

Extrusion and characterization of nanoclay filled polypropylene

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ABSTRACT

In recent years, the interest in nanocomposites has grown exponentially. However, the dispersion of polar nanoclay in an apolar thermoplastic matrix remains the key issue. In this manuscript, the process factors affecting the dispersion of nanoclays in a polypropylene matrix are studied. Both the processing of nanocomposites using twin screw and single screw extruders are compared. As the tensile properties of the material are influenced by the dispersion, these characteristics are used for a straightforward evaluation of the different processing parameters. The main goal of this study is to optimize the extrusion process parameters and to evaluate their influence on the strength properties of the material. Variations in properties were noticed for different screw speeds and for different compositions of the starting materials.

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1. Introduction

The interest in nanocomposites, based on nanofilled thermoplastics, has grown exponentially during the last decade. Numerous studies show their great potential due to the nano-enhanced properties such as improved strength, better fire retardancy and lower gas permeability [1-5]. The largest difference in comparison with common composite systems such as glass reinforced thermoplastics is the high aspect ratio (length/diameter of the particle) and the high specific surface of the filler particles. This implies that the usual loading capacity of nanofillers (< 10 wt %) is much lower than other common additives.

Different methods of producing nanocomposites have been proposed during the decade including melt processing, in situ polymerization, solution and latex methods [3]. Melt processing, however, has certain advantages such as the higher commercial applicability of the process, the absence of a solvent, and more flexibility in the formulation of the starting materials.

This research focuses on the processing of nanoclay filled polypropylene (PP), using both twin screw and single screw extrusion. With these polymer-layered silicate nanocomposites, it remains difficult to obtain the optimal dispersion of the individual polar clay platelets in an apolar matrix, such as polyolefins. The final dispersion of nanoclays in a polymer matrix can be divided in three different composite types: tactoids, intercalated and exfoliated. The latter being the most desired one, because of the higher specific surface of the individual platelets and hence the improved mechanical properties [6]. The use of compatibilizers improves the interaction between the apolar thermoplastic matrix and the polar organomodified clays [3].

In this paper, a general extrusion line for the production of nanocomposites is being proposed. The exfoliation/intercalation of the nanoclay is monitored by comparing the Young's modulus of the different materials. It has been proven that the level of exfoliation/intercalation of the clay platelets affects the *E*-modulus of the compounds in a positive way [7-9]. This is a straightforward and easy way to compare the different compounds without using difficult and expensive visualisation techniques such as electron microscopy [10]. The effect of the different processing parameters and compositions of the starting materials are being studied.

2. Experimental

2.1 Materials

The selected polyolefin was a polypropylene homopolymer PP 531P delivered by Sabc Belgium with a MFI of 0.30 g/10 min (230 °C and 2.16 kg), an elongation at break of 600 % and a melting temperature of 170 °C. Cloisite 15 A (CIA), delivered by Rockwood Clay Additives Germany, was chosen as a montmorillonite based clay, modified with a quaternary ammonium salt (2M2HT) to increase the interlayer distance between the individual clay platelets.

Priex 20070 (Pr70) and Priex 20095 (Pr95), delivered by Addcomp Holland, were used as compatibilizer agents to positively influence the interaction between the apolar polypropylene and hydrophilic organomodified clay. Both are polypropylene-grafted-maleic anhydride (PP-g-MA) with a grafting level of 0.10 wt % and 0.45 wt % respectively. The higher the level of grafting, the more exfoliation can be reached [11, 12].

The PP granules, compatibilizer and clay were metered in the required proportions by using volumetric feeding units. All the materials were dried at 80 °C during 6 h in a vacuum dryer before melt processing.

2.2 Extrusion machinery/ die

A tightly intermeshing co-rotating twin screw extruder ZSK 18 MEGAlab from Coperion was used to produce the PP nanoclay composites. The temperature settings from the hopper to the die were respectively 175 °C, 185 °C, 185 °C, 190 °C, 195 °C, 195 °C, 195 °C and 205 °C. This temperature profile was set as low as possible to minimize clay degradation as experienced in earlier tests and as mentioned in the literature as well. The onset degradation temperature of Cloisite 15A is approximately 210 °C [13].

