

Possible mechanism of interaction among the components in MAPP modified layered silicate PP nanocomposites

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Abstract

Model reactions were carried out with components frequently used for the preparation of intercalated or exfoliated polypropylene (PP) nanocomposites. The results prove that maleinated polypropylene (MAPP) can react chemically with the surfactant applied for the organophilization of the filler, if this latter contains active hydrogen groups. The reaction of hexadecylamine (HDA) and MAPP was detected by MALDI-TOF spectroscopy, DSC measurements and FTIR spectroscopy. Anhydride groups are consumed and mainly amide groups form in the reaction. The formation of cyclic imides could not be proved by the techniques used. MAPP reacts also with the surfactant adsorbed on the surface of the silicate in ionic form. On the other hand, *N*-cetylpyridinium chloride (CPCI) not containing active hydrogen atoms does not react with maleinated PP. Intercalated or exfoliated composites could be prepared from the silicate organophilized with HDA, while microcomposites formed from the filler treated with CPCI. Chemical reactions remove the surfactant from the surface of MMT and hydrogenated silicate sites are left behind. The high energy surface interacts either with the anhydride or the amide groups by dipole–dipole interactions. Even the unmodified polypropylene chains may be attached much stronger to the surface by London dispersion forces than to the silicate covered with aliphatic chains. Although the effect of competitive adsorption (MAPP, HDA) and mutual solubility of the components (PP, MAPP, surfactant, reaction products) cannot be neglected, chemical reactions play a crucial role in structure formation in PP nanocomposites containing a functionalized polymer. Direct interaction of the silicate surface and the functionalized polymer as well as the formation of hydrogen bridges seem to play a lesser role, but the relative influence of processes may change with the type of surfactant, functionalized polymer, surface coverage and processing conditions.

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1. Introduction

Layered silicate nanocomposites created much interest both in academia and industry since the successful preparation and application of PA/montmorillonite composites by the researchers of Toyota [1–4]. The nanocomposites prepared from PA 6 possessed excellent mechanical and thermal properties at very low filler content offering economical solution in several fields of application.

Nanocomposites have been prepared from a variety of polymers and layered silicates since then including polyimide, polystyrene, epoxy, polyurethane, etc. but the expected improvement in properties was not always achieved with all combination of materials [5–16].

Polypropylene is a commodity polymer, which offers probably the best price/performance characteristics among all thermoplastics. It can be modified in many ways and its fiber reinforced grades compete even with engineering polymers [17]. As a consequence considerable effort was dedicated to the preparation of layered silicate nanocomposites also with a PP matrix, but practically all attempts to produce a composite with acceptable properties from an organophilic silicate and a PP homo- or co-polymer failed [18–23]. The lack of exfoliation and poor properties were often explained with the incompatibility of the hydrophilic silicate and the hydrophobic polymer [18,20–23], although

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the silicate was usually covered with long chain aliphatic amines, which makes it hydrophobic in an extent that they cannot be dispersed in water. However, some time ago it was found that organophilic silicates can be exfoliated and homogeneously dispersed in PP if polypropylene functionalized with hydroxyl or maleic anhydride (MA) groups is added to the composite [17,20–27]. The presence of the functionalized polymer resulted in the considerable improvement of mechanical properties in several cases, the extent of which depended on the characteristics of the maleinated polymer and on processing conditions.

In spite of the clear effect of MAPP on the properties of PP nanocomposites and the numerous publications in this field, several contradictions exist about the factors influencing the extent of exfoliation and the character of the interactions leading to improved properties. Mulhaupt et al. [17,25–30] found that MAPP with a larger extent of functionalization results in a more considerable improvement in properties than a modified polymer containing less polar groups. On the other hand, Usuki and Hasegawa [19,22,31] observed complete exfoliation even at a very low MA content and independence of structure of the extent of molecular weight and functional group content. Balazs et al. [32,33] predicted miscibility between low molecular weight polymers and organophilic silicates, but other sources proved that complete exfoliation can be reached also with high molecular weight components [19,22–24,31,34,35]. Further inconsistencies can be observed also in the effect of shear, time of homogenization and in the extent of property improvement as well [23,31,36,37].

