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Quantitative estimation of the reinforcing effect of layered silicates in PP nanocomposites

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Abstract

Various polypropylene/layered silicate composites were prepared with different silicate contents. Montmorillonites with and without organophilization as well as three maleinated polypropylenes were used to change the extent of exfoliation and hence the properties of the composites. Structure was characterized by X-ray diffraction (XRD), scanning (SEM) as well as transmission electron microscopy (TEM) and tensile properties were also measured. The analysis of the tensile yield stress values of a large number of composites showed a broad range of variation in mechanical properties. XRD and TEM results do not reflect the differences in properties and they usually do not give quantitative information about the extent of exfoliation either. PP/clay composites containing maleinated PP, which do not exhibit a silicate reflection in XRD, may have very poor mechanical properties indicating small extent of exfoliation. The composition dependence of tensile yield stress of these composites may be described and evaluated quantitatively by a simple model developed earlier for particulate filled polymers. The use of a few simple assumptions most of which are supported by previous results allows us to estimate the extent of exfoliation quantitatively. The tensile yield stress of about 40 composites was analyzed with the model. Some of the composites were prepared by us, while results on others were taken from papers published in the literature. The analysis indicated that the extent of exfoliation is very low in most composites; it reaches maximum 8% of the theoretically possible value in the best case. This result is in agreement with our observation that complete exfoliation can be seldom reached in thermoplastic/clay composites; the structure is complex and hierarchical including large particles and individual silicate layers. The results prove that further efforts must be done to increase the extent of exfoliation in order to achieve reinforcement levels forecasted earlier.

Keywords: Nanocomposites; Layered silicates; Polypropylene

1. Introduction

Layered silicate polymer nanocomposites created much interest recently. Practically all papers published on this new class of materials emphasize their potential advantages in various applications [1] including high modulus, increased strength and heat resistance, decreased gas permeability and flammability, etc. [2,3]. One of their potential advantages is high level of reinforcement at low silicate content leading to stronger and lighter parts [2–10]. The basic idea behind this expectation is the extremely large interface created by the exfoliation of the layered silicate, which is a precondition of improved properties [11,12]. A large contact surface coupled with strong interaction of the components must lead to a significant increase in strength and stiffness [13–19]. As a consequence, good interaction is expected to exist between the finely dispersed silicate layers and the polymer matrix [1,4,20–22]. Naturally, orientation of the platelets parallel to the direction of the load is an additional condition to achieve considerable reinforcement [1]. Although an extremely large number of papers are published on the structure, properties, and advantages of layered silicate nanocomposites, very few of them contain information, which unambiguously proves the validity of this concept.

Among the numerous papers published on these materials only a few present information about composite properties measured at large deformations. Dynamic mechanical spectra

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and modulus values are published in numerous publications [23–31], since stiffness is expected to be the best indicator of the extent of reinforcement [21]. Several, rather successful attempts were made to model the modulus of layered silicate nanocomposites [8,15,32–34]. Structure is taken into account by the aspect ratio of the silicate particles and the extent of exfoliation is estimated from the results [35]. All these calculations assume that property improvement generally and reinforcement particularly is proportional to and increases with the extent of exfoliation [8,15,21,32–35]. However, stiffness always increases when inorganic fillers are added to the polymer [36–38]. Moreover, models describing the composition dependence of stiffness rarely include particle size, specific surface area or interfacial interaction. As a consequence, the extent of exfoliation estimated in this way may not give information about the strength of the composites. Properties measured at larger deformations, like tensile yield stress, tensile strength, or fracture resistance, are more sensitive to structure and interaction [39–41], but reports containing such results for layered silicate nanocomposites are scarce. Among the more than 100 papers collected by us on layered silicate PP nanocomposites, only about eight contained information about tensile characteristics measured at more than one silicate content.

PP nanocomposites cannot be prepared by the simple mixing of the polymer and the organophilic silicate; only micro-composites can be created in this way. Maleinated polypropylene (MAPP) is added in order to improve component interaction leading to a more homogeneous structure with an enhanced degree of exfoliation [19,23–25,42–48]. In such composites the X-ray diffraction (XRD) peak, which is characteristic for the silicate disappears from the difractogram and individual silicate layers can be detected by transmission electron microscopy (TEM) [23,25,47–49]. The strength and stiffness of the composites also surpass the corresponding properties of microcomposites indicating stronger interaction and possible exfoliation, which are prerequisites for improved reinforcement [45,47].

In an attempt to estimate the reinforcing effect of layered silicates in PP matrices, a relatively large number of PP composites containing neither sodium or organophilic montmorillonite were prepared and investigated in this study. The silicates were organophilized with different surfactants and MAPP was added to some of the composites to promote exfoliation. We also tried to collect and evaluate data available in the open literature. Using a simple model developed earlier [39,40], we compared the load-bearing capacity of various silicates in different PP matrices and estimated the extent of reinforcement using the theoretical surface area of completely exfoliated silicate [5,50,51].

2. Background

The mechanical properties of composites, including tensile yield stress, depend on composition, component properties, structure and interaction [19,41–48,52]. Usually, homogeneous distribution of the dispersed particles is assumed in particulate filled composites. If the particles have anisometric geometry, their orientation and orientation distribution must be also taken into account in order to estimate reinforcement. The effect of interaction depends on its strength and on the size of the contact surface. Strong interaction is assumed to prevail in polymer/layered silicate composites [1,4,20,22] in spite of the fact that the surface of the silicate is covered with a surfactant. Such treatment was shown to decrease interaction significantly in all composites containing traditional fillers [53–55]. On the other hand, the interface between the phases can be extremely large in nanocomposites, the specific surface area of the silicate is about 750 m^2/g [5,50,51] compared to the 3–5 m^2/g value of usual particulate fillers [56–59], which may compensate the effect of any occasional decrease in interaction.