The twin screw extruder was equipped with a slit die, as displayed in Fig. 1. This die was designed to imitate continuous large-scale plate extrusion. In order to retain sufficient extrusion pressure at the extrusion point (max. 50 bar), a small die of 19 mm × 2 mm was used. This die was conically shaped to keep the flow as homogeneously as possible during the final shape formation.

The screw configuration (Fig. 2) consisted of 10 different zones, with 3 degassing areas (marked with upward arrows) and a side feeder mounted on the 4 fourth zone, directly behind the first degasser. Also present are wide kneading blocks and distribution/mixing elements. This is a standard twin screw set-up for compounding, with the possibility of being altered. The first three zones induce the melting and the conveying of the polymer/compatibilizer feed. The fifth zone consists of three wide kneading blocks, with a staggering angle of 45 ° and which has the main objective to break up the agglomerates fed in the side feeder. Zones six and seven are a repetition of the previous two zones. Zone eight and nine consist of small kneading blocks and contribute mainly to the distribution of the nanoclay in the matrix and the melt homogeneity. The diameter of the screw is 18 mm and it has L/D ratio of 40. The maximum throughput is 40 kg/h.

Two different screw speeds were tested, 200 rpm and 300 rpm, as screw speed affects the residence time in the extruder. The total residence time in the extruder (hopper to die) is 49 s and 33 s for 200 rpm and 300 rpm, respectively. The residence time from the side feeder until the die (clay residence time) is 33 s and 29 s, respectively. The PP feed rate was adjusted at each screw speed to ensure a fully filled screw.

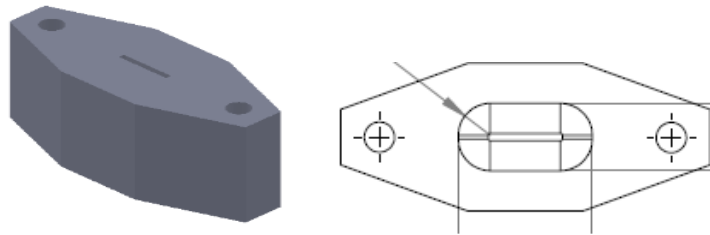


Fig. 1 Extrusion slit die (19 mm × 2 mm)

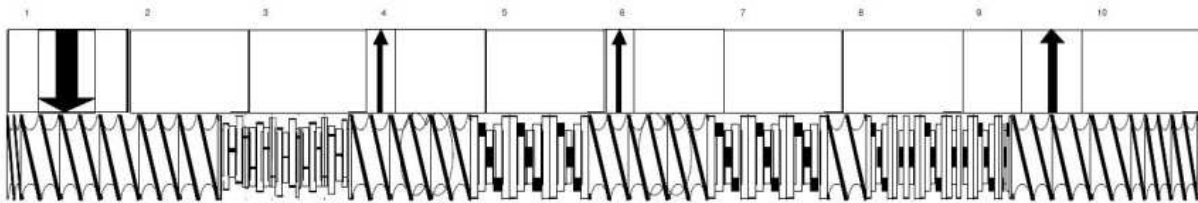


Fig. 2 Twin screw configuration

Concerning the single extrusion tests, an extruder from Brabender Plasti-Corder was used for producing the PP nanoclay composites. The temperature settings from the hopper to the die were respectively 175 °C, 185 °C, 190 °C, 195 °C and 205 °C.

The L/D ratio of the single screw extruder was 15. The single screw extruded compounds were produced by regranulating the twin screw extrudates and by adding them to the single screw extruder, equipped with the same slit die as shown in Fig. 1.

2.3 Sample denotation

Different compounds were produced using both single and twin screw extruders with different clay concentrations and different compatibilizer contents. The samples are denoted with PP/compatibilizer/Cloisite 15A, followed by the different weight percentages. For example, a sample with 5 wt % Priex 20070 and 3 wt % Cloisite15A is denoted with PP/Pr70/ClA 92/5/3.