Similarly contradictory are the explanations given for the mechanism of interaction among the components of PP/layered silicate nanocomposites containing functionalized polymers. The most frequent explanation is related to the hydrophilic or hydrophobic character of the components and involves some kind of undefined polar interaction between the silicate layers and the functionalized polymer [6]. Besides the undefined character of the interaction, this explanation does not take into consideration the presence of the aliphatic chains, which cover the majority of the silicate surface. An often cited explanation presented by Kato et al. [20–22] explains exfoliation and improved properties by the formation of hydrogen bonds between the oxygen groups of the silicate layers and the functionalized polymer. However, layered silicates contain active –OH groups only at their edges, thus interaction with them cannot lead to exfoliation [38–41]. Based on the study of Okada et al. [20–22], Reichert and Mülhaupt [17,25] mention the possibility of chemical reactions between MAPP and octadecylamine used for the organophilization of the silicate. However, they assume again that strong hydrogen bonds are induced between the polypropylene grafted with *N*-octadecyl-succinimide formed in the reaction and the silanol groups at the silicate surface. They also claim that the octadecyl group attached to the modified PP promotes hydrophobic interaction with the surfactant remaining on the surface of

the silicate. This latter explanation is contradicted by the experience that the strength of interaction between CaCO₃ and PP or PE decreases when the filler is covered by stearic acid, although both are very hydrophobic in nature [42–45]. Nevertheless, the occurrence of chemical reactions cannot be excluded between the very reactive MAPP and the amine used for treatment, in spite of the fact that it has been mentioned only as a possibility up to now [17,25,46]. For example, the formation of amide and imide groups was proved to take place in PA6/PP blends containing MAPP coupling agent [47–50].

Taking into consideration the uncertainty related to the effect of MAPP, the goal of our study was to shed more light onto the possible interactions acting among the components in layered silicate PP nanocomposites. With the help of model systems we also tried to verify the occurrence of possible chemical reactions among them, which may take place during the preparation of the composites. Based on the results of the experiments we propose a scheme, which might explain the effect of MAPP on the structure and properties of layered silicate nanocomposites containing such a functionalized polymer.

2. Experimental

Model reactions were carried out with the Licomont AR 504 (L504) maleic anhydride modified polypropylene oligomer produced by Clariant GmbH. The softening point of the product is 156 °C, its density 0.91 g/cm³, and acid number 40 mg/g, which corresponds to 3.5 wt% maleic anhydride (MA) content. The other components of the reactions were 1-hexadecylamine (HDA, $T_m = 45–48$ °C) and cetylpyridinium chloride monohydrate (CPCI, $T_m = 83–86$ °C). Nanofil 848 (Süd-Chemie AG) was used for the study of the interaction of organophilized montmorillonite (OMMT) and MAPP. This filler was treated with stearylamine, its density was 1.8 g/cm³, moisture content 2 wt%, organic content 25 wt% and its average particle size 3.5 μm. Montmorillonite organophilized with CPCI was prepared from a Wyoming bentonite (Steetley GWB) containing 92 wt% montmorillonite (MMT), 3 wt% quartz and 5 wt% feldspar. The theoretical ion exchange capacity of the Wyoming montmorillonite was 90 mequiv/100 g; complete ion exchange was carried out during treatment. The density of the final product was 1.8 g/cm³, volatile content 2 wt%, organic content 25 wt% and its average particle size 45 μm. Composites were prepared from the two organophilic silicates and a PP homopolymer (Tipplen H605, MFI = 3 g/10 min at 230 °C/2.16 kg) with or without 20 wt% MAPP (L504) in order to check the effect of the functionalized polymer on the gallery structure of the filler.

Calorimetric studies were done by using a Mettler DSC 30 cell controlled by a TA3000 system. Measurements were carried out on 5 mg samples with 10 °C/min heating rate between 30 and 200 °C using an open pan in order to avoid

the effect of volatile compounds possibly forming during reactions. The amount of reactants (HDA, CPCI) in the mixture changed between 0 and 40 wt%. Reaction products were analyzed by FTIR spectroscopy on films compression molded from the components at 190 °C. Spectra were recorded in the 4000 and 400 cm^{-1} wavelength range with 4 cm^{-1} resolution using a Mattson Galaxy 3020 instrument. Each spectrum was recorded in 16 scans. Composites were homogenized at 190 °C and 50 rpm for 13 min in a Brabender W 50 EH internal mixer attached to a Haake Rheocord EU 10 V driving unit. The gallery structure of the silicate was characterized by XRD using a Phillips PW 1830/PW 1050 equipment with $\text{Cu K}\alpha$ radiation at 40 kV and 35 mA.

