Composites Science and Technology 114 (2015) 34–41

Contents lists available at ScienceDirect

Composites Science and Technology

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

Transfer batch blending, an innovative solvent/solid assisted method for melt compounding to achieve good dispersion quality for polymer–clay-nanocomposites

Josef Hausner [a], Mazen Ziadeh [a], Bianca Fischer [b], Hussein Kalo [a], Jasmin Schmid [a], Raphael Kunz [a], Volker Altstädt [b], Josef Breu [a,*]

[a] *Lehrstuhl für Anorganische Chemie I, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany*
[b] *Lehrstuhl für Polymere Werkstoffe, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany*

ARTICLE INFO

Article history:
Received 15 December 2014
Received in revised form 5 March 2015
Accepted 23 March 2015
Available online 2 April 2015

Keywords:
A. Nano composites
A. Nanoclays
A. Polymers
E. Powder processing
Gas barrier

ABSTRACT

The specific interface area between filler and matrix is of key importance for the performance of nanocomposites and therefore blending methods that deliver the best possible dispersion quality, while at the same time being technically benign, are sought-after. Transfer batch blending, as proposed here, utilizes an organic separator compound that is highly volatile at melt compounding temperatures allowing for its easy removal, while being solid at room temperature allowing for easy handling and processing. As judged by particle size distributions for redissolved nanocomposites and TEM micrographs, the quality of dispersion achieved by this transfer batch blending is of comparably high quality as the quality achieved by solution blending and is clearly superior to the quality obtained by melt blending.

Permeability was chosen as the nanocomposite property used to probe dispersion quality as achieved by the different blending methods. For both fillers applied, organically modified natural montmorillonites and synthetic hectorites, transfer batch blending consistently delivered significantly higher reductions of the permeability suggesting that higher effective aspect ratios are achieved via the improved dispersion quality by transfer blending as compared to melt blending.

1. Introduction

Polymers are widely applied materials because of beneficial properties like lightweight and easy manufacturing. Nevertheless, for certain applications it is desirable to improve e.g. stiffness and toughness, flame retardancy or gas barrier. In this respect, polymer clay nanocomposites offer great potential and have for this reason received an ever growing attention from both academic and industrial researchers. Only small amounts of a clay nanofiller (<10 wt%) are required to gain significant enhancement of performance as compared to neat polymers [1,2]. Aside the properties of the filler itself, like aspect ratio and mechanical performance, the dispersion quality is of key importance for the performance of the nanocomposite. Suboptimal dispersion will reduce the specific interface area between polymer and filler and moreover, resulting aggregates of filler may represent failure spots [3]. Commonly four dispersion methods are applied for preparation of nanocomposites: In situ intercalative polymerisation, blending of the filler into liquid prepolymers, melt blending and solution blending [4,5] In all four methods, the filler has to be organophilized by organic modificators prior to blending to reduce surface tension.

In situ intercalative polymerisation disperses the layered silicate in the liquid monomer. Thereby the silicate swells meaning that at least part of the monomer is intercalated before the polymerisation is activated either by heat, by an organic initiator or a catalyst introduced via ion exchange in the interlayer gallery [6]. The second blending technique is similar to the first inasmuch as the filler is mixed via high shear mechanical stirring with a liquid prepolymer prior to crosslinking [7]. In melt blending organically modified clay is dispersed in the polymer matrix at temperatures above the softening point of a polymer, again at high shear rates [8,9]. This technique is the most favoured one in industry because of easy handling, upscaling and environmental friendliness. The fourth technique, solution blending, is a multistage process in which the organically modified clay is dispersed first in the same solvent as the polymer is dissolved in. Then both components are mixed and the solvent is evaporated [10]. This technique is known to provide good dispersion quality and thus optimal properties of polymer clay nanocomposites. The main advantage of solution

---

* Corresponding author. Tel.: +49 921552530; fax: +49 921552788.
E-mail address: josef.breu@uni-bayreuth.de (J. Breu).

http://dx.doi.org/10.1016/j.compscitech.2015.03.019
0266-3538/© 2015 Elsevier Ltd. All rights reserved.

blending is that it allows avoiding complete removal of the solvent throughout the blending process which in turn would inevitably trigger aggregation of the platy fillers into band-like aggregates [11]. In the overlapping areas of such band-like aggregates, external surface area is converted into internal interlayer area. Moreover, the larger the diameter of the platelets the larger the resulting interlayer area is going to be. For large platelets the absolute adhesion energy in these areas may become too high to allow disaggregation during melt compounding of powders of fillers partially aggregated to band-like structures and consequently the specific interface area is sub-optimal in the resulting compounds. Compound properties like toughness or barrier are, however, crucially dependant on the specific interface area achieved.

Solution blending is of course not technically benign and is only used in academia [3,11]. Moreover not all polymers are soluble, in particular high temperature thermoplastics are insoluble in common solvents. Therefore, a compounding technique is needed that combines the benefits of easy processing offered by melt blending of a solid filler material [12] while avoiding any “drying” steps that trigger aggregation to band-like structures [13].

Here we propose the utilization of a powdered transfer batch for melt compounding in which the clay platelets are separated from each other and hold at distance even in the powder by a molecular solid that is subsequently evaporated during compounding while polymer chains take over the role of spatial separators. As previously shown, the oxygen transmission rates (OTR) of thin films are a sensitive measure for the dispersion quality [3] and were applied here to compare compounds obtained by the new method with conventional melt blending and solution blending. Additionally the microstructure was characterized by conventional and transmission electron microscopy (TEM). To probe the influence of the lateral diameter of the clay platelets a natural montmorillonite and a synthetic hectorite are compared.