A simple model was developed earlier to describe the composition dependence of the tensile yield stress of particulate filled composites [39,40,60]. The model is based on the fact that an interphase forms spontaneously in composites and it assumes that yield stress changes proportionally to its actual value as a function of composition. Accordingly, the composition dependence of tensile yield stress can be described by the following equation [39,40,60]

$$\sigma_y = \sigma_{y0}\frac{1-\varphi}{1+2.5\varphi}\exp(B\varphi) \tag{1}$$

where σ_y and σ_{y0} are the yield stress of the composite and the matrix, respectively, φ the volume fraction of the filler in the composite and B is related to the load carried by the dispersed component, i.e. it depends on interaction [39–41,53,54]. The term $(1-\varphi)/(1+2.5\varphi)$ expresses the effective load-bearing cross-section of the matrix. At zero interaction all the load is carried by the polymer and the load-bearing cross-section decreases with increasing filler content. The same correlation can be used to describe the composition dependence of tensile strength, if the elongation of the composite is small, usually less than 100% [40].

The value of parameter B depends on all factors influencing the load-bearing capacity of the filler, i.e. on the strength of interaction and on the size of the contact surface. The effect of these factors on B is expressed as

$$B = (1 + A_f\rho_f l)\ln\frac{\sigma_{yi}}{\sigma_{y0}} \tag{2}$$

where A_f is the specific surface area of the filler (contact surface), ρ_f is its density, while l and σ_{yi} are the thickness and corresponding property of the interphase. The latter two parameters were shown to depend on the strength of matrix/filler interaction [61,62]. A detailed study of numerous composites proved that in composites containing stiff fillers or reinforcements a hard interphase forms, which increases the load-bearing capacity of the filler and contributes to reinforcement [63–65]. Only the formation of such a hard interphase explains that composite yield stresses exceeding the yield stress of the matrix are achieved occasionally [39]. Moreover, we must assume that such an interphase forms also in layered silicate nanocomposites leading to the observed reinforcing effect of the silicate. The load carried by the second component depends also on the properties of the matrix; the extent of reinforcement is larger in a softer than in a stiffer polymer. This factor must be also taken into account when composites prepared with different matrices are compared with each other.

The model was developed for composites containing spherical particles. The orientation of anisometric particles increases the load-bearing capacity of the filler and increases B. This is not taken into account explicitly in the model. However, random distribution of the silicate particles was shown in many cases, thus, the effect of orientation is neglected during the evaluation of the results. Nucleation or other effects related to the filler may change the properties of the matrix continuously and this effect can also bias the prediction of the model. In spite of these limitations, the validity of the model has been demonstrated for various heterogeneous systems from particulate filled polymers to blends and short fiber reinforced composites, in spite that the latter contain anisometric reinforcements [39,40,66–68]. The effect of particle size, strength of interaction, matrix properties, i.e. practically all factors listed above, could be analyzed quantitatively with the help of the model.

The tensile yield stress of three PP composites containing fillers with different particle size is plotted in Fig. 1 as a function of filler content. If the model is valid, we should obtain linear correlation when the natural logarithm of reduced yield stress is plotted against filler content, i.e.

$$\ln \sigma_{\mathrm{yred}} = \ln \sigma_{\mathrm{y}} \frac{1+2.5\varphi}{1-\varphi} = \ln \sigma_{\mathrm{y}0} + B\varphi \qquad (3)$$

The values plotted in Fig. 1 are presented in the linear form in Fig. 2 in order to prove the validity of the model for this case. Although linearity itself does necessarily means that the model can be used for the composites studied, the fulfillment of other conditions definitely confirms its applicability. Accordingly, the slope of the straight lines, i.e. reinforcement, increases with decreasing particle size (increasing specific surface area) as predicted by the model, since all other parameters are constant. Deviation from linearity always indicates structural effects like the aggregation of the filler, orientation of anisometric particles or phase inversion in blends [66,69]. The model might not be valid in layered silicate PP nanocomposites because of the extreme large specific interface area and the orientation of the anisometric platelets. However, the validity of the theory can be verified or disputed only by a detailed analysis of a large number of experimental data.

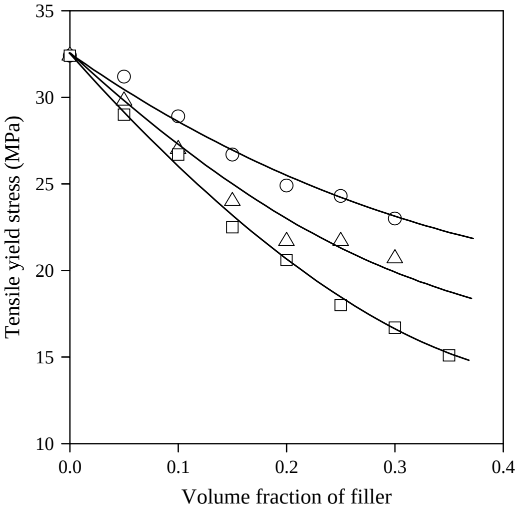

Fig. 1. Effect of particle size and filler content on the tensile yield stress of PP/CaCO$_3$ composites. Specific surface area (A_f): (○) 5.0, (△) 3.3, (□) 0.5 m^2/g.

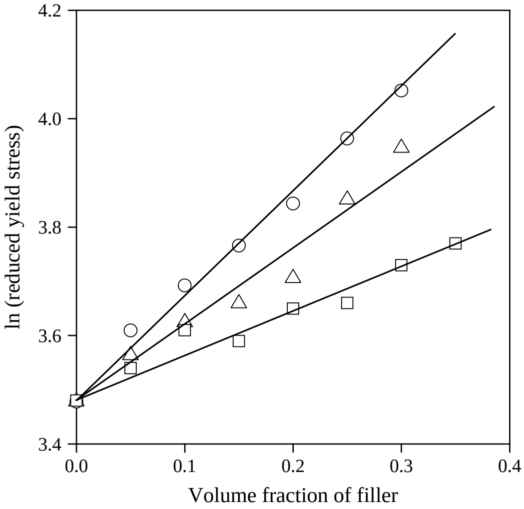

Fig. 2. Linear representation of reduced yield stress for the composites shown in Fig. 1 supporting the validity of the model (Eqs. (1)–(3)). Symbols are the same as in Fig. 1.