3. Results and discussion

The experiments were carried out in different stages and they are reported accordingly. First, model experiments were done with MAPP and surfactants frequently used for the organophilization of the filler. The behavior of hexadecylamine containing two active hydrogen atoms was compared to that of CPCI, which was expected to be inert because of the lack of hydrogens. The interaction of MAPP and organophilized fillers were investigated in the next stage followed by the study of the gallery structure of composites containing the usual components of layered silicate PP nanocomposites, i.e. PP, OMMT and MAPP.

3.1. Interaction of MAPP and surfactants

MAPP is a highly reactive compound, which is often used as compatibilizer or adhesion promoter in various heterogeneous polymer systems, but mainly in modified polypropylene. MAPP is used to promote stress transfer in glass or natural fiber reinforced composites [51–54] and as blending agent in PP/PA blends as well [47–50]. It has been proved on several occasions that the reactive MA group chemically reacts with the active –OH groups of starch and cellulose or with the amine group of silane coupling agents and polyamide [47–50]. At the beginning of our study we assumed that chemical reactions take place also during the preparation of layered silicate PP nanocomposites containing MAPP; the possibility of chemical reactions between the components was checked in model reactions. We used various means to reveal the occurrence of reactions and to analyze the reaction products. The MALDI-TOF spectra of the components and that of the reaction products are presented in Fig. 1(a)–(c). We refrain from the detailed analysis of the spectra for obvious reasons. However, we can establish at the first glance that drastic changes occur during the model reaction of HDA and MAPP. Both initial compounds consist of well defined components. MAPP contains oligomers with different molecular weight and possesses a broad molecular weight distribution (Fig. 1(a)),

while hexadecylamine consists of a few distinct components (Fig. 1(b)). The spectrum of the reaction product clearly prove that considerable changes took place during the heating of the two components, numerous compounds of the most various molecular weights formed in the reaction (Fig. 1(c)). Although the analysis of these products is practically impossible, we can conclude that the two components react with each other without any doubt. However, other techniques must be used for the identification of the main reaction products.

We hoped that the highly reactive MAPP groups take part in exothermic reactions with HDA and that the reaction can be detected by thermal analysis. Reactions were carried out in a DSC pan at constant weight with increasing amount of hexadecylamine. Three DSC traces are presented in Fig. 2, which clearly show the processes taking place during the heating of the mixture of HDA and MAPP. Three distinct peaks can be distinguished on each trace, all three are endothermic processes, but an exothermic reaction between the two components cannot be detected on them. The first two peaks belong to the melting of the amine; quantitative analysis proved that the area under the two peaks depends linearly on the amount of amine added to the mixture. The third endothermic peak is related to the melting of MAPP. We must call attention here to several observations. The area under this latter melting peak decreases continuously with increasing amine content and also the location of the peak shifts towards lower temperatures. These changes exceed the extent justified by changing composition in spite of the fact that the relative amount of MAPP decreased in the mixture with increasing HDA content. The only reasonable explanation is that an exothermic chemical reaction starts immediately after the melting of MAPP and the heat of reaction contributes to the melting of PP. As a consequence, the traces represent the sum of the exothermic reaction heat and the endothermic heat of melting. A closer scrutiny even reveals a small exothermic overshoot behind the melting peak of MAPP (see trace (c) in Fig. 2). These DSC traces further confirm the occurrence of chemical reactions during the simultaneous heating of MAPP and HDA.

The same experiments were carried also with cetylpyridinium chloride as the second component. As mentioned earlier, we did not expect any reaction to occur because of the lack of active hydrogen atoms in this compound. The DSC traces recorded during the heating of MAPP/CPCI mixture are presented in Fig. 3. Although they might resemble those shown in Fig. 2 at the first glance, distinct differences can be also observed between the two sets of traces. Contrary to HDA, CPCI possesses only a single well defined melting peak, which appears at around 80 °C. Considerable differences can be observed also in the melting range of MAPP as well. The area under the melting peak remains practically constant, independent of the amount of CPCI added to the reaction mixture. Variation in the peak area is caused only by the uncertainty of sample preparation,