2. Experimental

2.1. Materials

A commercial polystyrene (PS 158K, supplied by BASF SE, Ludwigshafen, Germany) with a melt index of 3.00 g/10 min (ASTM D1238), a glass transition temperature of 100 °C (ISO 11357) and a density of 1.04 g/cm^3 (ASTM D792) was used. Ethanol was supplied by VWR, Darmstadt, Germany. Tetrahydrofuran and the cationic modifier, di(hydrogenated tallow) dimethylammonium chloride (Arquad® 2HT-75), were purchased from Sigma Aldrich, Steinheim, Germany. Sodium dithionite was supplied by Merck, Darmstadt, Germany. 2-({2-[Bis(carboxymethyl)amino]ethyl}(carboxymethyl)amino)acetic acid (ethylenediaminetetraacetic acid disodium salt, Na_2H_2EDTA), trisodium citrate and sodium bicarbonate were purchased from Grüssing GmbH, Filsum, Germany. These chemicals were used without further purification. The fluorohectorite (Li-Hec) used was synthesised as described by Kalo et al. [14]. The cation exchange capacity (CEC) was determined to be 150 mmol/100 g. Montmorillonite clay PGV® (MMT) was supplied by Nanocor®, Arlington Heights, IL, USA. To remove accessory minerals that limit exfoliation of natural montmorillonites [15,16], MMT was purified as described below. The CEC of the purified MMT was determined to be 122 mmol/100 g.

2.2. Purification of MMT

MMT was purified in three steps to remove carbonates, amorphous binders like iron oxyhydroxides, and organic compounds. Purification is essential to assure phase pure and delaminated nanoplatelets. In the first step, the removal of carbonates, 50 g of MMT were dispersed in 750 ml deionised water and stirred until larger aggregates are dispersed. Then 28 g of Na_2H_2EDTA was added in small portions to reach a 0.1 M solution at a pH-value of 4.5. After stirring the dispersion at 55 °C for 2 h, further 150 ml of a 0.1 M Na_2H_2EDTA solution were added and stirring was continued for 30 min. In order to remove the EDTA complex and the excess of salt the dispersion was centrifuged (4000 rounds per minute (rpm), 5 min), resuspended in water and centrifuged again. Next, the removal of iron oxyhydroxides was achieved by the so-called dithionite citrate bicarbonate (DCB) method [17]. Herein the citrate is acting as a complexation agent, the bicarbonate serves as buffer at a pH of 7.3 and the dithionite as reducing agent for Fe (III). The suspension obtained after step one was placed in a beaker and diluted to 2 L. Na-citrate (155 g) was added in order to get a 0.3 M citrate solution. The suspension was buffered with 250 ml of 1 M sodium bicarbonate (21 g) solution and then the suspension was heated to 80 °C. 50 g dithionite were added in small portions and the suspension was then stirred at 80 °C until gas evolution stopped. After cooling to room temperature, the suspension was flocculated by adding 5 g of sodium chloride to facilitate washing (2×) by centrifugation (4000 rpm, 5 min). Finally the suspension was dialysed to lower the ionic strength and allow for exfoliation by osmotic swelling. The dialysis was stopped when the conductivity decreased to a value less than 50 μS.

In the last step organic compounds like humic acids were mineralized. Thereto the suspension was treated with ozone produced by an ozonizer for 24 h. The suspension was concentrated by rotary evaporation to 7 wt% for subsequent organophilization.

2.3. Organiophilization

MMT and Li-Hec were organophilized by the same procedure. Li-Hec was dispersed in deionized water (1 wt%). An amount of the organic modifier (Arquad® 2HT-75) corresponding to app. 1.2-fold excess of the CEC of the respective layered silicate was dissolved in 250 ml ethanol and added in portions under shaking to the layered silicate suspension. For equilibration the suspension was placed in an overhead shaker over night. The flocculated organically modified layered silicates were then centrifuged and washed two times with an ethanol water mixture (1:1), one time with ethanol and three times with THF. The samples of organophilized MMT (O-MMT) and Li-Hec (O-Hec) used for melt compounding were dried at 100 °C for 12 h and were then grinded in a mortar.

2.4. Nanocomposite preparation

The PS/clay nanocomposites containing 5 wt% inorganic filler were prepared by three different methods: (I) melt compounding, (II) solution blending, and (III) the new transfer batch method which is described in detail in the results and discussion section.

Melt compounding of dried powders of O-MMT and O-Hec with the polystyrol matrix was realized in a discontinuous co-rotating twin-screw microcompounder (DSM Xplore, 15 mL, MD Geleen, The Netherlands) at 210 °C, a mixing speed of 100 rpm and a mixing time of 5 min.

For solution compounding, 650 mL of THF suspensions of O-MMT or O-Hec (1 wt%) were thoroughly mixed with a suspension (266 g) of PS in THF (25 wt%). The united suspensions were casted into large glass basins (Ø = 23 cm) and the solvent was evaporated in vacuum for 3 h at 60 °C, then the temperature was increased for another 3 h to 100 °C. The nanocompound films were then ground and compounded as described above for the melt compounded samples for subsequent injection molding.