

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 as studied using light microscopy. The resulting improvements in mechanical properties were assessed and could be related to the improved dispersion. In some cases agglomerate free samples could be achieved after the three roll milling process.

Keywords:

A. Carbon nanotubes, A. Polymer-matrix composites (PMCs), Dispersion, Mechanical behaviour

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 increasingly 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 show 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 CNTs results in better CNT dispersion as assessed by light microscopy [2, 12, 14, 19, 20]. However, in many cases even after an extensive optimization process 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)/NanocylTM 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]. Next to 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 next to two roll mills to process and disperse a wide range of fillers in rubbers before crosslinking. Three roll milling, sometimes called calendaring, 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 melt 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/cm³ (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 diameters of 11±3 nm [28], a mean lengths of 0.8 µm [21], a deformation stress of agglomerates at 25% deformation of 0.64 MPa [1], a carbon purity of 95% and bulk density of 120-170 kg/m³ [29]. Nanocyl[™] NC7000 are characterized by an average nanotube diameter of 10±3 nm [28], a mean length of 1.3 µm [21], a deformation stress of agglomerates at 25% deformation of 0.39 MPa [1], a carbon purity of 90 %, a surface area of 250-300 m²/g [30] and a bulk density of 66 kg/m³ [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°C 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 with a roll diameter of 120 mm. A rotational speed of 300 min⁻¹ was set for the last roll, thus the previous roll was driven at 100 min⁻¹ and the first roll to come into contact with the material had a rotational speed of 33 min⁻¹. The gap sizes were set to provide a constant mass flow for each pass. A progressive increase of the shear rates was used in the first three passes by a stepwise reduction of the gap width, see table 1. The highest shear rate thus nominally was 250,000 s⁻¹ and applied 5 times.

As the unheated granule material was fed directly onto the first roll only a short period of time and a relatively bad thermal contact was available to heat the pellets before shearing them. Thus the first pass is not necessarily representative for further processing. In future work the feeding of the three roll mill will be done by continuous extrusion. This also alleviates problems arising through variations in the feeding rate, which may result in significant deviations of the nominal gap widths, especially for high feed rates of materials with very low melt flow indices.

The temperature of the rolls was sustained at 100°C for PCL and EVA masterbatches and at 180°C for PP nanocomposites throughout the process by a flow of heated silicone oil through the rolls. Thermal expansion is taken into account by recalibrating the machine at elevated temperature after a sufficiently long time to attain thermal equilibrium. For each material, batches of approx. 400 g were treated.

2.4. Characterization of the composite morphology

Light microscopy (LM) in transmission mode was performed to investigate the macrodispersion of CNT agglomerates within the matrices according to the standard ISO 18553. Thin sections with a thickness of 2.5 µm (PCL, EVA) or 5 µm (PP) were cut from the granules (composites without three roll mill treatment) or the pressed plates (samples after

three roll milling) using a microtome Leica 2055 (Leica Mikrosysteme Vertrieb GmbH, Bensheim, Germany) and were fixed with Entellan[®] (Merck KGaA, Darmstadt, Germany) on glass slides. The LM images were recorded using a microscope BH2 combined with a camera DP71 (Olympus, Deutschland GmbH, Hamburg, Germany). The agglomerate area ratio was determined from the LM images using the software ImageJ Version 1.43o by calculating the area ratio A_A (%) of the area of remaining MWCNT agglomerates A related to the total area of the image A_0 . According to the ISO-18553 standard only agglomerates with circle equivalent diameters $> 5 \mu\text{m}$ were regarded.

For the example of PCL based masterbatches, the length of the nanotubes before and after three roll milling was determined using a procedure described in [21]. To extract the nanotubes from the composites, chloroform was used and the nanotubes were measured in their length using TEM analysis.

2.5. Characterization of electrical, mechanical and other properties

Electrical measurements on the pressed films were made using a 4-point test fixture (external source electrodes spacing 16 mm and measuring electrodes spacing 10 mm) combined with a Keithley electrometer DMM 2000 (Keithley Instruments Inc., USA) on strips (5 mm x 55 mm x 0.3 mm).