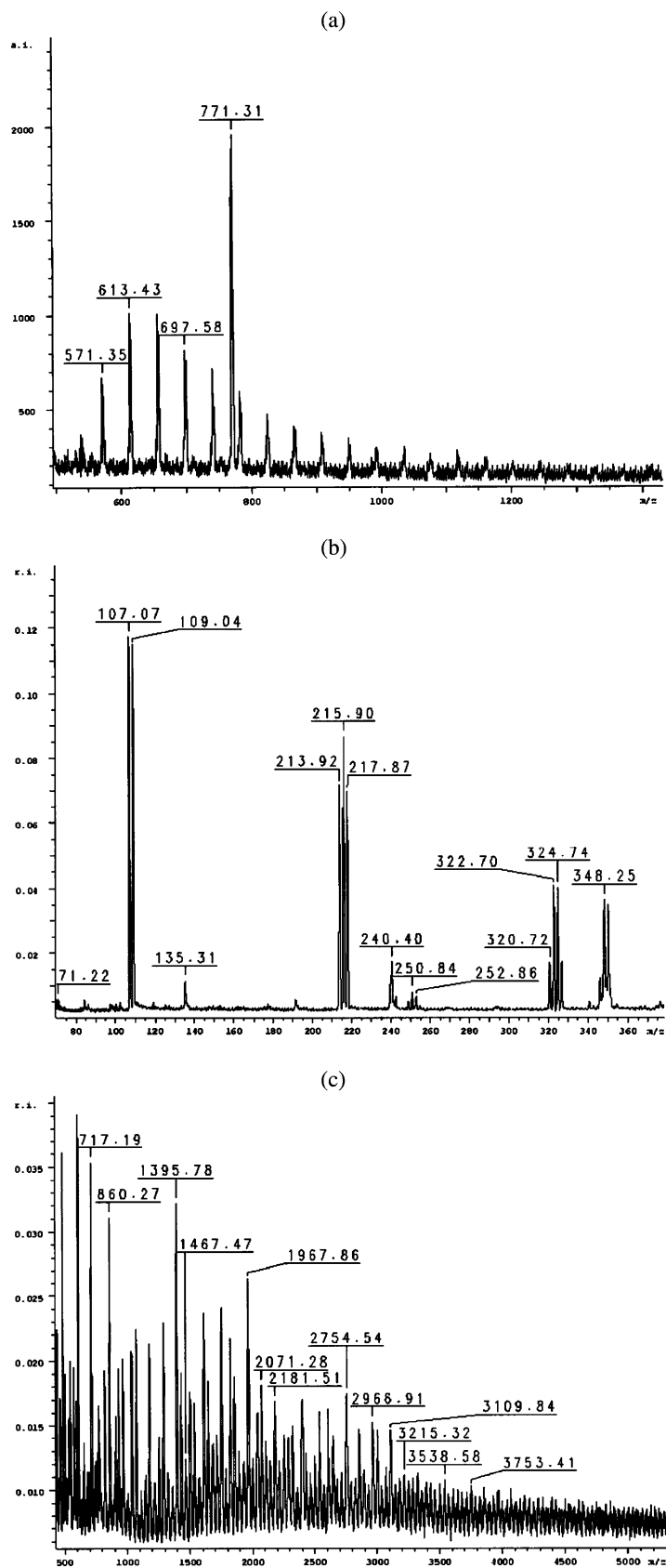


Fig. 1. MALDI-TOF spectrum of MAPP (a), HDA (b) and the reaction product of the two (c).

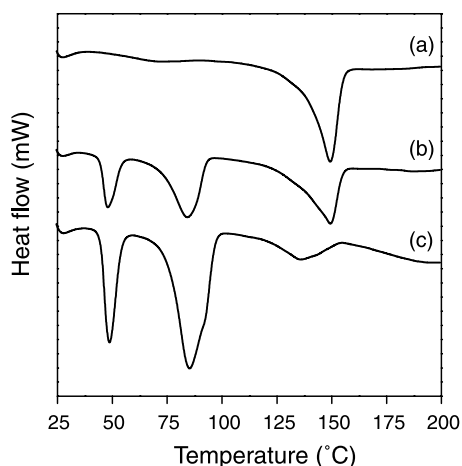


Fig. 2. DSC traces recorded during the reaction of MAPP and HDA. Heating rate: 10 °C/min (a) 0 wt% HDA, (b) 15 wt% HDA, (c) 35 wt% HDA.

and not by changing composition. The traces obtained during the heating of CPCI and MAPP supply a further proof for the reaction of HDA and MAPP, on the one hand, and prove that active hydrogen atom or atoms are needed for reactions to occur, on the other.