3. Experimental

Three different grades of silicates were selected for our composites. Sieved Wyoming GWB bentonite (Steetley Bentonite and Adsorbent Ltd) was subjected to ion exchange in order to produce sodium montmorillonite (NaMMT). NaMMT was treated with *N*-cetyl pyridinium chloride (CPCl) using the amount, which corresponded to the theoretical ion exchange capacity of the silicate in order to obtain one of the two organoclays used (CPCl–MMT) [70]. The density of the final product was 1.8 g/cm^3, its volatile content 2 wt%, organic content 25 wt% and average particle size 45 μm. Sodium montmorillonite (NaMMT) without treatment was used for comparison, to model a silicate without exfoliation. Nanofil 848, a commercial organoclay was supplied by Süd-Chemie AG (Germany). The silicate had the same characteristics as the one produced by us (see CPCl–MMT), but its average particle size was 3.5 μm. The silicate content of the composites changed between 0 and 10 vol% usually in seven steps.

We have used four maleic anhydride modified polypropylenes (MAPP) with different anhydride (MA) content and different molar mass to assist the exfoliation of the organoclay. Licomont AR 504 (MA content 3.5 wt%; $M_w = 2.4 \times 10^4$ g/mol; $T_m = 152$ °C; $\rho = 0.91$ g/cm^3) was supplied by

Clariant GmbH, Polybond 3200 (MA content 1.0 wt%; $M_w = 1.2 \times 10^5$ g/mol; $T_m = 157$ °C; $\rho = 0.91$ g/cm^3) was the product of Uniroyal Chemical Ltd, Orevac PP–C (MA content 0.1 wt%; $T_m = 151$ °C; $\rho = 0.9$ g/cm^3) was the product of Atofina Co., while Exxelor PO 1015 (MA content 0.25 wt%; $M_w = 2.1 \times 10^5$ g/mol; $T_m = 138$ °C; $\rho = 0.9$ g/cm^3) was obtained from Exxon Mobil Co. The composites contained 0 or 20 vol% MAPP, respectively, in most cases. The Tipolen H 605 grade polypropylene homopolymer (MFI = 3 g/10 min at 21.6 N and 230 °C) produced by TVK, Hungary was chosen as the matrix of our composites.

Homogenization was carried out in a Brabender W 50 EH internal mixer at 190 °C, 50 rpm for 10 min. The composites were compression molded into 1 mm thick plates using a Fontijne SRA 100 machine at 190 °C for 9 min. Dog-bone type tensile specimens were cut from the plates and tested with 50 mm/min cross-head speed using an Instron 5566 apparatus.

The gallery structure of the silicate was characterized by XRD using a Phillips PW 1830/PW 1050 equipment with Cu K_α radiation at 40 kV and 35 mA anode excitation. The morphology of the samples was examined by scanning (SEM) and transmission electron microscopy (TEM). 50–100 nm thick slices were cut at −80 °C with a LEICA Ultracut UCT microtome using a glass knife for the TEM measurements. TEM images were obtained with a Philips CM30 Twin STEM electron microscope fitted with Kevex Delta-Plus EDX and Gatan model 666 PEELS. A small piece of the sample was cut by a razor blade for SEM measurements. The specimens were polished and etched in a solution of $H_2SO_4/H_3PO_4/H_2O$ (10/4/1) and 0.01 g/ml $KMnO_4$ for 4 h. SEM images were recorded using a LEO Gemini 1550 FEG–SEM, fitted with a field Emission Gun, a Thermo Noran Vantage EDX system, and a Thermo Noran MAXray Parallel Beam Spectrometer.

4. Results

The reinforcing effect of layered silicates in PP is discussed in several sections. First the validity of the model is demonstrated for various PP/clay composites. Subsequently all data available, including those published in the literature, are analyzed and compared to each other. The consequences of the results obtained are discussed in a separate section.

4.1. Application of the model

The validity of the model is demonstrated by plotting yield stress values of various PP composites against composition using the corresponding expression derived from our model (Eq. (3)). We assume that neat montmorillonite (NaMMT) does not exfoliate at all and behaves like a regular particulate filler, while organophilized montmorillonite (OMMT) added to PP with a functionalized polymer (MAPP) results in intercalated or exfoliated nanocomposite. Several XRD patterns are compared to each other in Fig. 3. The shift in the silicate reflection is a sign of intercalation in the PP/OMMT composite (c), while the almost complete disappearance, at least in the detected 2θ range, of the reflection (d) indicates a considerable change in the structure of the composite prepared with the incorporation of a functionalized polymer (MAPP).

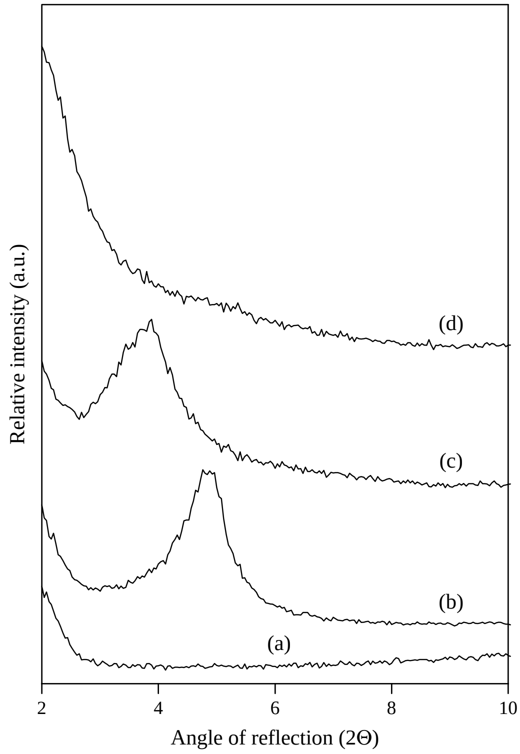

Fig. 3. XRD pattern of PP/clay composites and their components; disappearance of the silicate reflection upon the introduction of MAPP. (a) PP + 20 v/v % MAPP blend, (b) OMMT (c) PP + 2 v/v% OMMT, (d) PP + 2 v/v% OMMT + 20 v/v% MAPP.

