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Improvement of carbon nanotube dispersion in thermoplastic composites using a three roll mill at elevated temperatures

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ABSTRACT

The paper reports the effect of using of a three roll mill as additional dispersion step after twin-screw melt extrusion of nanocomposites containing thermoplastic polymers and multiwalled carbon nanotubes. The three roll milling technology was adapted to elevated temperatures of up to 180 °C and examples are shown for its use in processing of different pre-compounded thermoplastic polymer composites based on polypropylene, polycaprolactone and ethylene–vinyl acetate. The aim is to enhance the state of dispersion achieved by the previous melt extrusion step. In particular, depending on the state of dispersion before three roll milling and the adapted conditions, like number of runs and gap sizes, a reduction of number and size of remaining primary nanotube agglomerates was found. This was studied using light microscopy. The resulting improvements in mechanical properties were assessed and could be attributed to the improved dispersion. In some cases agglomerate free samples could be achieved after the three roll milling process.

1. Introduction

Thermoplastic materials containing carbon nanotubes (CNTs) offer many functional properties in the manufacture of electromagnetic shielding materials, electrostatically paintable materials, parts for automotive engineering, etc. Mechanical and electrical properties of such nanocomposites are determined through the properties of their constituents, their distribution and their interaction, and the process of the composites preparation. Some properties of the nanocomposites such as ultimate tensile strength, fracture toughness or electrical conductivity may be strongly affected by subtle changes in the particle dispersion and distribution. Due to their synthesis processes, most commercial nanotubes are produced in a strongly agglomerated structure, consisting of primary (as synthesized) agglomerates [1]. Due to the nanoscale diameter dimension of CNTs and high contribution of van-der Waals force the strength of such primary agglomerates can be very high [2]. In many cases remaining primary agglomerates can be observed after typical melt-mixing processes. However, remaining primary agglomerates reduce the fraction of CNTs which can contribute to electrical network formation, although conductivity may also be found in the presence of remaining agglomerates, if they are connected by exfoliated nanotubes and a continuous conductive path is formed by agglomerates [3]. On the other hand, remaining primary nanotube agglomerates act as defects under mechanical stress and lead to lower values of mechanical behaviour as compared to nicely dispersed CNTs [4]. The dispersion of CNTs in a polymer matrix is mainly influenced by CNT properties, like density of the primary agglomerates, length and diameter, surface properties, the polymer properties like viscosity and its interaction with the nanotubes, but also by the melt mixing conditions. These conditions mainly influence the shear forces and mechanical energy input into the mixtures, but also the melt viscosity which was shown to have a significant impact on the dispersion [5,6].

In the last years the influence of melt mixing conditions on the dispersion and the formation of networks of CNTs in polymer/nanotube composites has been intensively addressed. In that context also the effects on electrical, mechanical and other properties of such materials were studied [2,4,7–16]. The comparison of the CNT incorporation strategies, namely direct incorporation or masterbatch dilution, show that in composites prepared by masterbatch dilution better CNT dispersion as well as better mechanical properties, evidenced in higher values of elongation at break, can be achieved [17,18]. Other results show, that an increase in specific mechanical energy (SME) input during the dispersion process of

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CNTs results in better CNT dispersion as assessed by light microscopy [2,12,14,19,20]. However, in many cases even after an extensive optimisation of melt compounding, the composites still contain remaining agglomerates. Especially for materials like e.g. polyolefine [4], polycaprolactone [14], or polyamide [12,16] it is difficult to achieve nanocomposites free of CNT agglomerates. On the other hand, in recent investigations it was shown that increasing SME also increases nanotube shortening, as assessed using TEM on CNTs recovered from the nanocomposites by dissolving the matrix [5]. For melt mixed polycarbonate (PC)/Nanocyl™ NC7000 composite prepared by masterbatch dilution using twin-screw extrusion a significant shortening of the nanotube length to about 30% of the initial length was quantified [21]. Apart from the use of dispersion additives (like e.g. in [22]), another way to optimize the CNT dispersion could be specialized subsequent treatment of nanocomposites still containing remaining agglomerates after a typical melt extrusion processes.

This work focuses on the potential of three roll milling at elevated temperature of 100 °C and higher which to our knowledge was so far not reported in literature to be used for CNT based thermoplastics with melting points above 60 °C. This dispersion method was already found to be very suitable for epoxy systems and is now increasingly used in epoxy/CNT systems [23–27]. It is also used to produce polymer films and is an alternative to two roll milling to process and disperse a wide range of fillers in rubbers before crosslinking, as well. Three roll milling, sometimes called calandaring, is a high shear mixing and dispersion method. It is typically employed when a fine particle size and a narrow particle size distribution are of importance. It can be employed for lab scale quantities as well as on an industrial scale. The machine EXAKT 120HT-250 used in this work is based on a design with a roll diameter of 120 mm similar to EXAKT 120EH-250. The operating principle is based on relative movement of the roll surfaces in the gap formed by the adjacent rolls. The gap widths as well as the rotational speeds of the rolls are set electronically. In the type of three roll mill used, the speed difference of one roll to the next is approximately 1:3.