The qualitative analysis presented above is further corroborated by the quantitative evaluation of the DSC traces. The heat of reaction was calculated as the difference of the measured and calculated heat of melting of MAPP. According to Fig. 4 this area increases continuously up to certain amine content then reaches a constant value. It is obvious that after the consumption of all MA groups the heat of reaction cannot increase any more. The same procedure was carried out also with the traces recorded on the MAPP/CPCI mixture. In accordance with the results of the qualitative analysis, the difference in the area does not change with amine content and varies around zero in the range of the standard deviation of the determination

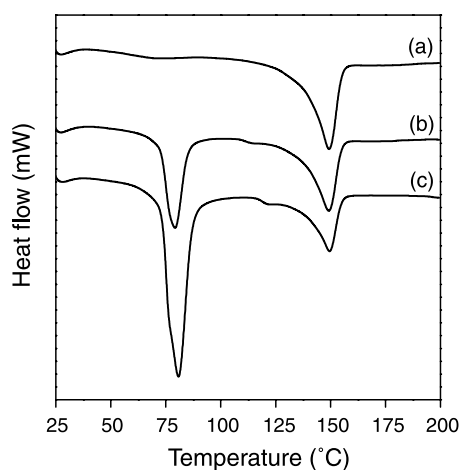


Fig. 3. DSC traces recorded on the mixture of MAPP and CPCI at 10 °C/min heating rate. (a) 0 wt% CPCI, (b) 15 wt% CPCI, (c) 35 wt% CPCI.

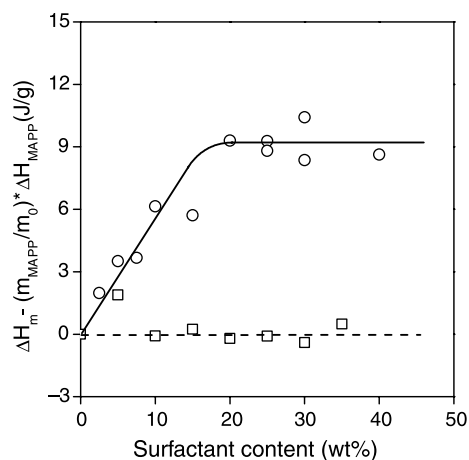


Fig. 4. Dependence of the overall heat of reaction on the surfactant content of the mixture. Symbols: (○) HDA, (□) CPCI.

supplying further proof for the reaction of HDA and the lack of it for CPCI.

DSC measurements are not able to identify the reaction products in any way. A detailed analysis of these latter was carried out by FTIR spectroscopy. The overall spectra of the two components and that of the reaction product obtained with 20 wt% HDA is presented in Fig. 5. Numerous vibrations appear in the spectra, the majority of which belong to the $-\text{CH}_2-$ and $-\text{CH}_3$ groups of the aliphatic chain of the two components. In further analysis we focus our attention to the wavelength range between 2000 and 1400 cm^{-1} , where the characteristic bands of the anhydride, the amine and those of the possible reaction products, the amide and imide groups appear. Already the overall spectra indicate considerable differences in the chemical structure of the three materials, the disappearance of some vibrations and the appearance of others. Moreover, the characteristic peaks of MAPP and HDA overlap with each other. The three spectra are presented in the range mentioned above in Fig. 6. The three characteristic peaks of the anhydride group can be clearly distinguished in the spectrum of MAPP at 1856 cm^{-1}

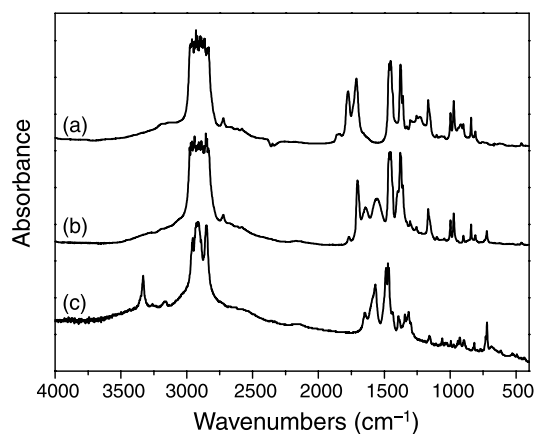


Fig. 5. Overall FTIR spectra of MAPP (a), HDA (c) and their reaction product at 20 wt% HDA content (b).

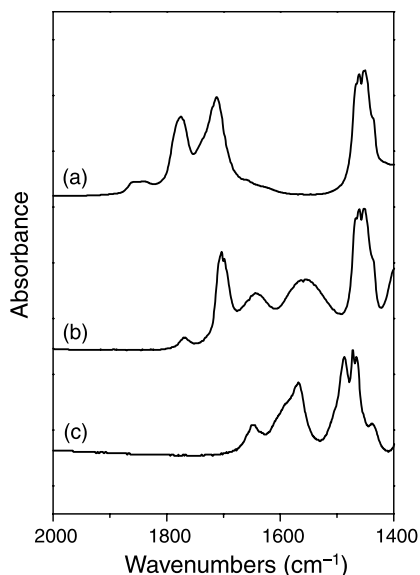


Fig. 6. FTIR spectra of the components and their reaction product in the wavenumber range of importance. Notation is the same as in Fig. 5.

