more than 200 MPa) if 1% of thermally treated MMT + HEMA is reinforcing the PA 6.