To compare the mechanical properties of the composites, tensile tests were performed on miniature dog bone tensile bars in accordance to DIN EN ISO 527-2. The tensile properties (E_t Young' modulus, σ_Y yield stress, σ_M maximum stress, σ_B stress at break, ϵ_Y strain at yield point, ϵ_M strain at maximum stress, ϵ_B strain at break) were measured on bars with a length of 20 mm, a measuring length of 8 mm, a thickness of 0.5 mm, and a width of 2 mm punched out from the pressed plates. The values shown represent average values of 10 measurements and typical stress-strain curves were selected for presentation in the graphs. The variation coefficient for all stress values was lower than 5%, whereas elongation at break values varied up to 30%.

High-temperature size exclusion chromatography was carried out by means of a Varian GPC2220 system combined with a refractive index detector. For the example of EVA masterbatches the molecular weight of the EVA matrix was determined before and after three

roll milling and compared with results on pure EVA. For this, the composites were dissolved in 1,2,4-trichlorobenzene at 160°C and the nanotubes were filtered out. A universal calibration was used. The measurements were performed in 1,2,4-trichlorobenzene at a temperature of 160 °C and 1.0 mL min⁻¹ flow rate.

For EVA and its masterbatches differential scanning calorimetry (DSC) using a Netzsch DSC 204F1 Phoenix instrument in nitrogen atmosphere was performed between -100°C and 150°C, at a scan rate of ±10 K/min. The glass transition temperature T_g, the melting temperature T_m and the melting enthalpy ΔH_m were determined from the second heating runs.

3. Results

3.1. PCL masterbatches

For PCL masterbatches containing 7.5 wt% MWCNT NanocylTM NC7000, the influence of processing conditions in twin-screw extrusion was studied extensively [14]. This concentration was selected after preliminary investigations indicated this to be a filling level where a broad variation of mixing conditions was possible, which was not the case when using higher CNT concentrations. An increase of specific mechanical energy input (SME) during mixing generated either by higher rotation speeds and/or lower throughputs was found to improve the macroscopic CNT dispersion significantly. Furthermore, the use of distributive screw configurations containing mixing elements was found to be advantageous for the dispersion process of MWCNTs in the PCL matrix. According to the extrusion optimisation study performed for PCL/CNT composites, a minimum area ratio of remaining MWCNT agglomerates of 2.2% was found.

Figure 1 shows light microscopic images of thin sections of the specific PCL/CNT masterbatches containing 7.5 wt% NanocylTM NC7000 or Baytubes[®] C150P selected or produced, respectively, for this study. The starting materials still contain primary undispersed CNT agglomerates and do not differ significantly concerning the number and size of those agglomerates. The agglomerate area ratio was found to be 3.7% for the PCL/NC7000 masterbatch and 3.3% for the PCL/ Baytubes[®] C150P masterbatch.

The additional treatment with the three roll milling process significantly improves the CNT dispersion, leading to only few small undispersed CNT agglomerates in the case of NanocylTM NC7000 as filler, indicated by an agglomerate area ratio of 0.5%. Interestingly, this finding cannot be generalised for different CNT grades, as the three roll mixing of the

PCL/CNT masterbatch with Baytubes[®] C150P leads to a much lower improvement in CNT dispersion. The agglomerate area ratio decrease only to 1.9%. Even if the smaller agglomerates disappeared after the treatment, some agglomerates in the size of those existing before three roll milling can be observed, meaning that the dispersion aim of this additional procedure could not be achieved under these conditions. This finding can be attributed to the significant differences in the CNT agglomerate structures leading to higher critical agglomerate deformation stress for the Baytubes[®] grade as compared to Nanocyl[™] NC7000 [1].

The stress-strain behaviour of PCL and the PCL masterbatches is shown in Figure 2. The addition of 7.5 wt% MWCNTs to the PCL leads to an increase of yield stress and stress values beyond yield stress, however the samples break at lower strain values in comparison to the pure PCL (ϵ_B 1330 MPa). Thereby, the typical stress-strain behaviour is quite similar when comparing Baytubes[®] C150P and Nanocyl[™] NC7000 with slightly higher stress values for the latter. The elongation at break ϵ_B is significantly higher when using Baytubes[®] C150P with 503% in comparison to 306% for composites containing Nanocyl[™] NC7000.