(unsymmetrical stretching modes of C=O in a saturated ring anhydride), 1775 cm^{-1} (symmetric C=O stretching) and at 1712 cm^{-1} (carboxylic acid) (spectrum a). In the spectrum of HDA the vibration of the amine group appears at 1550 cm^{-1} accompanied by a smaller peak at 1650 cm^{-1} . New peaks appear in the spectrum of the reaction product, which can be identified as the amide I ($1680\text{--}1630\text{ cm}^{-1}$) and amide II ($1570\text{--}1515\text{ cm}^{-1}$) bands of the secondary amide. Further proof for the formation of this group is the appearance of the amide III band at 1260 cm^{-1} . Because of the vibration of various groups overlap with each other and the position of some bands shifts as an effect of changing environment, both the assignment of peaks, as well as their quantitative analysis is very difficult. Nevertheless the qualitative analysis of the spectra proves again that chemical reactions take place in the melt of MAPP and HAD, indeed, leading to the formation of amides. We cannot exclude the formation of cyclic imides either, but their existence cannot be proved unambiguously since the characteristic vibration of the imide group appears also in the same range, around $1770\text{--}1700\text{ cm}^{-1}$.

In spite of the difficulties of quantitative evaluation, an attempt was made to determine changes in the intensity of characteristic vibrations as a function of the amine content of the reaction mixture. We deconvoluted the main peaks mentioned in the previous paragraph, altogether nine vibrations, and determined the area under the peaks. Changes in the relative intensity of the anhydride carbonyl (1775 cm^{-1}), carboxylic acid (1712 cm^{-1}) and amide I (1655 cm^{-1}) vibrations are plotted against amine content in Fig. 7. The vibration of the $-\text{CH}_3$ group of MAPP appearing at 973 cm^{-1} was used as internal standard during the evaluation. The content of the acidic carbonyl does not change significantly as a function of amine content, but this

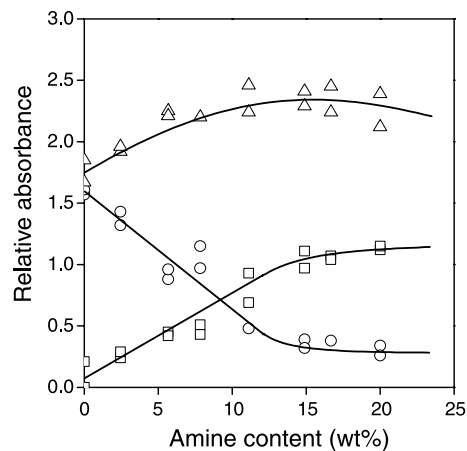


Fig. 7. Quantitative analysis of the changes in the intensity of the vibration of selected functional groups. Symbols: (○) anhydride, (□) amide, (△) carbonyl.

is not very surprising, since the vibration of the acidic carbonyl group in the two compounds cannot be separated and both contribute to the overall intensity of the band detected at around 1712 cm^{-1} . With increasing amine content the peak shifts from 1713 to 1703 cm^{-1} , which also proves that the environment of the carbonyl group is modified considerably with changing composition. The intensity of the characteristic band of the cyclic anhydride group (1775 cm^{-1}) decreases continuously with increasing amine content. This change might result from the hydrolysis of the anhydride, but the simultaneous increase in the intensity of the amide II vibration (1550 cm^{-1}) proves the formation of this latter group. The slope of the composition dependence of both functions changes at around $10\text{--}15\text{ wt}\%$ amine content just like that of the composition dependence of the reaction heat (Fig. 4), which further supports the consistency of the results. However, we must emphasize again that the analysis of FTIR spectra is very difficult because of the overlapping of various vibrations. The location of practically all peaks changes with amine content, which also warrants further caution.