The tensile yield stress values of composites (c) and (d) investigated by XRD (Fig. 3) are plotted against composition in Fig. 4. Corresponding values of PP/NaMMT composites are also shown in the figure for comparison. Numbers in brackets

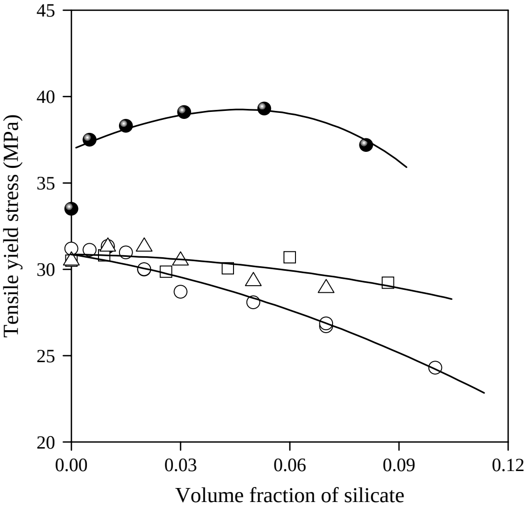

Fig. 4. Effect of silicate content on the tensile yield stress of various PP/clay composites. See the details in Table 1. Symbols: (□) PP/NaMMT (34), (△) PP/OMMT (37), (○) PP/OMMT/MAPP (41), (●) PP/OMMT/MAPP [71] (22).

in the caption of Fig. 4, and also in all subsequent figures, identify the composites and the source of the data evaluated. Information about all composites evaluated can be found in Table 1. The yield stress of all composites prepared by us decreases with increasing filler content. The average particle size of NaMMT is claimed to be approximately 2–3 μm, but its distribution covers a very wide range. The specific surface area of this silicate is 26.0 m^2/g measured by the BET method, which is somewhat larger than the usual value of particulate fillers. However, we must take into account also the large internal surface of the filler [5,50,51] here, which is not accessible for PP, but a part of it is measured by nitrogen. On the other hand, the anismetric particle shape of the silicate may also lead to some additional reinforcement like in talc filled PP. The composition dependence of the yield stress of the composites containing the organophilized MMT is very similar to that obtained for composites prepared with NaMMT. We can explain this behavior by assuming that only negligible exfoliation could be achieved in the absence of MAPP, thus both silicates have approximately the same reinforcing effect. However, the performance of the composite containing both OMMT and MAPP is rather surprising. The yield stress values of these composites are significantly smaller than those of the other two materials, i.e. PP/NaMMT and PP/OMMT composites, in spite of the fact that the silicate reflection almost completely disappeared from the XRD pattern of this material, or it moved out of the detection range of WAXS indicating significant intercalation and/or exfoliation. In Fig. 4, we

Table 1
Mechanical properties of PP/clay composites published in the literature and reinforcing effect (parameter B) calculated from them

No.	Polymer	MAPP		Silicate		σ_{y0} (MPa)	σ_{y0c} (MPa)	B	Refs.
		Type	(wt%)	Type	Treatment				
1	PP	–	0	Somasif	C6	33.3	32.1	3.6	[19]
2	PP	–	0	Somasif	C8	33.3	32.8	3.3	[19]
3	PP	–	0	Somasif	C12	33.3	32.7	3.1	[19]
4	PP	–	0	Somasif	C16	33.3	34.1	2.4	[19]
5	PP	–	0	Somasif	C18	33.3	36.3	0.2	[19]
6	PP	Epolene E43	20	Somasif	C6	33.1	33.4	3.5	[19]
7	PP	Epolene E43	20	Somasif	C8	33.1	33.8	3.3	[19]
8	PP	Epolene E43	20	Somasif	C12	33.1	33.7	5.6	[19]
9	PP	Epolene E43	20	Somasif	C16	33.1	33.7	5.3	[19]
10	PP	Epolene E43	20	Somasif	C18	33.1	33.1	5.4	[19]
11	PP	Hostapr. HC5	20	Somasif	C6	33.2	35.1	4.2	[19]
12	PP	Hostapr. HC5	20	Somasif	C8	33.2	34.1	4.9	[19]
13	PP	Hostapr. HC5	20	Somasif	C12	33.2	36.2	7.2	[19]
14	PP	Hostapr. HC5	20	Somasif	C16	33.2	34.5	8.3	[19]
15	PP	Hostapr. HC5	20	Somasif	C18	33.2	33.9	8.8	[19]
16	PP	Hostapr. HC5	20	Somasif	C18	33.0	34.9	7.8	[45]
17	sPP	–	0	Somasif	C18	16.1	16.1	2.6	[47]
18	sPP	Hostapr. HC5	20	Somasif	C18	18.7	26.1	4.2	[47]
19	sPP	Lico. AR 504	20	Somasif	C18	15.3	17.5	6.3	[47]
20	PP	–	–	MMT	C16+EM	26.0	26.6	15.6	[74][a]
21	PP	Epolene E43	diff.	Cloi. 20A	mix.	33.5	34.9	4.6	[71][b]
22	PP	Epol. G3003	diff.	Cloi. 20A	mix.	33.5	37.6	4.3	[71][b]
23	PP	Polybond 3150	diff.	Cloi. 20A	mix.	33.5	37.5	3.6	[71][b]
24	PP	–	–	Cloi. 20A	mix.	33.5	36.0	2.7	[71]
25	MAPP	Polybond 3150	100	Cloi. 20A	mix.	32.3	34.7	4.9	[71]
26	PP	–	–	MMT	Fluor-C18	28.5	32.6	0.3	[12]
27	PP	–	–	MMT	2C18	28.5	26.5	5.7	[12]
28	MAPP	Bynel	100	Nmer 131	mix.	4.7	4.9	5.4	[12]
29	MAPP	Orevac PP–C	100	MMT	CPCl	17.4	18.1	2.5	[c]
30	MAPP	Orevac PP–C	100	Nfil 848	C18	17.4	17.8	3.4	[c]
31	PP	Lico. AR 504	20	MMT	CPCl	25.5	24.5	3.7	[c]
32	PP	–	–	MMT	CPCl	33.9	30.7	2.2	[c]
33	PP	–	–	Nfil 848	C18	33.9	33.5	1.8	[c]
34	PP	–	–	NaMMT	–	33.9	30.8	2.8	[c]
35	MAPP	Exxcelor	100	MMT	CPCl	27.8	27.2	2.6	[c]
36	MAPP	Exxcelor	100	Nfil 848	C18	27.8	28.9	2.4	[c]
37	PP	–	–	Nfil 848	C18	30.5	32.0	1.8	[c]
38	PP	Exxelor	20	Nfil 848	C18	32.0	31.7	1.5	[c]
39	PP	Polybond 3200	20	Nfil 848	C18	33.4	32.3	2.1	[c]
40	PP	Lico. AR 504	20	NaMMT	–	25.5	25.5	2.7	[c]
41	PP	Lico. AR 504	20	Nfil 848	C18	31.2	31.9	0.6	[c]