Even if the MWCNT content in both composites is well above the percolation threshold p_c (in PCL with Nanocyl[™] NC7000 at 0.37 wt% [14]), according to findings of generally higher p_c -values when using Baytubes C150P (e.g. [4, 31]), the concentration difference between the filling level of 7.5 wt% and the percolation threshold concentration may be lower in the case of Baytubes, explaining the still higher elongation at break. For the composites after three roll mill treatments (TRT) the typical stress-strain behaviour is unchanged but the samples break at significantly higher elongation. For PCL/ Baytubes[®] C150P the ϵ_B value increased from 503% to 948% and for Nanocyl[™] NC7000 composites from 306% to 711%. The increase of elongation at break ϵ_B is evidence for an improvement of CNT dispersion in the composites after the three roll mill treatment and corresponds to the findings from microscopic investigations. The Young's modulus E_t increased from 146 MPa for pure PCL to 326 MPa (Nanocyl[™] NC7000) or 377 MPa (Baytubes[®] C150P) for the PCL masterbatches. An additional increase of Young's modulus could be found after the three roll mill treatment up to 407 MPa (Nanocyl[™] NC7000) or 432 MPa (Baytubes[®] C150P).

For the PCL masterbatch containing Baytubes[®] C150P the shortening of the nanotubes due to the three roll milling was investigated. Interestingly the nanotubes dissolved from the

masterbatch after extrusion, as well as those after the three roll milling, showed approximately the same length x_{50} of 380 +/- 5 nm. This indicates that a strong nanotube shortening took place during the masterbatch extrusion (initial length of Baytubes[®] C150P 770 nm) which is not increased after the three roll milling. For comparison, in a composite based on a high viscosity polycarbonate with 0.75 wt% Baytubes[®] C150P processed using a DACA small-scale mixer for 5 min a value for x_{50} of 350 nm was found.

3.2 EVA masterbatch

As a second example, the low melting matrix of EVA was selected and a masterbatch with 15 wt% Baytubes[®] C150 P was produced using twin-screw extrusion. The macrodispersion of the EVA masterbatch before and after TRT as observed by transmission light microscopy on thin sections is shown in Figure 3. After the three roll mill treatment the number of agglomerates of Baytubes[®] C150P as well as their sizes decreased. However, it needed seven runs with increasing shear rates in the three roll mill to achieve an EVA masterbatch which was completely free of remaining primary agglomerates.

The stress-strain behaviour of EVA and EVA masterbatches is shown in Figure 4. It was found that the addition of 15 wt% Baytubes[®] C150P to the EVA leads to a significant increase in the values of stress at break (from 6.6 MPa to 7.6 MPa) combined with a strong decrease in elongation at break ϵ_B (651% to 91%). The Young's modulus increased from 30 MPa to 63 MPa. After the three roll mill treatment (TRT) an increase in stress at break up to 9.3 MPa and elongation at break ϵ_B up to 132% was found. Additionally, the Young's modulus increased up to 90 MPa. The increase in all the key values of the stress-strain diagram is again an indication for the improved CNT dispersion after the three roll mill treatment as it was shown using light microscopy.

As the treatment of the composites was performed in air environment, the arguments of decreasing of molecular weight of the matrix due to the three roll milling may apply.

Therefore, for the example of the EVA, GPC investigations were performed on the pure EVA material before and after TRT as well for the masterbatches. Interestingly, no significant differences could be observed between pure and treated EVA, and also the value of M_w for the EVA masterbatch is the same before and after three roll milling (50,000 +/- 3000 g/mol). This indicates that in principle the process should be applicable without harming the matrix.

Furthermore the results of mechanical measurements, show significant improvements after TRT and indicate that polymer degradation has not taken place at a significant level.

In addition, the DSC study showed that the three roll milling did not affect the glass transition temperature T_g (-32°C), the melting temperature T_m (81°C) or the melting enthalpy ΔH_m (44 J/g) of the masterbatches, so that changed crystallinity can be also excluded as reason for enhanced mechanical properties.

3.3 PP composite

In order to check if the observed effects can be also found in composites with CNT contents typical for practical applications, a PP composite containing 4 wt% Nanocyl™ NC7000 was produced and investigated. The as extruded PP composite contains some residual primary agglomerates as shown in Figure 5. After three roll mill treatment of 7 runs the composite was nearly free of agglomerates (see Figure 5). This is significant as despite an intensive optimization of the extrusion process varying feeding position [4], screw configuration, screw speed, temperature, and throughput during the production of that composite, composites which were free of agglomerates could not be achieved using melt extrusion.