The reaction products of MAPP and CPCl were analyzed in a similar way. The spectra of the two components and that of the reaction product are presented in Fig. 8 in the same range as for HDA. Based on our original assumption and on the results of DSC measurements, we expected that the spectrum of the product would be a simple combination created from the spectra of the components without any new vibrations. Rather surprisingly, the spectrum of the product does not correspond to expectations. The intensity of the vibration of the anhydride group (1775 cm^{-1}) decreases almost to zero and its location shifts to lower wavenumbers (1768 cm^{-1}). The carbonyl band also shifts, the intensity of a peak detected at 3385 cm^{-1} increases with amine content, and smaller changes can be observed in the intensity or location of other vibrations as well, which are completely unexpected and rather difficult to explain. A more thorough

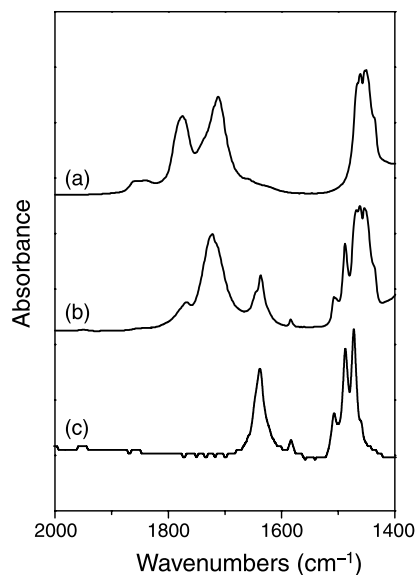


Fig. 8. FTIR spectra recorded on MAPP (a), CPCl (b) and their mixture of 20 wt% surfactant content (c).

analysis of the reaction components and the spectra revealed that CPCl contains water; it is partly present as a monohydrate (see vibration at 3385 cm^{-1}), which results in the immediate hydrolysis of the anhydride. The presence of the Cl^- ion further modifies the location of some vibrations. The analysis unambiguously proved that in spite of the fact that the spectrum of the compound does not correspond to the combined spectra of the components, MAPP and CPCl do not react with each other to form covalent bonds.

3.2. Interaction of MAPP and OMMT

Although the model experiments presented above unambiguously prove that MAPP and HDA react chemically with each other under the conditions of the experiments and probably also under those of composite preparation, we cannot assume a priori that similar reactions take place when the surfactant is attached to the surface of a silicate. As a consequence, similar experiments as described above were carried out also with montmorillonites organophilized with HDA or CPCl, respectively. We refrain from the detailed presentation of all results, only the most important conclusions of the FTIR analysis are shown here for the filler treated with hexadecylamine. The spectra of MAPP, OMMT(HDA) and the reaction product, respectively, are presented in Fig. 9. Although the intensity of the vibrations characteristic for the reaction product is much smaller than before because of the presence of the silicate, the spectra resemble very much those presented in Fig. 5. Fortunately the silicate does not absorb in the wavelength range of interest, thus the qualitative analysis of the spectra can be carried out in the same way as before. We can observe again a decrease in the intensity of the vibration

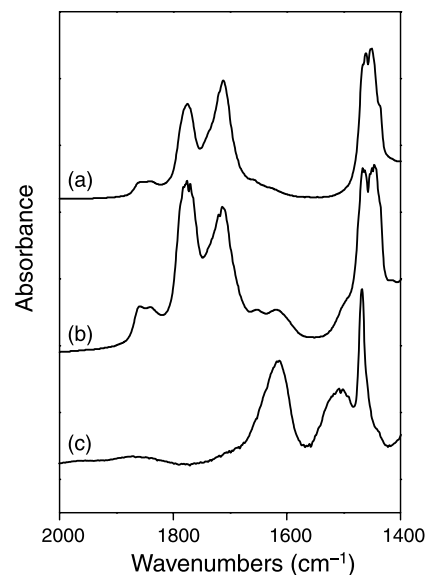


Fig. 9. FTIR spectra recorded on MAPP (a), and their reaction product obtained at 20 wt% filler content (b) OMMT organophilized with hexadecylamine (Nanofil 848) (c).

characteristic for the anhydride and the appearance of amide vibrations in the product.

