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ORIGINAL PAPER

PP/clay nanocomposite: optimization of mixing conditions with respect to mechanical properties

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Abstract Polypropylene/clay nanocomposites were studied with focus on optimization of mixing conditions. Two different types of commercial nanofillers Dellite® were used (Dellite® 72T and Dellite® 67G). Effect of various concentrations of fillers on morphology and mechanical properties was investigated. Conditions of preparation were varied with respect to mixing time and speed of rotation of kneaders. Results of morphology study showed that nanocomposites contained agglomerates of nanofillers. The comparison of the filler types revealed that better dispersion and distribution was found for nanocomposites containing Dellite 72T which had also better tensile strength. Optimum mixing time was 30 min. 3D graphical analysis showed that the optimum speed of rotation was 60 rpm and with increasing clay content (2–10 wt%) the tensile strength increased.

Keywords Polyolefine · Clay · Nanocomposites · Morphology · Mechanical properties

Introduction

The nanotechnology is a science field which started during the 1990s. The nanocomposite is a material composed from polymer matrix and a filler called nanofiller because of its nano dimensions. Group of polymeric materials, e.g. polypropylene, polyethylene, polyamide and polystyrene, represent materials used as polymer matrix [1–8]. Montmorillonite, vermiculite or saponite are clay minerals used as nanofiller [9–13]. The reason of preparation of nanocomposites was expectation of achieving of unique properties that cannot be obtained by micro-size

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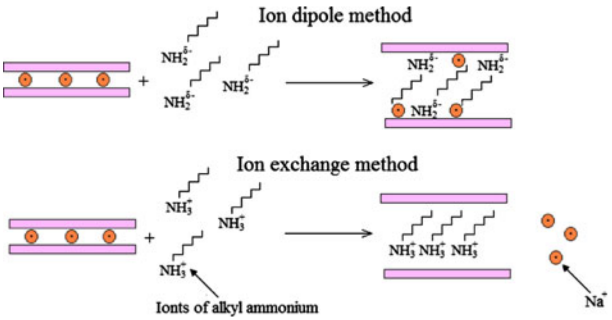

Fig. 1 Principles of modification of clay minerals

fillers. The presence of nanofiller improves mechanical and barrier properties and flame resistance [14].

However, the proper preparation of these unique materials is very difficult. This is because polyolefins are hydrophobic and montmorillonite is hydrophilic [14]. The preparation of nanocomposites starts by modification of natural clay mineral, e.g. montmorillonite. The name of modification is organofilization. Organofilization of clay mineral, respective montmorillonite, can be performed by two different methods. The first method is called ion dipole method that can be performed in melt, and therefore it is called “dry” method.

The second method is ion exchange reaction. Ion exchange method is called wet method due to washing of by-product Na$^+$ [15]. Both principles of modification of clay minerals are shown in Fig. 1.

The modification can influence the intercalation or exfoliation of clay minerals. The degree of intercalation has three levels which are shown in Fig. 2 [16]. The first level is called phase separated because one can find two phases, polymer and clay (polymer does not enter between clay plates). The second level is intercalated. Polymer enters between clay plates to a lower extent which causes increase in plates distance. The highest level is exfoliated—plates of fillers have random orientation in polymeric matrix. This structure is called nanostructure.

The preparation technique can influence the level of intercalation of filler. The Toyota Corporation prepares nanocomposites in two steps. The mineral clay is modified by organic compound in the first step; the compounding of polymer matrix, maleic anhydride modified polymer with modified nanofiller is mixed in the second step. The processing temperature is above the melting point of the polymers; a compounding device can be single screw extruder or twin screw extruder [15].

Conditions of compounding can influence consequent degree of intercalation or exfoliation that results in a change of mechanical properties. The first quantity is time of compounding; the second is the speed of rotation of screw or kneaders [16]. Theoretically, higher speed of rotation should cause better dispersion and distribution of plates of the filler.