The mechanical properties of the already talc filled polypropylene were only slightly changed upon the additional incorporation of the MWCNTs (Figure 6), namely the elongation at break ϵ_B decreased (from 13% to 9%) and stress values beyond yield point increased slightly whereas the modulus was not influenced (at 754-758 MPa). After the 7th run of three roll treatment (TRT), an increase of all the measured values could be observed in comparison to the untreated composite. Especially the stress values above the yield point were higher and elongation at break comes back to the value of PP (14%) while the Young's modulus remains unaffected. The improved CNT dispersion observed in LM after the three roll mill treatment is again illustrated by a slight improvement of mechanical properties as compared to extruded composites.

3.4 Electrical properties

In addition to morphological and mechanical properties, also the electrical properties of the composites based on PCL, EVA and PP were determined. In the PCL and EVA masterbatches the amount of nanotubes added led to conductive composites in the well percolated range. The samples showed electrical volume resistivities of 10 Ohm cm (PCL +7.5 wt% Nanocyl™ NC 7000) and 4 Ohm cm (EVA +15 wt% Baytubes® C150P). The three roll treatment did not change these resistivity values significantly. Interestingly, also in the PP composite with 4 wt% Nanocyl™ NC7000 having an electrical volume resistivity of 10 Ohm cm the three roll milling treatment did not change the values significantly (20 Ohm cm after the 7th run). Also here, the amount of 4 wt% MWCNTs is well above the percolation concentration p_c of about 0.5 wt % [4].

However, for composites with CNT contents near the electrical percolation threshold one can assume that small improvements in dispersion may lead to improvements in electrical properties. This was shown e.g. for composites based on polycarbonate with 0.5 wt% when improving dispersion by increasing the SME input in small-scale mixing [2].

4. Summary

The technology of three roll milling, well established for epoxy systems to incorporate nanoscaled fillers like carbon nanotubes, was employed to thermoplastic nanocomposites. As this equipment has the advantage of an intensive treatment of the full composite volume through decreasing gaps during multiple runs, even difficult to disperse filler agglomerates can be destroyed. This is achieved by strong shear and elongational forces acting on the primary filler agglomerates. For three different cases, two masterbatches and one lower concentration composite, it could be shown that three roll milling is quite efficient in reducing the size and number of agglomerates which existed after the melt extrusion of these composites. This was shown for PCL masterbatches filled with two different industrial nanotubes, for an EVA masterbatch and also for a PP composite. However, as typical in three roll-milling of epoxy systems, several runs were needed to achieve samples free of agglomerates and only in some

cases the number and size of agglomerates could be reduced significantly. The enhanced dispersion is reflected in changed mechanical properties. In the stress-strain curves of the treated composites with enhanced dispersion, especially the elongation at break ϵ_B is increased after the three-roll-milling treatments. From the simultaneous improvement of stress and strain at break also on an improved work of fracture and possibly higher impact values can be concluded.

The results show that three roll milling in principle is suitable to disperse MWCNT agglomerates also in thermoplastic matrices. In the presented study, which to our knowledge is the first describing the use of a three-roll mill for thermoplastic nanocomposites with pre-compounded CNTs, the process was not yet fully optimized. So far, the first runs were needed to heat up the composites. The perspective is to combine a twin-screw extruder directly with a three roll mill so that the very small gaps between the rolls assure the elimination of agglomerates still existing after the extrusion. This will be the focus of next investigations.

Acknowledgements

We thank the German Federal Ministry of Education (BMBF) for financial support within the Innovation Alliance Inno.CNT. project CarboDis. BMBF 03X0042M and M. Heber (IPF) for her technical support. In addition, we thank O. Starkova and L.A.S.A. Prado (TUHH) for the DSC investigations.

