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Polypropylene-Clay Nanocomposites: Comparison of Different Layered Silicates

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Summary: In former studies of the preparation of polypropylene(PP)-clay nanocomposites, different types of layered silicates were used. However, the obtained results were not comparable due to different preparation conditions and types of silicates. The aim of this work was the investigation of the influence of different layered silicates on the properties of the resulting nanocomposites. FT-IR-spectra, SAXS, TEM micrographs, elemental analysis, mechanical properties and surface tension measurements were used for the comparison of the four different layered silicates under investigation.

Keywords: clay; layered silicates; nanocomposites; polypropylene; surface tension measurements

Introduction

In the last years, polymer nanocomposites containing layered silicates have gained great attention due to their academic and industrial importance[1–6]. They have shown a significant improvement in mechanical, thermal, especially flame-retardant, and barrier properties with small amounts of inorganic fillers compared to conventional filler composites. Improved properties were obtained with loadings of only 1–10 wt% of modified layered silicates. Polypropylene as one of the most widely used and low cost polyolefin is very interesting as matrix polymer for such nanocomposites. Before preparing the nanocomposite, the clay has to be transferred to a more organophilic form to obtain a better interfacial adhesion to the nonpolar polypropylene. Clay modification is generally achieved by ion exchange reactions of the intergallery sodium cations of the layered silicates by organophilic cations (like alkyl ammonium ions). To produce polypropylene layered silicate nanocomposites by a melt mixing method, maleic anhydride grafted polypropylene (PP-g-MA) has to be used as compatibilizer [7,8]. The aim of the present paper is to evaluate the influence of four different layered silicates on the polypropylene

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nanocomposite properties. Therefore, a fixed standard composition of the nanocomposite as well as a standard preparation technology was used in order to obtain an expressive result.

Experimental

Four different types of layered silicates were used to produce organophilic modified clays: Nanofil 757 (Germany; CEC = 75 mmol/100 g), denoted MM(1), and Nanofil 918 (Turkey; CEC = 100–110 mmol/100 g), denoted MM(2), both types are products of Süd-Chemie AG (Germany). The second one is a natural clay with Ca-cations in the intergallery, which have to be exchanged by Na-cations in order to produce a silicate fully exchangeable by organic cations like alkylammonium compounds (activation) in aqueous media. Additionally, Cloisite Na^+ (CEC = 95 mmol/100 g) from Southern Clay (USA), denoted MM(3), and Somasif ME100 (CEC = 70 – 80 mmol/100 g) from CO-OP Chemicals (Japan), denoted MM(4), were used. These four layered silicates were modified with dimethyldistearylammonium chloride (DSQ) from Clariant (Genamin DSAC) according to a standardized method described elsewhere [9]. The corresponding nanocomposites [NC(1)–NC(4)] were produced in a batch technology via a master-batch of organoclay and PP-g-MA (Polybond 3200 from Crompton). The batch concentration is calculated on the basis of the ash content of the organoclay intending to produce a formulation containing 7.5 wt% PP-g-MA and 5 wt% inorganic residue[10] in the nanocomposite after dilution with PP-homopolymer (Moplen HF500N from Basell). The density of pure montmorillonite and hectorite in the sodium form is about 2,0 – 2,7 g cm^{-3} depending on the content of water surrounding the sodium ions and differs from cation exchanged form. The density of the organoclays varies due to different amounts of DSQ with respect to the CEC. In order to make the nanocomposites comparable, we decided to focus on the inorganic residue, giving a more precise similarity in the nanocomposite on volume and mass fraction of the filler used, taking into account the more or less "molecular" level of dimensions, rather to use a fixed weight fraction of the organoclay, which would definitely lead to different volume fractions in the nanocomposite.

Instrumental

FT-IR-Spectra were taken on a Bruker IFS66V. Clay materials were measured either as powder, in reflection mode, or as KBr disks. SAXS data were collected on a KRATKY compact camera

(AntonPaar Graz, Austria), and TEM-pictures were made using ultrathin cuts with a Philips CM 20. Elemental analysis was performed with an Elementar VARIO EL CHNS analyzer. Batches of the modified silicates with PP-g-MA were prepared on a cokneader MKS 30-18 (Buss, Switzerland) followed by compounding with PP (200-220 °C; 300 rpm; 10 kg/h) on a co-rotating twin screw extruder ZE 25 (Berstorff, Germany) to obtain the nanocomposite with the focused clay content. Mechanical analysis was done according to CAMPUS conditions. The inorganic residue was determined gravimetrically after burning in a microwave oven at 550 °C/10 min.
The modified organoclay samples were characterized by FT-IR-spectroscopy, SAXS, elemental analysis and a method to determine the surface tension reported earlier [11,12]. Tensile bars were made by injection moulding from the corresponding nanocomposites and were characterized by mechanical analysis, SAXS and TEM.