[a] Composition calculated for the inorganic content of the composite.
[b] MAPP content changed proportionally to silicate content.
[c] Results obtained in this study.

include also results taken from Ref. [71] for comparison. The yield stress of the composites reported by the authors exceeds considerably our values indicating better reinforcement. Obviously, the disappearance of the silicate reflection is not a sufficient proof for exfoliation and does not give any indication about the performance of the composites. The combination of component properties and processing conditions [72] must have led to the difference in reinforcement obtained in our composites and in those prepared by Svoboda et al., respectively [71].

The natural logarithm of reduced yield stress (Eq. (3)) is plotted against composition in Fig. 5. Linear correlation exists between the quantities plotted for our composites, which indicates that the model might be valid also for nanocomposites. Although, as mentioned above, linearity is not and unassailable proof for the validity of the model, structural effects (aggregation, orientation, phase inversion, changing matrix properties, etc.) always yielded a non-linear correlation in earlier studies, thus, we may assume that these are absent in this case. The slope of the straight line derived from published results [71] is larger than the values obtained for our own composites indicating increased reinforcement in the former case, which might be the result of better intercalation or exfoliation. The relatively poorer performance of our PP/OMMT/MAPP composite needs further study and explanation. Several issues need to be emphasized at this juncture. Although we obtained a straight line for all composites, the intercept with the ordinate occasionally differs from the value of the matrix polymer (● in Fig. 5). We must take into account the fact here that the properties of the functionalized polymer often differ considerably from that of the matrix. Because of modification, the crystallinity, stiffness and strength of MAPP is usually smaller than that of the matrix polymer, especially if a homopolymer is used. As a consequence the properties of the PP/MAPP blend differ considerably from that of PP, but the blend serves as a matrix for the silicate. Accordingly, the value of σ_{y0} also changes in Eqs. (1) and (2) leading to the different intercepts with the ordinate as observed in Fig. 5. In order to eliminate the effect of variation in matrix properties, we plot relative yield stress, i.e.

$$\ln \sigma_{\text{yrel}} = \ln \frac{\sigma_y}{\sigma_{y0}} \frac{1+2.5\varphi}{1-\varphi} = B\varphi \tag{4}$$

in most subsequent figures. In relation of the data taken from the paper of Svoboda et al. [71] we must mention that the authors kept constant the silicate/MAPP ratio during their experiments. This led to a continuous change in the composition and properties of the matrix, which resulted in the slight deviation from linearity of the ln σ_{yrel} vs. φ plot and to the strong deviation of the last point from the calculated line.

Our analysis was extended to include also data taken from the literature in order to check the validity of the approach even further. Experimental yield stress values taken from several sources are plotted against composition in Fig. 6. Different fillers and matrices were used in these composites leading to dissimilar changes in properties as a function of silicate content. Because of the variation in components and processing conditions, comparison is difficult. If we plot the results according to Eq. (4), we obtain straight lines again with different slopes, i.e. the extent of reinforcement changes from one composite to the other (Fig. 7). The difference in the reinforcing effect of the various silicates may arise from variations in interfacial adhesion, but we are convinced that they are caused mainly by the changing extent of exfoliation. Whatever is the explanation, we can establish that the model can be applied also to nanocomposites. We obtained straight lines practically in all cases similarly to other systems studied earlier [39,40,66–68] indicating that layered silicate PP nanocomposites are heterogeneous polymer systems and can be treated accordingly. As a consequence, all results available were analyzed in the way presented above and the reinforcing

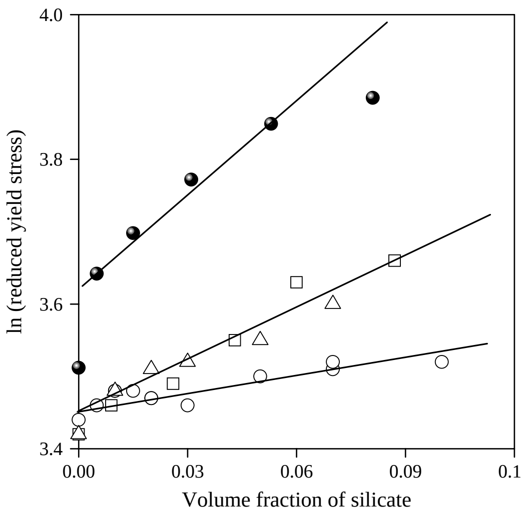

Fig. 5. Reduced tensile yield stress of the composites shown in Fig. 4 plotted against filler content in linear form. Symbols are the same as in Fig. 4.

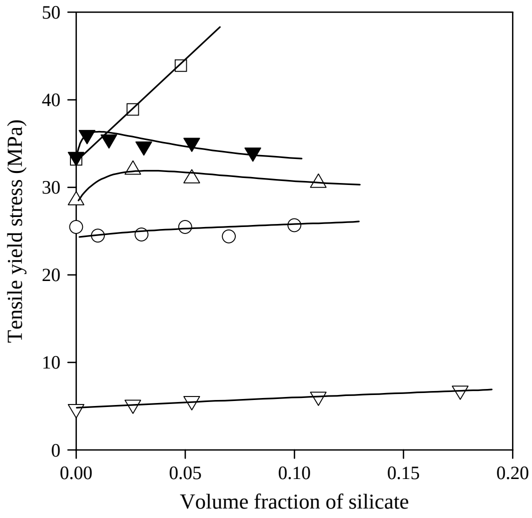

Fig. 6. Tensile yield stress of several PP/OMMT/MAPP composites plotted as a function of silicate content. See the details in Table 1. Symbols: (□) Reichert [19] (15), (▽) Chen [73] (28), (○) this paper (31), (▼) Svoboda [71] (24), (△) Manias [12] (26).