The difference between single and twin screw extrusion is denoted as SE (single extruder) and TSE (twin screw extruder).

2.4 Characterization

Tensile properties (ASTM D638 – specimen Type IV) were measured four weeks after the production using an Instron 5565 dynamometer, with a load cell of 5 kN at a crosshead speed of 50 mm/min. The specimens were stamped out of the produced plates. The specimens were fully crystallized, so no effects of post-crystallization could occur. The elastic modulus was calculated as the slope of the linear (elastic) part of the stress-strain curve. Tensile property values reported in this paper represent an average from measurements on at least five specimens per compound.

The crystallinity of the specimens was determined using a Netzsch DSC 204F1 at a heating rate of 10 °C/min, under a nitrogen atmosphere. The crystallinity of the different compounds was calculated as follows [14]:

$$x_c = \frac{\Delta H}{(1 - \Phi)\Delta H^0} \quad (1)$$

where ΔH is the apparent enthalpy of fusion per gram of composite, ΔH^0 is the heat of fusion of a 100 % crystalline PP, and Φ is the weight fraction of organoclay in the specimens.

Statistical analysis of the results was performed with SPSS19 through a one-way ANOVA test, with $p = 0.05$ significance level.

3. Results

First the results of the different processing parameters for the twin screw extruder are discussed in subsections 3.1, 3.2 and 3.3. Afterwards (subsection 3.4), a comparison between twin and single screw extruders is made.

3.1 Influence of the % wt compatibilizer

Fig. 3 illustrates the elastic modulus with different % wt compatibilizer with the same amount (5 wt %) of Cloisite 15A. The screw speed (*ss*) was kept constant at 200 rpm. The higher the amount of coupling agent, the higher the free maleic anhydride concentration, leading to a better compatibility between the apolar PP and the polar clay platelets. This is expressed by a likewise increasing modulus value. The progress of the modulus seems to level out after the use of 10 % compatibilizer. Indeed, while there is a significant difference between the modulus of specimens with 5 wt % and 10 wt % compatibilizer ($p = 0.014$), there is no significant difference in modulus between the specimens with 10 wt % and 20 wt % compatibilizer ($p = 0.089$). Additionally, the results clearly evidence a rise in mechanical properties with the addition of nanoclay to the virgin PP material, regardless of the amount of compatibilizer.

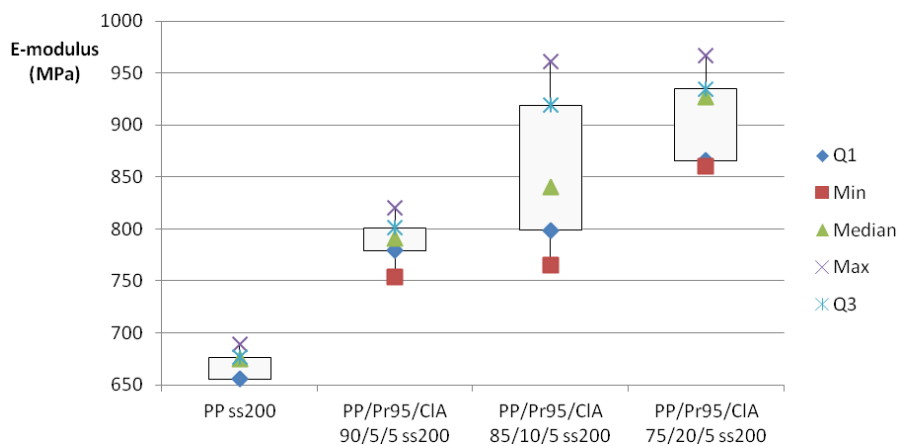


Fig. 3 *E*-modulus of PP/nanoclay with different % wt compatibilizer (5 wt % nanoclay)

3.2 Influence of the rate of nanoclay to compatibilizer

The influence of different percentages nanoclay were tested with the same constant amount of compatibilizer (5 wt %). Fig. 4 shows the evolution of the *E*-modulus for the compounds with different clay concentrations (0 wt %, 3 wt %, 5 wt %).