This research describes preparation of polypropylene–montmorillonite nanocomposite. Dellite® (Dellite 72T and Dellite 67G) was used as filler. Various speeds

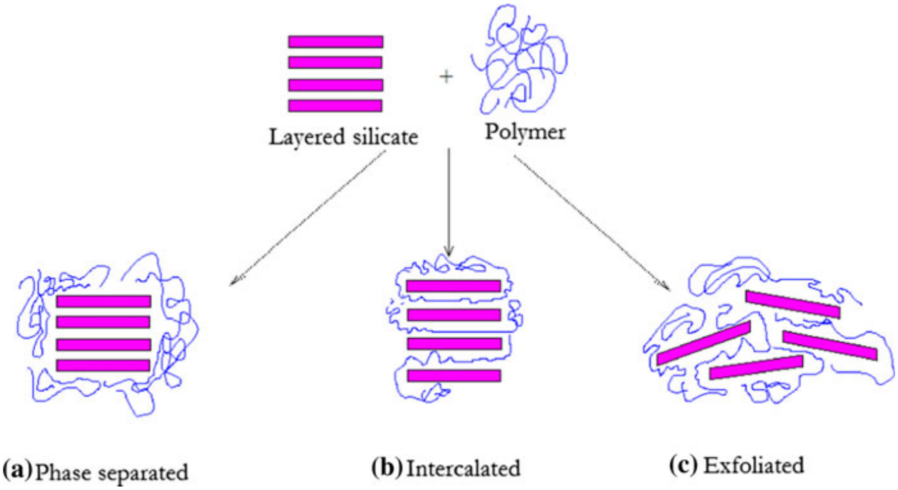

Fig. 2 The level of intercalation/exfoliation of nanofiller in polymeric matrix

of rotation and times of compounding were used in our study; the concentration of nanofiller varied too. Degree of intercalation or exfoliation of filler was obtained by X-ray diffraction and supported by transmission electron microscopy (TEM). Also tensile properties were evaluated.

Experimental

Materials

Three types of materials were used in this research: polypropylene (PP), maleic anhydride modified polypropylene (Table 1) and filler. Polypropylene Mosten GB 003 produced by Chemopetrol Litvinov, Czech Republic was used as the polymer matrix. Maleated polypropylene was supplied by ExxonMobil Chemical Europe, Belgium. Two types of nanofiller Dellite were used (D 72T, D 67G); their concentration was selected 2, 4, 6 and 10 wt%. The nanofillers were supplied by Laviosa Chemical Mineraria S.p.A., Italy.

Table 1 Specifics of polymeric materials

Polymeric materials	Density (g/cm^{-3})	Melt flow index (g/10 min)
Polypropylene Mosten GB 003	907.0	3.2[a]
Maleated polypropylene Exxelor PO 1015	900.0	22.0[b]

[a] At 230 °C

[b] At 190 °C

Table 2 Composition of nanocomposites

	Filler (g)	Polypropylene (g)	PP–MA (g)
2 wt%	1.0	46.5	2.5
4 wt%	2.0	45.5	2.5
6 wt%	3.0	44.5	2.5
10 wt%	5.0	42.5	2.5

Preparation of the polymer–clay nanocomposites and samples

All nanocomposites in this work were prepared by melt mixing in a Brabender Plasticorder compounder. There were two variables: speed of rotation and time of compounding.

Conditions of preparation were the following: the speeds of rotations were 40, 60 and 80 rpm; the times were 10, 20, 30 and 40 min. The temperature of compounding was the same for all samples, 220 °C. The charge was 50 g and it contained the pure polymer, maleic anhydride modified polypropylene and filler (Table 2).

Sample preparation and evaluation techniques

X-ray diffraction measurement (XRD) was performed on diffractometer URD 6, the reflex mode, angle range was 3–30° with a step of 0.05° and the time interval was 5 s. Specimens were prepared by compression moulding. Conditions of preparation were following: the temperature of moulding was 220 °C and time of moulding was 7 min, followed by 8 min cooling. Conditions were the same for all samples.

Transmission electronic microscopy (TEM) was obtained by JEM 200CX (JOEL). The ultra thin specimens were cut with an ultracryomicrotome LEICA ULTRACUT UCT at −110 °C. TEM pictures were take on device JEM 200CX (JOEL) at 100 kV. Pictures were digitalized by using digital camera DXM1200 Nikon. The digital camera was controlled by a computer.