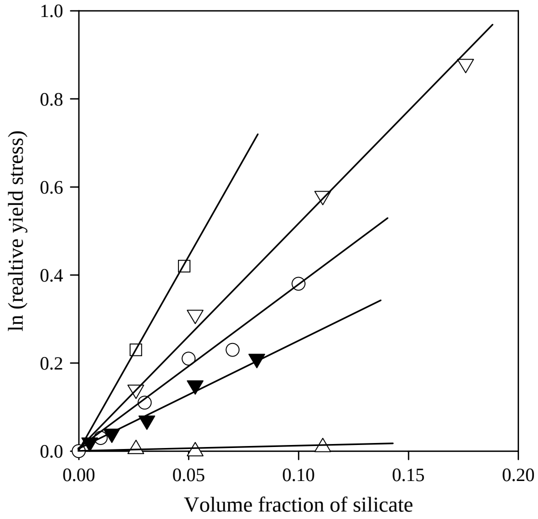

Fig. 7. Relative tensile yield stress of the composites shown in Fig. 6 plotted as function of silicate content in the linear form of Eq. (4). Symbols are the same as in Fig. 6.

effect of the silicate was estimated from the slope of the straight lines, i.e. using the value of parameter *B*.

4.2. Reinforcement

Yield stress values were analyzed in the way presented above for all PP nanocomposites prepared by us and for those which we could find in the open literature. A few data taken from the literature are presented in Fig. 8 as an example. Relative yield stresses are plotted in the figure to eliminate the effect of different or changing matrix properties. *B* values characterizing reinforcement cover a very wide range from 2 to 15, in spite of the fact that all composites are claimed to have intercalated or exfoliated morphology.

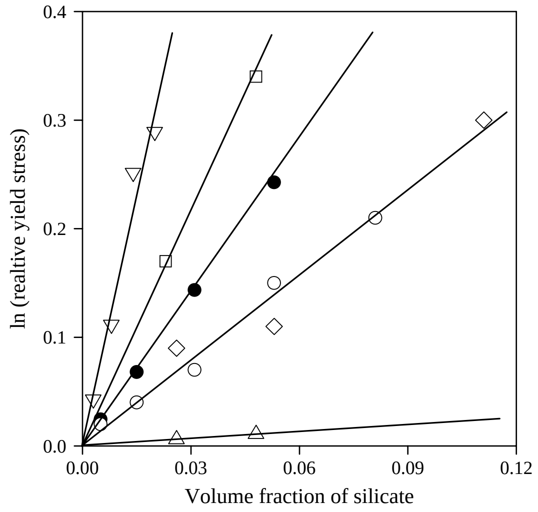

Fig. 8. Evaluation of yield stresses according to Eq. (4). Results taken from the literature in the entire range of reinforcing effects. Symbols: (▽) Liu [74] (20), (□) Reichert [19] (13), (●) Svoboda [71] (22), (○) Svoboda [71] (24), (◇) Kaempfer [47] (17), (△) Reichert [19] (5). See the details in Table 1.

The results of the calculations are compiled in Table 1. The table contains the most important information about the composites (type of PP, functionalized polymer, silicate), parameter *B* and calculated matrix yield stress values (σ_{y0c}). This latter is very important, since the extent of reinforcement, i.e. *B*, depends on its value as mentioned before. If the same filler is used in different matrices, A_f and ρ_f are constant. We may also assume that σ_{yi} and l do not vary much either because the strength of interaction characterized by the reversible work of adhesion (W_{AB}) differs only slightly for the composites involved. The effect of W_{AB} on *B* is smaller than that of A_f or σ_{y0} anyway [53–55]. Accordingly we simplify Eq. (2) to obtain

$$B = a + b \ln \sigma_{y0} \tag{5}$$

The role and importance of matrix yield stress is demonstrated in Fig. 9, in which parameter *B* is plotted against $\ln \sigma_{y0}$ according to Eq. (5). The relationship between the value of *B* and $\ln \sigma_{y0}$ is linear in Fig. 9, which is a strong indication that the assumptions listed above are reasonable. LDPE, plasticized (pPVC) and unplasticized PVC (uPVC), as well as PP composites containing a $CaCO_3$ filler were prepared in order to obtain the correlation. Additional reinforcement can be estimated by the deviation from the linear correlation in the vertical direction.

In further treatment, we assume that only microcomposites form if the composites do not contain a functionalized polymer. The value of parameter *B* is relatively small for these composites. Occasionally, the introduction of the functionalized polymer changed the properties of the matrix considerably as shown by the difference between the measured (reported, σ_{y0}) and calculated (σ_{y0c}) matrix yield stress values (Table 1). However, σ_{y0} is usually given for the PP matrix polymer and not for the PP/MAPP blend, as it should be. In some other cases the difference between the measured and calculated σ_{y0} values is surprisingly small. Since, *B* values do not give a direct estimate of the extent of reinforcement, we plotted *B* against the calculated matrix yield stress (σ_{y0c}) of the

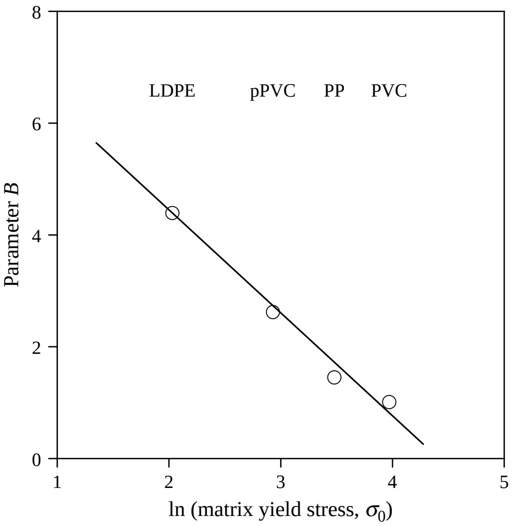

Fig. 9. Effect of matrix yield stress on the relative load bearing capacity of the filler (parameter *B*) [39].