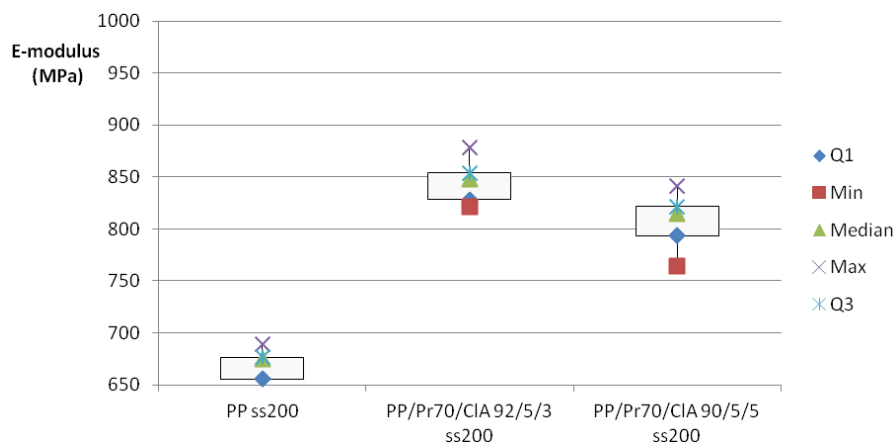


Fig. 4 *E*-modulus of PP/nanoclay with different % wt nanoclay (5 wt % compatibilizer)

Compared to the virgin PP material, an increase of about 25 % in modulus value is observed for the samples containing 3 % nanoclay. However, while still higher than that of virgin PP, the modulus for specimens with a higher (5 %) concentration of clay are significantly lower ($p = 0.002$). Once more, these results indicate that an optimum rate of nanoclay to compatibilizer would exist and that, when surpassed, insufficient amounts of compatibilizer are present to harmonize the dispersion of the polar nanoclay in the apolar PP. Based on these observations, the amount of compatibilizer mixed into the compound is maintained at twice the amount of nanoclay used for the remaining experiments.

3.3 Influence of the screw speed

A visualisation of the results for different screw speeds is given in Fig. 5 (pure PP samples) and 6 (nano filled PP). The elastic modulus of the tested virgin PP stays mostly constant at around 650 MPa for the different screw speeds. There is no significant difference for varying the screw speed within the elastic modulus ($p = 0.147$). This is expected, as there is no filler present.

Fig. 6 displays the elastic modulus results for two different compounds at two different screw speeds each. Regardless of their specific composition, all samples have increased the mechanical properties compared to the virgin PP. Furthermore, both compounds show a significant loss in elastic modulus for higher screw speeds ($p_1 = 0.021, p_2 = 0.045$).

The screw speed of the extruder affects the residence time in the extruder. A higher residence time can lead to a higher degree of intercalation/exfoliation of the nanoclay in the PP matrix, which in turn will improve the mechanical properties [15]. By increasing the residence time of the nanoclays in the extruder, the different polymer molecules have more time to penetrate between the interlayers of the organoclays. This intercalation/exfoliation leads to a higher elastic modulus of the samples at lower screw speeds.

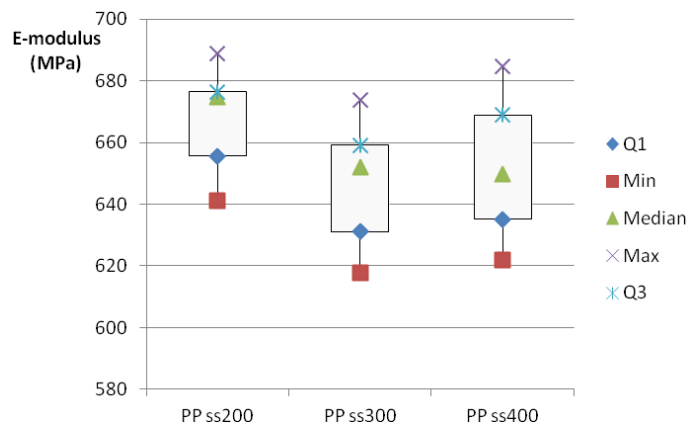


Fig. 5 E-modulus of pure PP at different screw speeds (200 rpm, 300 rpm and 400 rpm)