Results and Discussion

To prepare polypropylene based nanocomposites four different layered silicates MM(1)–MM(4) were used. Figure 1 shows for better visibility a cutout of the IR-spectra of MM(1)–MM(4). There are only insignificant differences in the IR-spectra due to the different amounts of not exchangeable ions M^{II+}/M^{III+} like Fe and Mg cations. These cations are responsible for the negative charge of the platelets, which is compensated by the exchangeable sodium ions in the intergallery. The synthetic hectorite MM(4) used for comparison is a three-layer silicate produced by heating talc and Na_2SiF_6 for several hours in an electric furnace at high temperatures (CO-OP Chemicals, Japan)[13]. Therefore, in the IR-spectra of MM(4) the Si–OH stretching band in the region of 3600 cm^{-1} is missing, which is the difference in the part of the IR spectra not shown. Beside those bands, different amounts of quartz (SiO_2) can be found in the IR spectra of the four different clay materials MM(1)–MM(4) (see Figure 1).

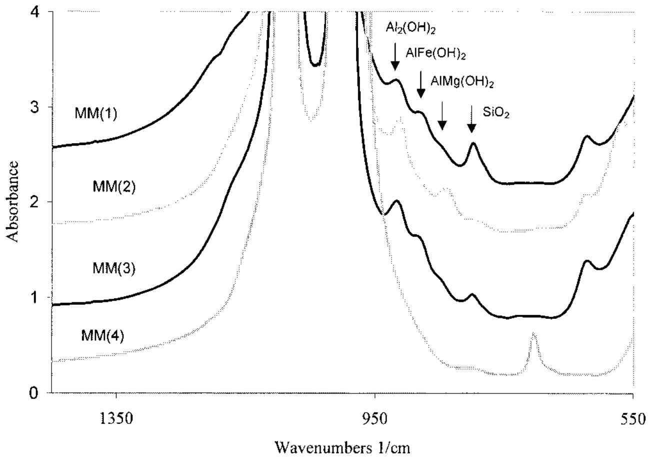

Fig. 1: FT-IR-Spectra of MM(1)–MM(4) silicates in the region of 550–1400 cm^{-1}

MM(1)–MM(4) were modified with DSQ in a stoichiometric ratio of 1/1 taking into account their different cation exchange capacity (CEC). The exact amount of DSQ in the modified clays DSQ MM(1)–DSQ MM(4) was obtained by elemental analysis, see Table 1. The given cation exchange ratio n/CEC was determined from the carbon value of the elemental analysis and is close to the theoretical value of 1.00 (100%).

Table 1: Elemental analysis of cation exchanged layered silicates and surface tension γ_{sv}

Sample	Carbon content [%]	Nitrogen content [%]	n / CEC	Surface tension γ_{sv} [mJ/m^2]
Unmodified MM	-	-	-	44.2
DSQ MM(1)	24.88	0.673	1.02	27.5
DSQ MM(2)	29.97	0.872	1.01	27.5
DSQ MM(3)	29.47	0.834	1.04	26.5
DSQ MM(4)	24.48	0.630	0.99	26.5

The surface tension γ_{sv} of the modified clays DSQ MM(1)–DSQ MM(4) measured according to method given in reference [11] are also given in Table 1. There are only neglected differences in the surface tension values of DSQ MM(1)–DSQ MM(4) - 26.5–27.5 mJ/m^2. But the aim of the modification to obtain a more hydrophobic silicate powder can be realized as reflected in the great difference in the surface tension of modified with respect to unmodified layered silicate. The surface tension of polypropylene determined in melt at 185 °C by using axisymmetric droplet shape analysis was about 20 mJ/m^2 [14]. Consequently, there is still a gap existing between the surface tension of modified clay and polymer matrix, which makes a compatibilizer necessary.
The *d*-spacings of the unmodified layered silicates are about 0.9 – 1.2 nm and result from sodium ions surrounded by different amounts of water molecules. After modification with DSQ the observed interlayer distances increase compared to the pristine silicate *d*-spacings. As shown in Figure 2, the four different layered silicates DSQ MM(1)–DSQ MM(4) differ in the interlayer distances reaching from about 2.7–3.2 nm. As expected, the clay MM(1) with the lowest cation exchange capacity shows the smallest *d*-spacing in the modified form.