An ongoing adaption of the technology to higher temperatures currently allows the processing of low melting thermoplastics at temperatures up to 180 °C. This three roll milling treatment of thermoplastic–CNT composites is expected to gently disperse difficult to individualize remaining agglomerates due to the shear and elongation forces present in the gaps of the three roll mill with comparatively low and gradual energy inputs. In contrast to twin-screw extrusion all volume elements of the nanocomposite and thus all remaining agglomerates are forced through the narrow gaps between the rolls. By that treatment, it can be expected that the shortening is lower compared to generating similar dispersion states by increasing SME in melt mixing, so that a better property profile may be achieved.

In order to first study the efficiency of three roll milling on the dispersion, precompounded masterbatches based on polycaprolactone (PCL) and ethylene–vinyl acetate (EVA) as well as a polypropylene (PP) based composite containing commercial multiwalled CNTs (MWCNTs) were used. These composites were pre-compounded using a twin-screw extruder. The envisioned final configuration will be the direct and continuous feeding of the three roll mill at the end of an extruder. For this basic study however the ambient temperature nanocomposite pellets were fed directly into the three roll mill and processed in several runs with decreasing gaps. Thus, the initial runs were needed just for heating up the materials to the final working temperature of the three roll mill. After several runs, size and number of agglomerates were observed by light microscopy. In addition, mechanical and electrical properties of the treated composites were investigated and molecular weight, thermal property and CNT length analyses were performed for some examples.

2. Experimental part

2.1. Materials

As polycaprolactone (PCL) the homopolymer CAPA® 6800 (Perstorp, UK) with a molecular weight of 80,000 g/mol and a melt flow index of 3 g/10 min (2.16 kg at 160 °C, ASTM D1238) was applied.

As ethylene–vinyl acetate (EVA) the type ELVAX® 420 (DuPont™) with a melt flow index of 15 g/min (ASTM D1238) was used.

In addition, an impact modified polypropylene (PP) filled with 20 wt% talc with a density of 1.04 g/cm^3 (ISO 1183 A) and a melt flow index of 15 g/10 min (ISO 1133) was employed as matrix.

As nanotubes, two different commercially available MWCNT materials were used; namely Baytubes® C150P (Bayer MaterialScience AG, Germany) and Nanocyl™ NC7000 (Nanocyl S.A., Belgium). Baytubes® C150P are characterized by an average nanotube diameter of 11 ± 3 nm [28], a mean length of 0.77 μm [21], a deformation stress of agglomerates at 25% pressure deformation of 0.64 MPa [1], a carbon purity of 95% and bulk density of 120–170 kg/m^3 [29]. Nanocyl™ NC7000 are characterized by an average nanotube diameter of 10 ± 3 nm [28], a mean length of 1.34 μm [21], a deformation stress of agglomerates at 25% pressure deformation of 0.39 MPa [1], a carbon purity of 90%, a surface area of 250–300 m^2/g [30] and a bulk density of 66 kg/m^3 [1].

2.2. Preparation of composites

MWCNT based PCL and EVA masterbatches as well as the PP composite were compounded using an intermeshing co-rotating twin-screw extruder ZE25 (Berstorff, Germany), for which the conditions varied for the different thermoplastics. For morphological, electrical, and mechanical measurements the compounded pellets were compression moulded into circular plates (60 mm diameter, 0.5 mm thickness) using a hot press (Model PW 40 EH, Paul Otto Weber GmbH). For comparison, unfilled reference materials were processed in the same way.

The PCL masterbatches containing 7.5 wt% MWCNT were produced using a dispersive mixing screw configuration with many back-conveying elements and an L/D ratio of 36 (screw 2 in [14]). The CNTs (Baytubes® C150P or Nanocyl™ NC7000) were fed gravimetrically into the hopper. For the compounding process, an increasing temperature programme from 180 °C to 220 °C, a screw speed of 500 min^{-1}, and a throughput of 5 kg/h were used. Compression moulding was performed at 180 °C for 2 min at 50 kN followed by fast cooling up to room temperature.

The EVA masterbatch filled with 15 wt% Baytubes® C150P was compounded using a screw configuration having an L/D ratio of 48 containing mainly mixing elements. The CNTs were again fed gravimetrically into the hopper. An increasing temperature ramp from 90 °C to 110 °C, a screw speed of 500 min^{-1}, and a throughput of 10 kg/h were used. Compression moulding was performed under the same conditions as for PCL.

The PP composite containing 4 wt% Nanocyl™ NC7000 was produced using a distributive mixing screw configuration with an L/D ratio of 48 (similar to screw 5 in [14]). The CNTs were fed using a separate side feeder attached at 14 D. For the compounding process an increasing temperature programme from 180 to 200 °C, a screw speed of 500 min^{-1}, and a throughput of 10 kg/h were used. Compression moulding to plates was performed at 200 °C for 2 min at 50 kN. The samples were cooled down rapidly.

2.3. Three roll mill treatment

The three roll mill EXAKT 120HT-250 (with HT standing for high temperature) used in this work was developed based on a design