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Figures and captions

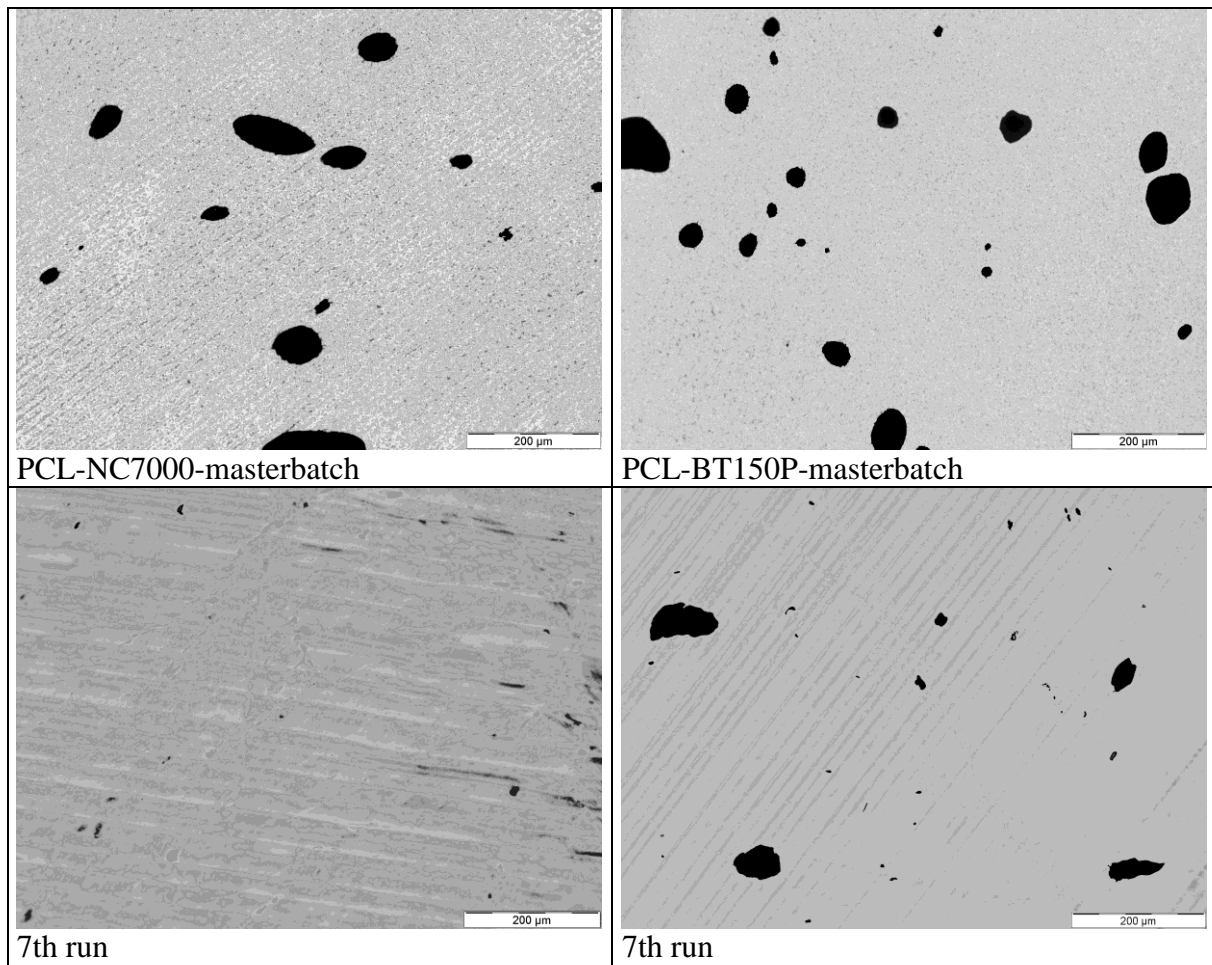


Fig. 1: Light microscopy images of PCL masterbatches containing 7.5 wt% NanocylTM NC7000 (left column) or Baytubes[®] C150P (right column) after extrusion and the 7th run through the three roll mill

