



Macromolecular Nanotechnology

Stiffening mechanisms in vermiculite–amorphous polyamide bio-nanocomposites

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ABSTRACT

Sub-micron thick flakes were obtained by sonication of vermiculite that was first exfoliated by either thermal shock or chemical treatment with hydrogen peroxide. Dimer fatty acid polyamide nanocomposites with a mixed morphology were prepared via a solution–dispersion technique. The large (in the micrometre range) vermiculite flakes assumed random orientations in the matrix. BET surface area measurements indicated flake thickness below 100 nm but SEM showed that thicker flakes were also present. Filler content was varied up to 30 wt.%. At this loading, the tensile strength doubled, the modulus increased fivefold but the elongation-at-break decreased by a factor of ten. Dynamic mechanical analysis suggests that three stiffening mechanisms were operating. The reinforcing effect of the high stiffness inorganic flakes is the primary contributor. Together with the chain confinement effect, that expresses itself in an apparent increase in the glass transition temperature, this provided an adequate rationalisation of the stiffness variation below T_g . However, an additional stiffening effect is indicated at temperatures above T_g . The mechanism may involve dynamic network formation based on fluctuating hydrogen bonding interactions between the matrix polymer chains and the filler particles.

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1. Introduction

Polymer nanocomposites are high performance materials promising to meet new application requirements and to replace existing materials [1–3]. Adding clay-based nanoparticles can significantly improve properties such as heat resistance, stiffness, strength, toughness, impact resistance, barrier properties, rheological properties, and flame retardancy [4–9]. In this regard high particle aspect ratios are desirable and are achieved by extensive delamination and even exfoliation of clay flakes. Exfoliated structures are favoured by strong interfacial adhesion and appropriate mixing processes that also effect homogeneous dispersion of clay layers within the polymer matrix [10].

Conventional polymer nanocomposites are prepared using surfactant modified clays. It is well-known that the nature of the surfactant plays an important role as it determines the degree of clay exfoliation that can be achieved. However, these surfactant molecules need to be chosen very carefully such that interaction with the polymer chains in the matrix is favoured

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above surfactant–clay and surfactant–surfactant interactions [8,9]. Unfortunately the use of cationic surfactants introduces problems including limitations with respect to thermal stability. Hence surfactant-free organo-modifications are of interest [11]. In polyamides it is possible for the polymer chains themselves to provide the required organo-modification when amine functional groups are present, e.g. at the chain ends. Dimer fatty acid-based polyamides are of this type and they are soluble in lower carboxylic acids, e.g. formic acid or acetic acid [12]. When these polyamides are dissolved in acidic solvents, the amine functional groups at the ends of some chains become protonated. Thus, it is possible for these cationic polymer end groups to displace the exchangeable cations present in clays to facilitate exfoliation of the clay sheets [11]. The technique also allows organo-modification of the external surfaces of nano-sized clay sheets suspended in an acidic solution. This may facilitate clay dispersion and to prevent restacking when they are ultimately compounded into the polymer matrix. That was one of the objectives of the present communication. However, instead of a smectite clay, submicron vermiculite nano-flakes were used. These were prepared by either first exfoliating the vermiculite via thermal shock or by suspending it in a H_2O_2 solution followed by ultrasound dispersion in the liquid phase.

The “vermiculite” of commerce features the desirable property that it expands by more than eight times in volume when heated rapidly to elevated temperatures [13–17] or by treating it with H_2O_2 [18,19]. Heating a vermiculite flake results in the rapid transformation of the interlayer water into steam. This generates high pressure that causes the flakes to separate and to expand in a worm-like manner. This expansion can reach 30 times the original flake thickness while the original basal dimensions of the particles remain unchanged [16,18,20]. Vermiculite can also be exfoliated by treatment with H_2O_2 [18,19]. Exfoliation into submicronic and even nanoflakes can be accomplished by subsequent sonication using high power ultrasound [18,21–25].

Dimer fatty acid polyamides find application as thermoplastic hot melt adhesives and as injection mouldable polymeric encapsulants for electronics packaging [12,26]. These applications may benefit from improvements in the matrix strength and stiffness. The present communication compares the effect of submicron vermiculite flakes, prepared by either thermal or H_2O_2 exfoliation followed by sonication, on the mechanical properties of such polyamide/bio-nanocomposites. A primary objective of the present study was to gain an understanding of the stiffening mechanisms operating in amorphous polyamide–vermiculite nanocomposites.

2. Experimental

2.1. Materials

Acetic acid 100% (glacial), ammonium chloride and de-ionized water were obtained from Merck Chemicals and used as received. The amorphous copolyamide, Euremelt 2138 (E2138), was supplied by Huntsman Advanced Materials. According to the supplier, this grade polyamide has a softening point in the range of 138–148 °C and an amine value of ca. 4 mg KOH g^{-1} polymer. Vermiculite grade Superfine (1 mm) was obtained from Mandoval Vermiculite.

2.2. Sample preparations

The raw vermiculite was first washed with de-ionized water to remove soluble compounds and organic impurities by flotation. The washed material (N-VMT) was dried at 60 °C for 48 h. The ammonium exchanged vermiculite (A-VMT) was prepared as previously described [11]. A typical procedure was as follows: Vermiculite (100 g) was suspended in 500 mL of a 1 M solution of NH_4Cl ($\text{pH} \approx 5$) and stirred for 2 h at ambient conditions. The solid was separated by sedimentation and the supernatant decanted and replaced with fresh NH_4Cl solution. This procedure was repeated five times. Then the NH_4^+ -vermiculite was washed with a large volume of de-ionized water until all Cl^- was removed (checked with AgNO_3 solution). The flakes were allowed to air dry. The resulting product was then exfoliated using either thermal shock or by suspension in a H_2O_2 solution.

Thermal exfoliation was achieved by exposing the material for 5 min to a temperature of 700 °C in a convection oven. The expanded samples were sonicated at 20 kHz and 375 W using an ultrasound probe (Sonics & Materials Inc., Model Vibracell VC375, 12.15 mm diameter). Typically, 2 g of TE-VMT was suspended in 300 mL of de-ionized water and sonicated for 2 h. The slurry was allowed to settle for 2 h. Thereafter the supernatant was decanted. Water was added to the residue and the sonication proceeded for another 2 h. This process was repeated for a third time at which stage the remaining residue was discarded. Afterwards all samples obtained in this way were combined to obtain the sonicated thermal-exfoliated vermiculite filler.

A similar procedure was used to prepare the sonicated hydrogen peroxide-exfoliated vermiculite filler. Instead of de-ionized water, 30% H_2O_2 solution was initially used as medium. The chemical exfoliation was first performed by the suspending 100 g amounts in 500 mL of 30% H_2O_2 solution at room temperature for 48 h. After the first sonication the process used for the thermal-exfoliated vermiculite was followed. The combined hydrogen peroxide exfoliated and sonicated vermiculite samples were then washed with a large amount of de-ionized water to remove any residual H_2O_2 .

The sonicated vermiculite flakes were recovered by filtration and heated at 150 °C for 48 h to remove residual water. The filler powders were then re-dispersed in acetic acid at a solids content of 5 wt.%. Part of these dispersions was used to

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