The interlayer distance obtained from DSQ MM(4) is hardly comparable with those of the three clay samples DSQ MM(1)–DSQ MM(3), because of the differences in the layered silicates: MM(1)–MM(3) are natural montmorillonite, belonging to the family of dioctahedral smectites, and MM(4) is a synthetic hectorite belonging to the family of trioctahedral smectites. The interlayer distances from the batch composites DSQ MM(1) PB–DSQ MM(4) PB remain nearly the same compared to the original modified silicates, concluding, that there is no intercalation of polymer into the galleries. The prepared composites NC(1)–NC(4) are best described as partly exfoliated. The TEM images of NC(1)–NC(4) reflect, that the layered silicates in the nanocomposites are exfoliated to some extent, see Figure 3. Both, stacks of multilayer and isolated exfoliated platelets can be observed. The low-magnification TEM image (see Figure 3 left) shows that the modified layered silicate NC(2) is well dispersed throughout the polymer matrix.

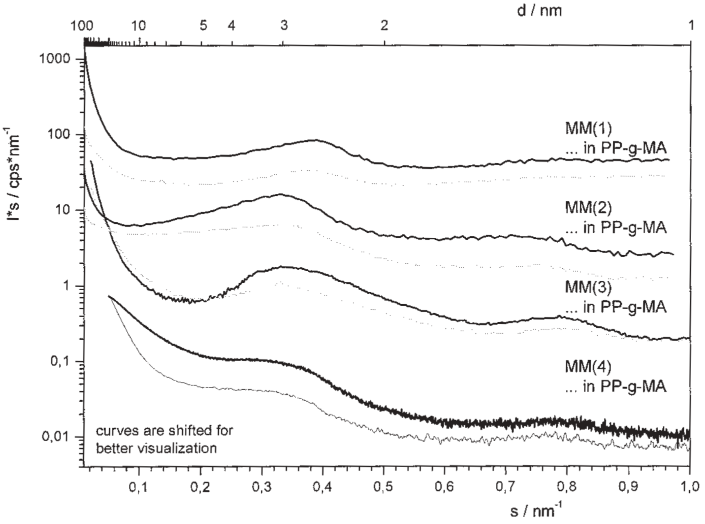

Fig. 2: SAXS curves for DSQ modified MM(1)–MM(4) and for the clay/PP-g-MA batches [DSQ MM(1) PB–DSQ MM(4) PB] to determine interlayer spacing distances (d)

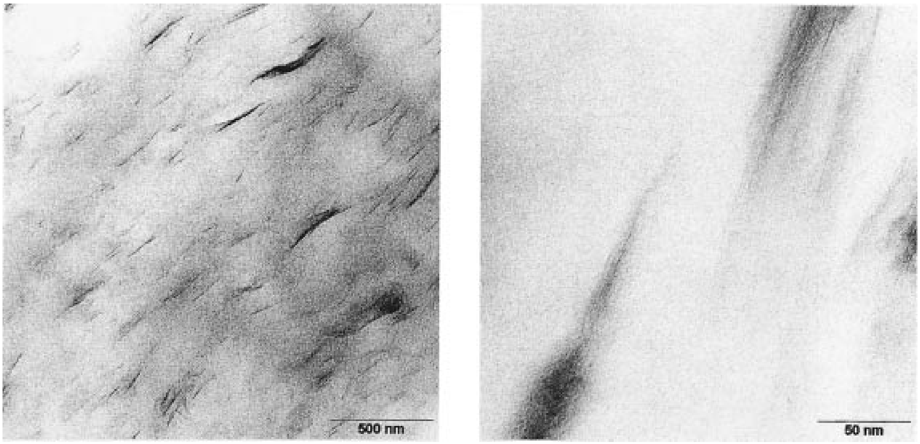

Fig. 3: TEM-micrographs of DSQ modified MM(2) in PP/PP-g-MA (left: low magnification; right: high magnification)

There exists a complex relationship between the properties of the layered silicates and the properties of the corresponding nanocomposites. Only the nanocomposites obtained from the natural clays MM(1)–MM(3) are comparable to each other due to the differences in the composition of the layered silicates.