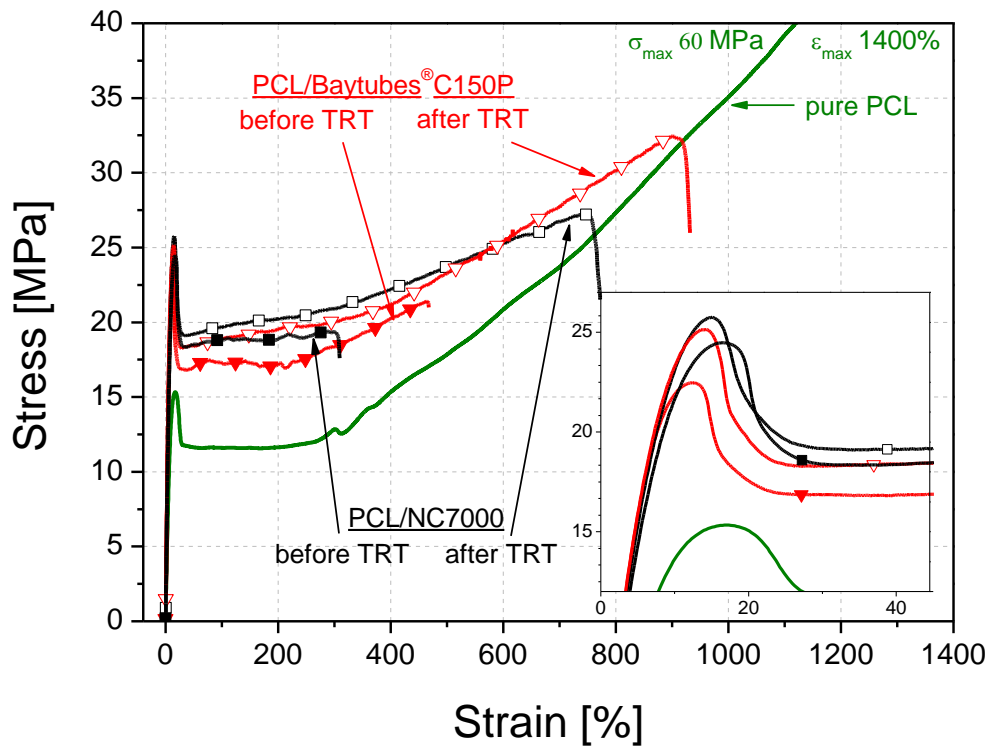


Fig. 2: Stress-strain behaviour of PCL and PCL masterbatches with 7.5 wt% MWCNTs after extrusion and three roll milling treatment (TRT, 7th run)