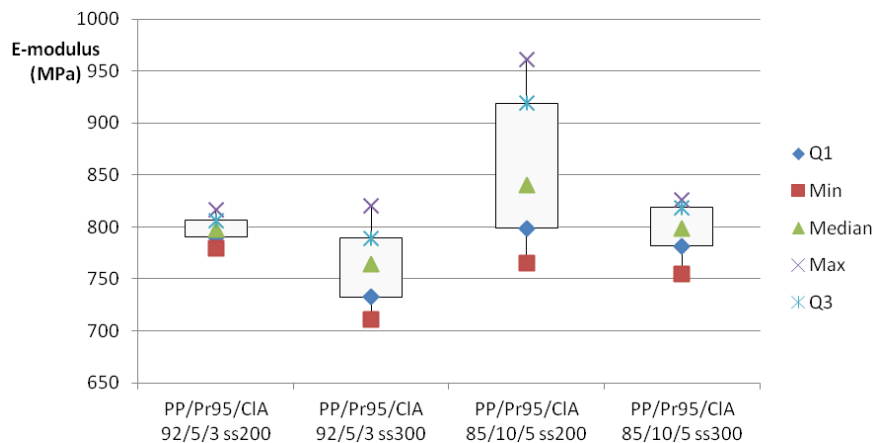


Fig. 6 E-modulus of PP/nanoclay composites at different screw speeds

3.4. Comparison between twin and single screw extrusion

The mixing conditions of an extruder are very important for the production of nanocomposites [16, 17]. Twin screw extrusion is normally used to produce nanocomposites due to the higher mixing capabilities in comparison with single screw extrusion. A lower mixing capacity leads to a loss in penetration possibilities for the polymeric chains into the organoclays and hence lowers the intercalation/exfoliation.

In Fig. 7, the resulting difference in mechanical properties is shown. The standard deviations of the different measurements are not mentioned; they are in the order of 30 MPa for each sample. When processing the regranulated extrudate of the twin screw extrusion with a single screw extruder, the *E*-modulus of the samples drops substantially, indicating that previously exfoliated nanoclay particles have once more cluttered together in larger (less reinforcing) aggregates.

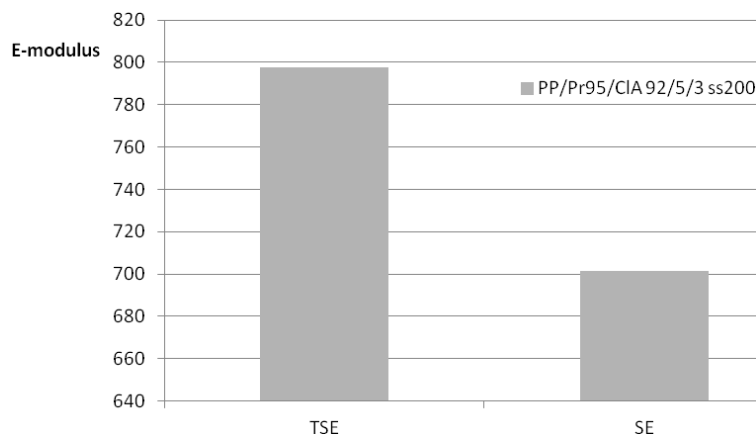


Fig. 7 Comparison of the *E*-modulus of different samples produced with twin (TSE) and single screw (SE) extrusion

3.5 Degree of crystallinity

The incorporation of clay into the PP matrix induces a minor increase in crystallinity from 40 % to 43 %. Adding only the compatibilizer to the virgin PP is in fact observed by a minor reduction of crystallinity (Table 1).