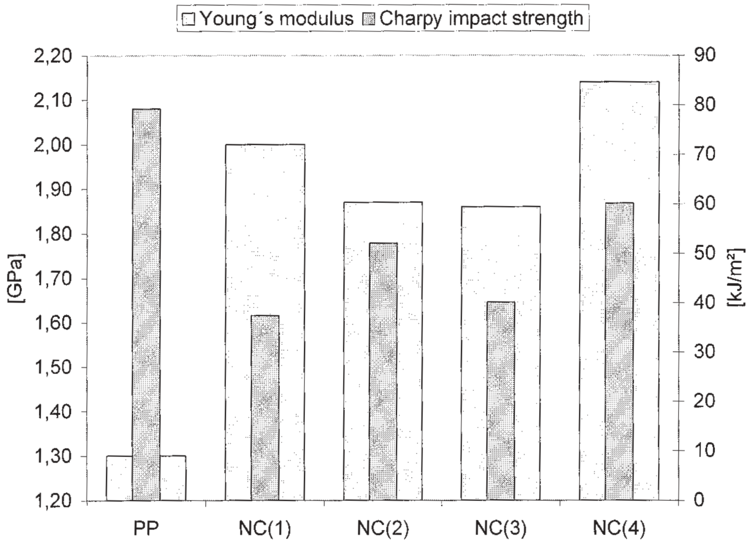

Fig. 4: Young's modulus and impact strength of NC(1)–NC(4) in comparison to PP

The experiments concerning the mechanical properties (see Figure 4 and Table 2) show the influence of the cation exchange capacity and the different amounts of organic molecules on the impact strength and Young´s modulus. The highest impact strength was found in the nanocomposite NC(2) with the clay with the highest CEC, the lowest in NC(1) with the clay having the lowest CEC. The differences in the notched impact strength and the tensile strength are inferior, but show the same general trend. Unfortunately, there is at present no possibility to accurately quantify the degree of exfoliation and therefore it is not clear, if the differences in mechanical properties result from different aspect ratios of the distributed clays, due to agglomerates and/or to different primary particle sizes. According to Morgan and Gilman[15] it is necessary to analyze SAXS-curves and TEM micrographs to get an idea of the clay-platelet dispersion. On the other hand, new rheological experiments leading to the shear thinning factor give only a qualitative degree of exfoliation within the layered silicate[16]. But for a correct analysis the mean size and size distribution of different layered silicates and their agglomerates would be necessary.

Table 2: Mechanical properties of nanocomposites based on DSQ modified layered silicates

Sample	Residue [%]	σ_Y [MPa]	ε_Y [%]	E_t [GPa]	a_{cU+23} [kJ/m^2]	a_{cA+23} [kJ/m^2]	HDT B [°C]
PP	-	30.5	9.5	1.33	79.2	3.9	85
NC(1)	5.1	35.1	6.8	2.00	37.4	3.6	111
NC(2)	5.2	35.2	7.4	1.87	52.1	4.2	105
NC(3)	4.7	34.3	7.8	1.86	40.1	3.6	104
NC(4)	4.8	36.2	7.0	2.14	60.1	4.3	109

Conclusion

In this work nanocomposites of four different layered silicates in polypropylene were compared. Three natural clays (montmorillonite) with different cation exchange capacities (CEC) and a synthetic hectorite were used. The nanocomposites were prepared in a batch technology with a focus of 7.5 wt.-% PP-g-MA and 5 wt.-% inorganic residue. The mechanical properties show the influence of the CEC on the strength and the modulus, when comparable clays (natural clays MM(1)-MM(3)) are used. MM(1) with the lowest CEC shows also the lowest impact strength in the corresponding nanocomposite whereas the highest impact strength is found in the composite NC(2) with the clay MM(2) having the highest CEC. The obtained results from NC(3) were intermediate. Although different amounts of alkylammonium ions were found in the modified clay samples due to their different CEC, the surface tension measurements show nearly the same results. Therefore, the surface tension is surprisingly more influenced by the differences in the organic modifiers[17] than by the cation exchange capacity of the layered silicates. The influence of the sizes of the platelets on the strength and modulus is at present hardly to quantify because of the difficulties in a suitable model and analytical methods. For a better understanding of the characteristics of the layered silicates in the polymer matrix further experiments have to be done.

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