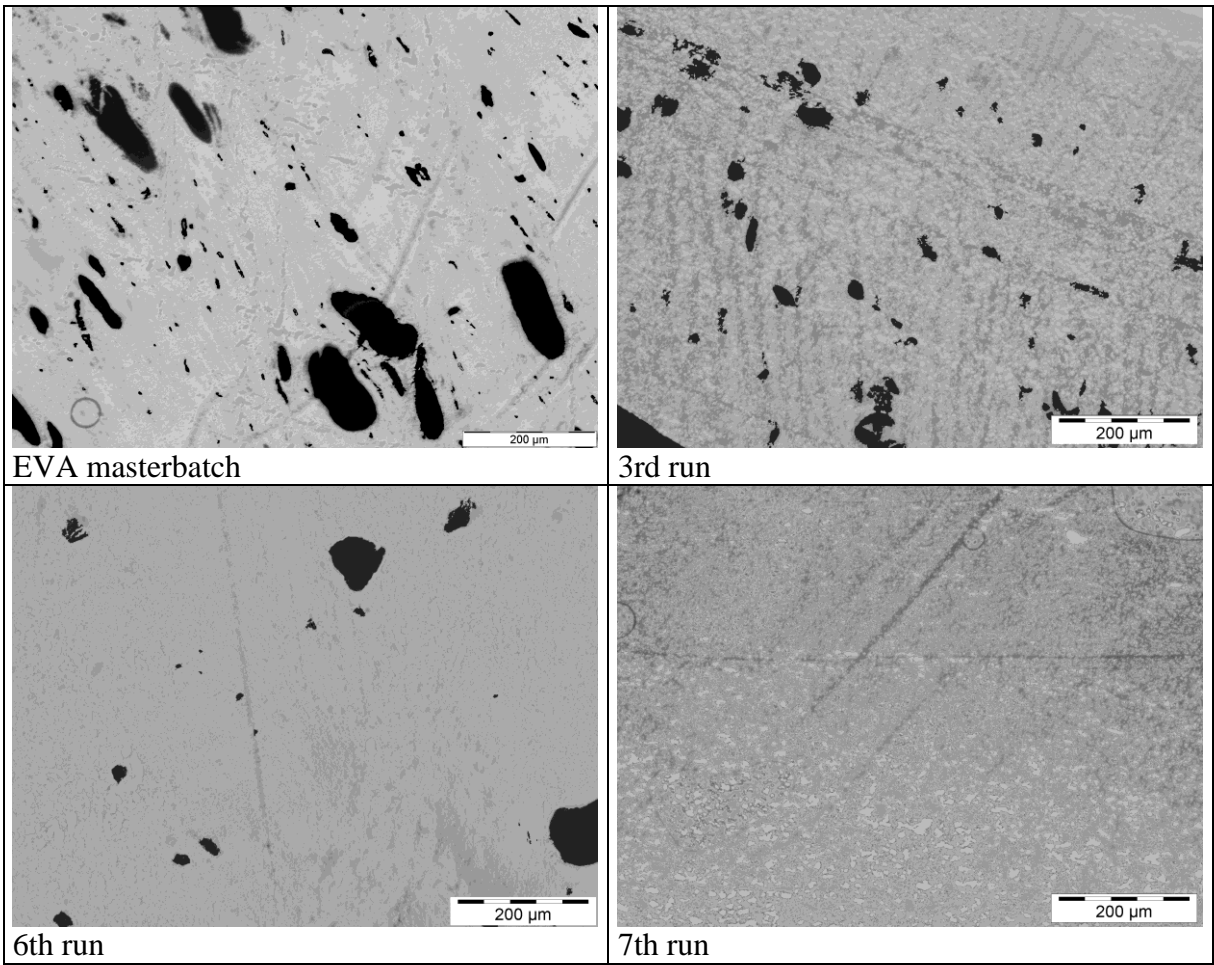


Fig. 3: Light microscopy images of EVA masterbatches containing 15 wt% of Baytubes[®] C150P as produced by extrusion and after the 3rd, 6th and 7th run through the three roll mill

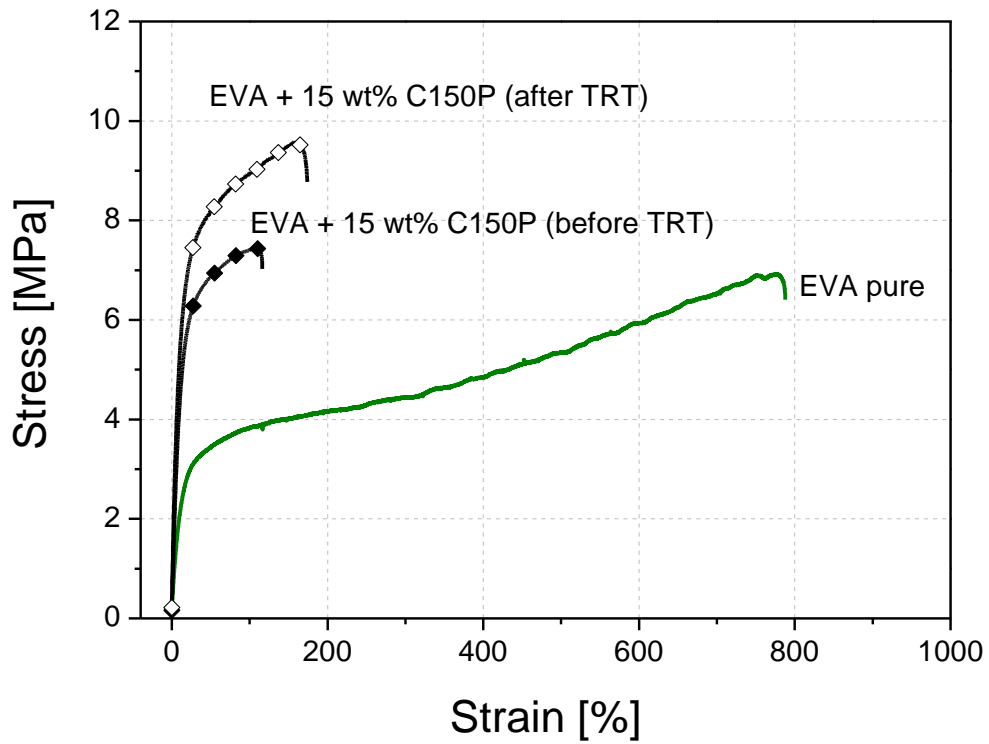


Fig. 4: Stress-strain behaviour of EVA and EVA masterbatches with 15 wt% MWCNTs after extrusion and three roll milling treatment (TRT, 7th run)