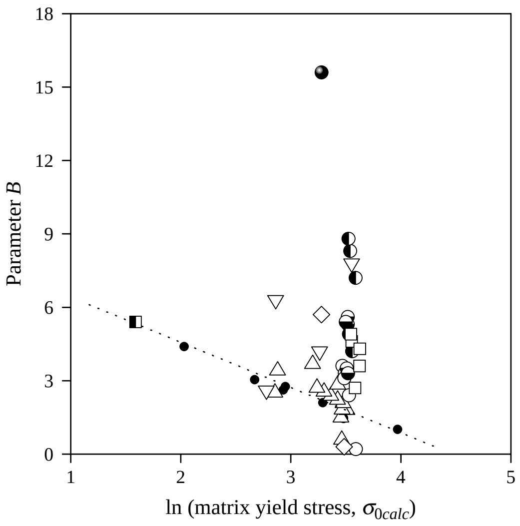

Fig. 10. Estimation of the reinforcing effect of layered silicates in PP composites (Eq. (6)). Symbols: (○) Reichert [19] (1–5), (◒) Reichert [19] (6–10), (◐) Reichert [19] (11–15), (□) Svoboda [71] (21–25), (△) this paper (29–41), (◉) Liu [74] (20), (▽) Walter, Kaempfer [45,47] (16–19), (◇)Manias [12] (26–27), (◧) Chen [73] (28), (●) $CaCO_3$ reference line (dashed) shows the effect of changing matrix properties.

composites in Fig. 10. The dashed line obtained for different polymer/$CaCO_3$ microcomposites is also shown in the figure as reference. The plot indicates that the relatively large B values obtained for syndiotactic PP (see symbol ▽ at around 2.7 ln σ_{y0c}, composite no. 19 in Table 1) are rather misleading, since the difference from the straight line is relatively small compared to some of the iPP samples. It is interesting to note that the value published by Chen et al. [73] falls on the reference line (◇ at 1.6 ln σ_{y0} value), i.e. the extent of reinforcement is negligible in that case, in spite of the fact that they used MAPP as matrix. We must reflect also on the largest reinforcement achieved by Liu et al. [74]. They swelled OMMT with an acrylate containing also peroxide. The reaction must have modified the structure and properties of the matrix considerably leading to the large value. If we exclude this composite from our evaluation we must establish that the best PP/silicate composites were prepared and the largest reinforcement was achieved by the group of Mülhaupt [19,47]. We may conclude from the data presented in Table 1 and Fig. 10, that the extent of exfoliation, thus also reinforcement differs significantly for the various combinations of materials studied. This statement contradicts somewhat conclusions drawn from the experimental results by the authors, who claimed a considerable extent of exfoliation, i.e. very similar structure, in most cases when MAPP was used. Some of the possible factors influencing the results presented in Table 1 and leading to this apparent contradiction are discussed in Section 5.

5. Discussion

Several assumptions were made during the analysis presented above and some factors, which may or do influence composite properties were completely neglected. The orientation of anisometric particles considerably influences the extent of reinforcement, but parameter B does not take into account this factor explicitly (Eq. (2)). However, TEM micrographs taken from nanocomposites often show completely random distribution of the exfoliated layers. Moreover, even if the various technologies used for the preparation of the composites lead to some orientation of the layers, this effect is included in the value of B implicitly and thus also in the reinforcing effect of the silicates. Accordingly, our statements on reinforcement are valid, but conclusions related to the extent of exfoliation might not be completely right, because B may vary due to changing orientation.

Changes in the properties of the matrix were taken into account by Eq. (5) and by the plot shown in Fig. 9. However, we assumed that the strength of interaction is the same in all composites leading to similar l and σ_{yi} values. Eq. (2) can be expressed in the simplified form of Eq. (5) only in this case. The surface free energy, or surface tension, of inorganic fillers is large, while these surface characteristics are relatively small for polymers [75]. If we cover the high energy surface of a filler with an organic substance, like a surfactant, interaction decreases considerably [53–55,75]. If only secondary forces act between the polymer and the filler, the differences caused by the type and amount of the surfactant used for treatment must be negligible [55]. Stronger interactions may develop between the components of micro- or nanocomposites when functionalized polymers are used. However, in the case of complete exfoliation, the more than two orders of magnitude increase in the specific surface area of the filler from about 3 to 750 m^2/g affects reinforcement much more than any changes in the strength of interaction, naturally apart from the possible formation of covalent bonds.

We can use the results collected in Table 1 also for the estimation of the extent of exfoliation. Naturally, we must assume that the effect of orientation and interaction is small compared to that of the changing contact surface. If we accept

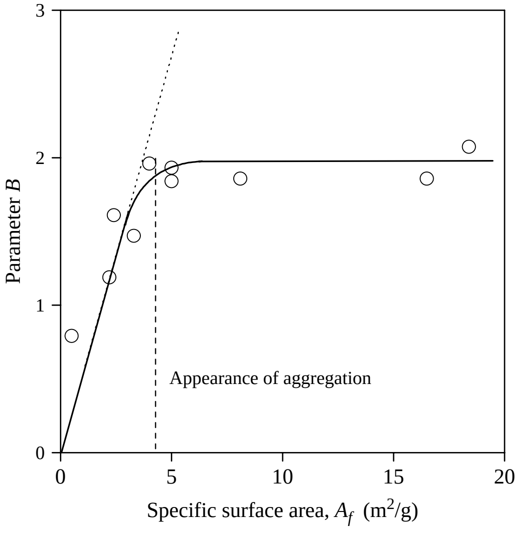

Fig. 11. Correlation between parameter B and the specific surface area of the filler (A_f) for PP/$CaCO_3$ composites.