Mechanical properties were tested on tensile test machine Instron 8871. All specimens were tested at following conditions: moving clamp distance was 50 mm and the rate was 50 mm/min for all specimens. The temperature was 23 °C. The test was performed according to the standard CSN EN ISO 527-3.

Results and discussion

XRD measurement of pure montmorillonite and PP/clay nanocomposites

Figure 3 shows X-ray pattern of PP filled with 4 wt% of both nanofillers. The conditions of preparation were: 80 rpm, 10 min. As can be seen, both curves contain peaks which show presence of agglomerate of nanofiller. However, the X-ray pattern shows that PP/Dellite 72T has better level of dispergation of filler in comparison with PP/D 67G which comes from the fact that peak has moved to lower

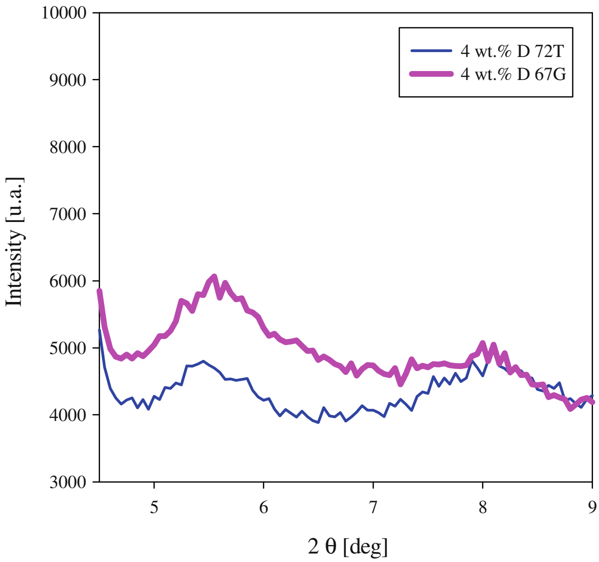

Fig. 3 X-ray pattern of PP/clay nanocomposites mixed at 80 rpm for 10 min

angle (compare 5.55° with 5.4°). TEM pictures confirmed the results of intercalation and/or exfoliation from XRD as follows.

TEM images of PP nanocomposites

TEM images were obtained for PP filled with 4 wt% of D 72T and D 67G mixed for 10 min at 80 rpm, see Fig. 4. Better dispersion and distribution of nanofiller were obtained for samples containing Dellite 72T. The thicknesses of particles were 150 nm, as can be seen at Fig. 4a. Figure 4b shows agglomerate of nanofiller. The dispersion and distribution of nanofiller were better in case of PP/Dellite72T.

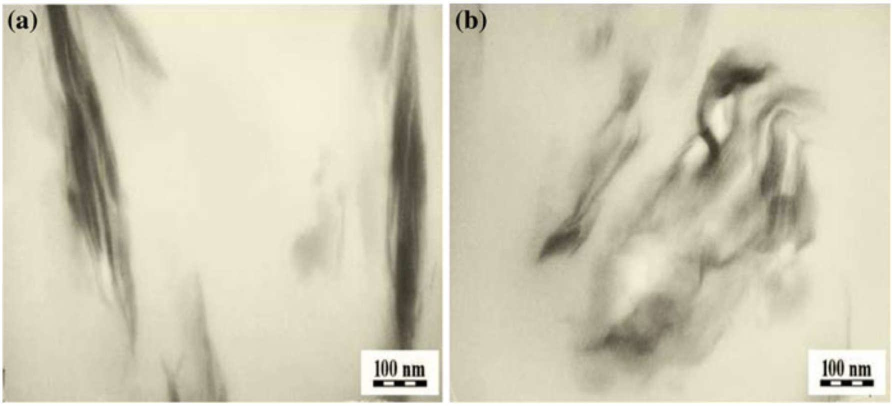

Fig. 4 TEM pictures of PP/4 wt%: **a** Dellite 72T and **b** Dellite 67G (80 rpm/10 min)