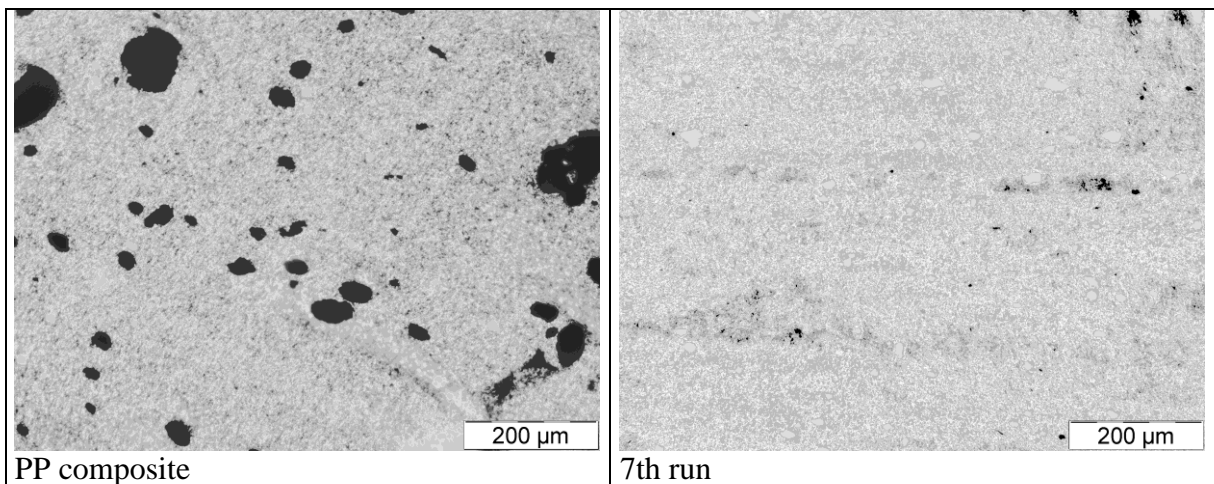


Fig. 5: Light microscopy images of PP composites containing 4 wt% of NanocylTM NC7000 after extrusion and the 7th run through the three roll mill

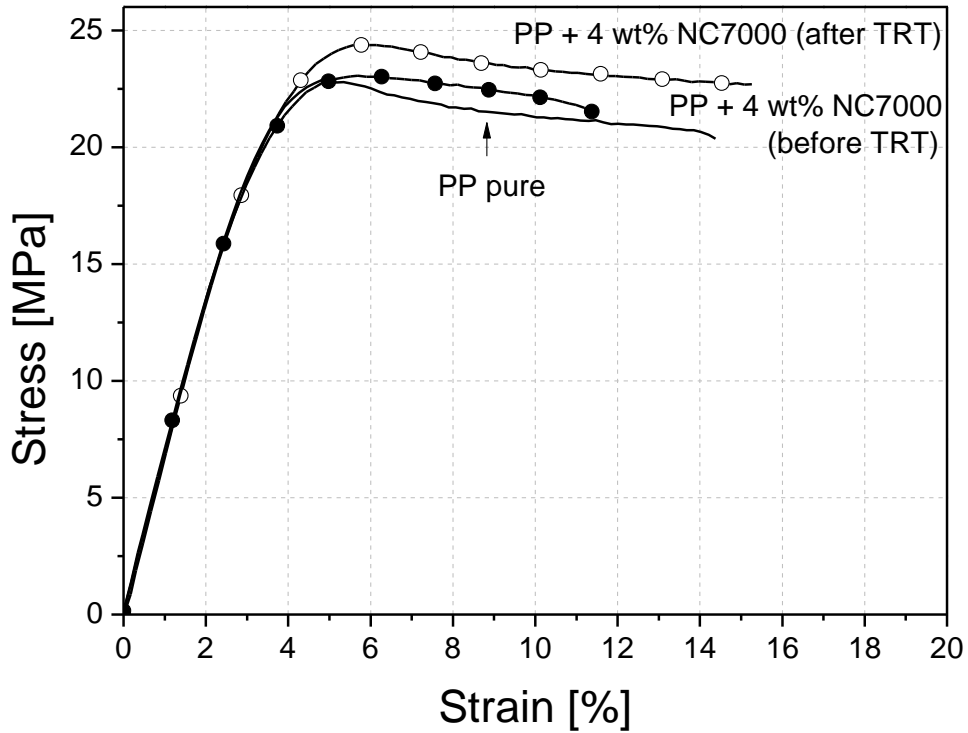


Fig. 6: Stress-strain behaviour of talc modified PP and PP based composites with 4 wt% NC 7000 after extrusion and three roll milling treatment (TRT, 7th run)

Tables

Table 1: Settings of the three roll mill for the dispersion process. In total seven passes were performed. The material was fed directly onto the first roll and sheared in Gap1 and then in Gap2, after which it was repeatedly fed into the machine for the next pass.

Pass number	Gap1 [μm]	Gap2 [μm]	Rotational speed [min^{-1}]	Nominal shear rate in gap2 [s^{-1}]
1	120	40	300	31,000
2	40	13	300	96,000
3, 4, 5, 6, 7	13	5	300	250,000