Table 2
Estimation of the extent of exfoliation from parameter *B* determined in PP composites

Filler	Parameter *B*	Specific surface area (m^2/g)	Extent of exfoliation (%)	Refs.
$CaCO_3$	1.5	3.3	0	[51]
NaMMT	1.8	26.0	0	a
NaMMT	195[b]	750	100	[5,54,55]
OMMT	15.6	57.5[c]	8	[74]

[a] Results obtained in this study.

[b] Calculated from published specific surface area assuming complete exfoliation.

[c] Calculated from the largest *B* value published.

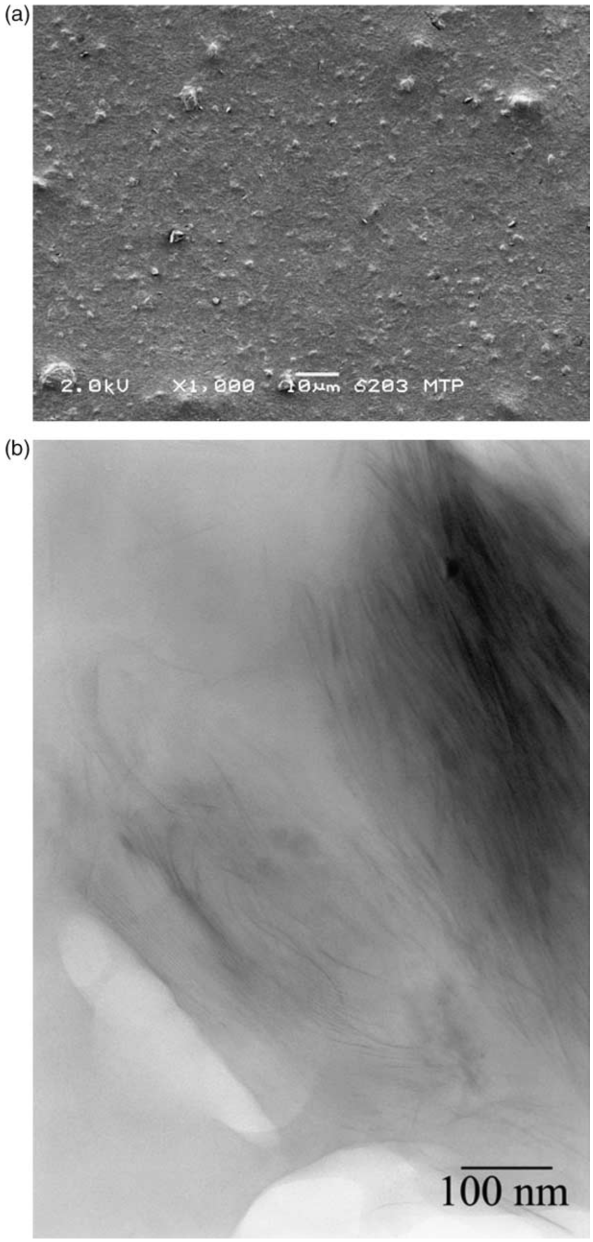

Fig. 12. Structure of a PP/OMMT/MAPP composite containing 20 vol% MAPP and 2 vol% silicate, (a) SEM, (b) TEM.

this assumption we can rearrange Eq. (2) into the following form

$$B = a_2 + b_2 A_f \tag{6}$$

i.e. the extent of reinforcement depends linearly on the specific surface area of the filler. The validity, and also the limitation, of Eq. (6) is shown by Fig. 11, in which *B* is plotted against A_f for PP/$CaCO_3$ composites. At large particle size the correlation is linear indeed, while it deviates from linearity at large specific surface areas, due to the aggregation of the filler. In nanocomposites, a small contact surface (A_f) may develop between the phases either because of low extent of exfoliation, or because of the aggregation of already exfoliated layers, but the result on composite properties is exactly the same. Mechanical properties, e.g. σ_y, will change accordingly, i.e. small specific surfaces result in small *B* values. Table 2 gives an estimate for the extent of exfoliation. A PP/$CaCO_3$ composite is used again as reference. The theoretical value of parameter *B* of around 195 was calculated for complete exfoliation from data published for the specific surface area of montmorillonite [5,50,51]. Although the value of 15.6 reached with PP composites [74] represents a considerable improvement compared to traditional microcomposites, it is far from the theoretical prediction obtained for silicates. A *B* value of 15.6 indicates an extent of exfoliation of about 8%.

One may argue that the disappearance of silicate reflection from the XRD traces and TEM micrographs clearly prove complete exfoliation. Our experience shows that complete exfoliation is rearely reached and the structure of PP nanocomposites is rather complicated. We presented the XRD pattern of a nanocomposite in Fig. 3 in which the silicate reflection was absent. A SEM micrograph taken from the etched surface of the same composite is shown in Fig. 12(a). Particles are clearly visible on the surface; exfoliation is obviously far from complete. On the other hand, a TEM micrograph taken from the same composite is presented in Fig. 12(b). Individual silicate layers and intercalated clay particles dominate structure in this part of the sample. The *B* value obtained for composite 41 was 0.6. The combined evidence of all results clearly proves that exfoliation is not complete and the structure of the composites is complex.

6. Conclusions

The comparison of the tensile yield stress of a large number PP/layered silicate composites showed widely differing mechanical properties. The usual techniques used for the characterization of structure, i.e. XRD and TEM, do not reflect the differences in properties and they do not give any reliable information about the extent of exfoliation either. PP/clay composites containing also maleinated PP and not exhibiting a silicate reflection in XRD may have very poor mechanical properties reflecting small extent of exfoliation. The composition dependence of tensile yield stress of these composites may be described and evaluated quantitatively by a simple model developed earlier for particulate filled polymers. Using a few simple assumptions, most of which are supported by previous experience, it is possible to estimate quantitatively the extent of exfoliation. We analyzed the tensile yield stress of about 40 composites, some of which were prepared by us, while results for others were published in the literature. The analysis indicated that the extent of exfoliation is very low in most composites; it reaches maximum 8% in the best case. This result is in complete agreement with our observation that complete exfoliation usually cannot be reached in thermoplastic/clay composites, their structure is complex and further efforts must be done to increase the extent of exfoliation in order to achieve reinforcement levels forecasted earlier.

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