Table 3 Data of tensile strength of PP/clay nanocomposites

	2 wt%		4 wt%		6 wt%		10 wt%	
	D 72T	D 67G	D 72T	D 67G	D 72T	D 67G	D 72T	D 67G
Pure PP	12.7	12.7	12.7	12.7	12.7	12.7	12.7	12.7
40 rpm/10 min	26.2	25.2	31.9	21.6	32.9	25.8	32.0	30.6
40 rpm/20 min	32.1	27.8	31.9	27.6	33.0	26.9	32.0	31.7
40 rpm/30 min	30.7	24.8	32.4	27.0	33.0	24.5	28.9	32.8
40 rpm/40 min	28.4	30.7	33.5	28.2	30.9	23.1	33.0	31.3
60 rpm/10 min	27.2	27.9	29.9	27.2	29.7	24.3	28.7	25.6
60 rpm/20 min	33.7	30.5	29.4	27.4	32.4	26.8	30.2	32.3
60 rpm/30 min	34.3	28.2	33.3	29.1	32.5	25.8	30.5	33.1
60 rpm/40 min	33.0	25.9	31.8	26.3	32.1	25.0	34.0	31.0
80 rpm/10 min	32.4	29.4	32.4	25.0	33.1	24.2	31.5	30.8
80 rpm/20 min	28.1	27.1	33.4	28.6	28.4	29.0	32.8	31.8
80 rpm/30 min	28.6	26.6	32.5	26.5	30.7	30.3	32.1	32.4
80 rpm/40 min	34.5	28.7	32.8	24.9	28.0	27.5	22.4	31.5

Mechanical properties of PP/montmorillonite nanocomposites

Mechanical properties (tensile strength) were measured for all prepared nanocomposites and compared with the pure polymer matrix. Measured data are shown in Table 3.

As can be seen from Table 3, all prepared nanocomposites had higher tensile strength in contrast with pure polypropylene matrix. The maximum of tensile strength was obtained for PP filled with 2 wt% of Dellite 72T (80 rpm/40 min) and the minimum was found for PP/4 wt% of Dellite 67G (40 rpm/10 min).

Figure 5 shows dependence of tensile strength on the concentration of both types of nanofillers.

Figure 5 shows dependence of tensile strength (TS) on concentration of nanofiller. Specimens were prepared at 80 rpm for 10 min. As can be seen from Fig. 5, the dependences had different shape of curves. The curve of TS of PP/Dellite 72T shows a dramatic increase in range 0–2 wt% and then the value is almost constant. PP/Dellite 67G has the same rapid increase in range 0–2 wt%, but then it decreases with the minimum at 6 wt% and then it increases again with the maximum being at 10 wt%. The difference could cause by different types of fillers. The following Fig. 6 represents dependence of TS on the mixing time.

As can be seen from Fig. 6, the maximum of TS was found to be at 30 min of mixing for all three speeds of rotation of kneaders. The shape of curves had the same tendency; however, the rapid increase of value of TS can be observed only for 60 rpm. The other speeds showed only gradual increase up to 30 min and then a gradual decrease.

In order to observe the influence of speed of rotation and clay concentration on TS in one figure we have created a 3D graph, see Fig. 7. TS is almost linearly

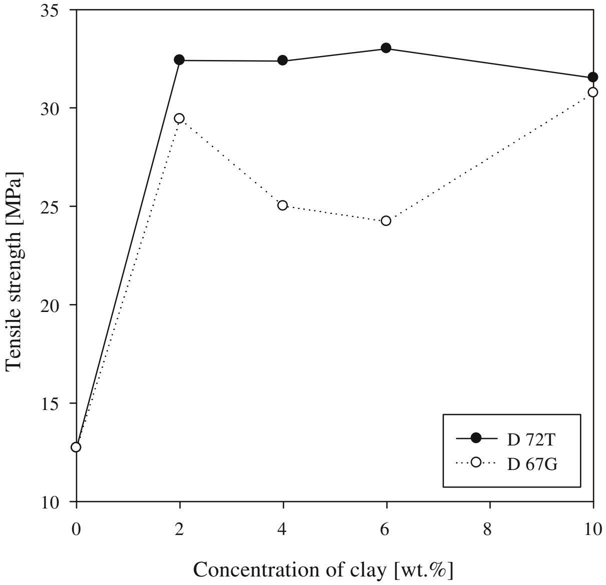

Fig. 5 Dependence of tensile strength on concentration of clay of nanocomposites (80 rpm/10 min)