Table 1 Crystallinity of different compounds

Composition	Wt %	Cryst %
PP	100	40
PP/Pr95	95/5	39
PP/Pr95/CIA	92/5/3	43
PP/Pr95/CIA	90/5/5	43

4. Discussion

In a first aspect of this study, the influence of composition on the mechanical properties of nanoclay-filled PP was investigated. The elastic modulus of the extruded compounds is known to be a marker for the degree of exfoliation of the nanoclay platelets [7-9]. It was found that the ratio of 2 : 1 coupling agent to nanoclay resulted in the best mechanical properties. Increasing the amount of compatibilizer beyond this ratio did not result in significantly higher properties, indicating that the maximal dispersing effect is obtained at this ratio. Likewise, larger amounts of nanoclay did not result in higher modulus values, suggesting that the reinforcing effect on the nanoclays is subordinate to the dispersing effect of the compatibilizer. These findings are validated by existing literature, where a compatibilizer/organoclay ratio of 2 : 1 is commonly used for the intercalation/exfoliation of organomodified clays in an apolar matrix such as PP [18].

Secondly, the impact of the screw speed was investigated. While the properties of the virgin PP were unaffected by the screw speed, it was observed that the modulus of the nanoclay-filled compounds rose with reduced screw speed, due to the related extended residence time of the polymer in the screw. It must be mentioned that during this study, the feed rate of the twin screw extruder was adjusted to the different screw speeds to reach the same filling degree in the screw. By changing the feed rate, the output of the extruder is being changed simultaneously. We noted an increase in output of 0.6 kg/h between the used screw speeds of 200 rpm and 300 rpm. This increase also affects the residence time in the extruder and will likewise have its influence on the mechanical properties of the final extrudate [19].

Finally, the crystallinity of the extruded compounds was quantified. Given that the elastic modulus of a polymer will increase with higher grades of crystallinity [20, 21], it is necessary to quantify this aspect so that an improvement in mechanical properties will not wrongly be ascribed entirely to the dispersion and exfoliation of the mixed-in nanoclays. However, it was found that the addition of the nanoclay enlarged the crystalline fraction with only a few percent, which is not sufficient to account for the large differences in modulus values. Worth mentioning is that the coupling agent by itself did not result in an increased crystallinity, while the addition of nanoclays did. This is attributed to the smaller size of the nanoclays and their entirely different structure from the PP matrix (as opposed to the coupling agent, which is PP-based). Both qualities make them more suitable as locations for heterogeneous nucleation of the crystalline phase during cooling.

The current screw set-up allows us to produce nanoclay filled polypropylene with a maximal increase in elastic modulus of up to 25 %. Similar results have previously been reported with similar processing methods by different researchers [7, 12, 22].

Within the current study, the degree of exfoliation of the nanoclay platelets has been evaluated by comparing the tensile modulus of the extruded specimens. As this is a derivative method, it is only possible to classify the different samples relatively to one another. Quantitative analysis of the exact degrees of dispersion and exfoliation of the nanoclay within the different compounds is only possible through visualization methods such as electron microscopy and xray diffraction [23-25]. These future experiments will give new insights in terms of to which degree the maximum possible nanoclay exfoliation has already been achieved with the current screw configuration and what level of further improvement may be expected by adapting the said configuration.

5. Conclusion

The following conclusions can be drawn from the obtained results:

1. A lower screw speed (TSE) results in stiffer nanoclay-filled polypropylene;
2. When increasing the clay content, one has to increase the compatibilizer concentration as well. A 2:1 ratio of compatibilizer to nanoclay is preferable;
3. Twin screw extrusion is more suited for the production of nanoclay filled polypropylene than single screw extrusion, due to the higher mixing capacity and hence the better dispersion and higher Young's modulus of the samples;
4. The crystallinity of the samples is slightly improved by the addition of nanoclay particles.

Notes and acknowledgements

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