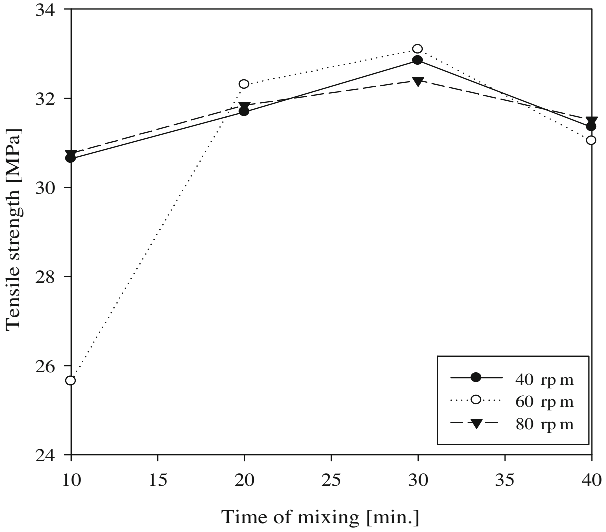

Fig. 6 The dependence of TS on time of mixing (PP/10 wt% of Dellite 67G)

increasing with clay content and the maximum values of TS were found at 60 rpm. At low speed of rotation, the shear stress is not sufficient for good intercalation. At high speed of rotation, there is a possibility of decrease of molecular weight of PP and the temperature increases which causes decrease in viscosity. Decrease in viscosity means less efficient mixing and eventually lower TS. There is an optimum

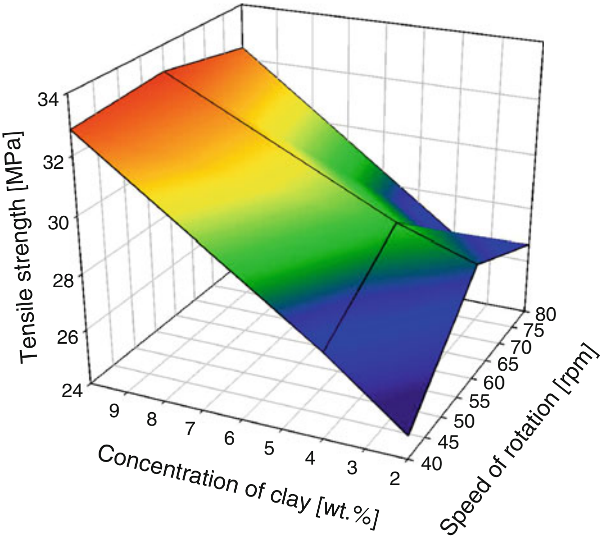

Fig. 7 Tensile strength as a function of clay concentration and speed of rotation of kneaders for PP/Dellite 67 after 30 min of mixing

in speed of rotation (60 rpm) when the mixing is the most efficient and the TS reaches maximum values.

Conclusion

Two types of nanofillers, various concentrations and conditions of preparation were used in this study. The morphology was studied by X-ray diffraction and transmission electron microscopy; mechanical properties were tested with focus on tensile strength.

X-ray diffraction and TEM pictures showed that the level of intercalation or exfoliation was not perfect because the nanocomposites contained agglomerates of filler. However, PP/4 wt% Dellite 72T (80 rpm/10 min) had the distribution, dispersion and intercalation better than the rest of prepared nanocomposites.

Testing of mechanical properties revealed that all nanocomposites had higher tensile strength in comparison with the pure polypropylene. The maximum of tensile strength was obtained for PP filled by 10 wt% of Dellite 72T (34.0 MPa). The minimum of tensile strength was obtained for PP filled by 4 wt% of Dellite 67G (21.6 MPa).

Optimum mixing time was found to be 30 min. The 3D graphical evaluation illustrated that the tensile strength increases with clay content, and there is an optimum for speed of rotation (60 rpm) when the composites had the highest tensile strength.

In future, we would like to study other types of fillers and compare mechanical properties with Dellite 72T and 67G.

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