The changes in the intensity of the three characteristic vibrations (anhydride, carbonyl, amide) were evaluated quantitatively just as before. The $-\text{CH}_2-$ vibration of the PP chain appearing at 1376 cm^{-1} had to be used as internal reference since the silicate adsorbs in the range of 973 cm^{-1} , which was used as reference vibration in the model experiments (see previous section). Unfortunately, besides the smaller intensity of vibrations, this change of reference band further decreased the accuracy of the analysis. The relative intensity of the three groups is plotted against OMMT content in Fig. 10. The results strongly corroborate the conclusions drawn from the qualitative analysis and agree well with those obtained in the model reaction of HDA and MAPP although some differences can be also

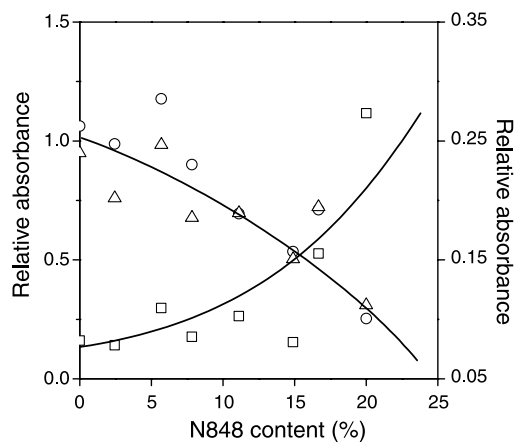


Fig. 10. Effect of the filler content of the reaction mixture of MAPP and OMMT on the intensity of selected groups. Symbols: (○) anhydride, (□) amide, (△) carbonyl.

observed. The amount of cyclic anhydride group decreases drastically, while that of the amide increases slightly with changing composition. The increase is continuous and we do not observe any change in the slope of the functions, because the number of amine groups is much smaller than that of the available MA groups. Filler content could not be increased sufficiently to reach equivalence. Unlike in the model reactions, the intensity of the acidic carbonyl vibration also decreases, which is very difficult to explain at the moment.

These results indicate that the same chemical reactions take place between the surfactant attached to the silicate surface than with the free compound. As a result of the reaction, the surfactant is removed from the surface and hydrogenated silicate sites are left behind. The high energy surface may interact either with the anhydride or the amide groups by dipole–dipole interactions, but even unmodified polypropylene chains may be attached to the surface by London dispersion forces much stronger than to the silicate covered by aliphatic chains. Although the functionalized polymer may interact with the silicate surface directly as suggested by some authors, chemical reactions undoubtedly occur because of the high reactivity of MAPP and strongly influence the interaction of the components, as well as the structure of the composite. Nevertheless, because of the complexity of the system, the effect of competitive adsorption (MAPP, HDA) and mutual solubility (PP, MAPP, surfactant, reaction products) cannot be neglected either. However, we do not believe that hydrogen bridges considerably contribute to component interactions.

3.3. Composite structure

The final proof for the occurrence and effect of chemical

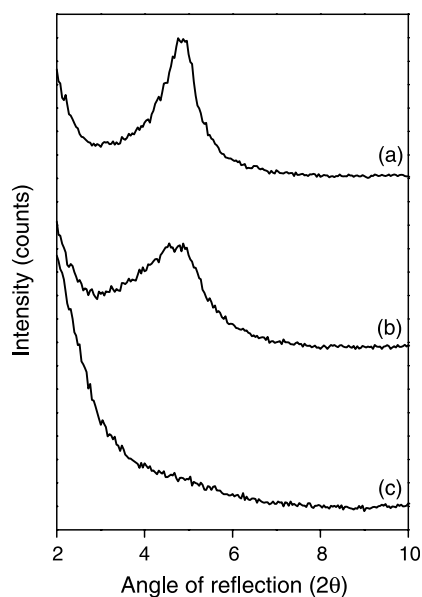


Fig. 11. XRD spectra of Nanofil 848 (a) and PP composites prepared from it; (b) 0 wt% MAPP, (c) 20 wt% MAPP. Silicate content: 2 wt%.

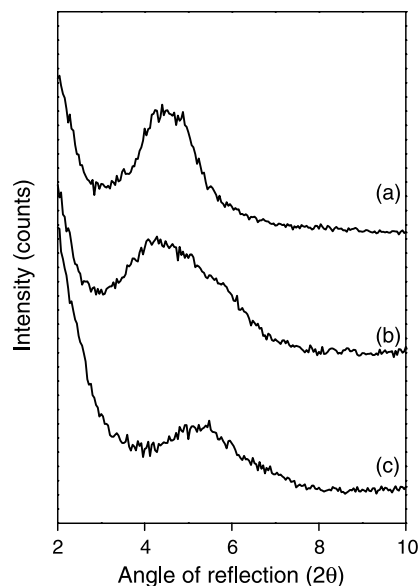


Fig. 12. Gallery structure of OMMT organophilized with CPCI (a) and that of its composites containing 0 wt% (b) and 20 wt% MAPP (c). Silicate content: 2 wt%.

reactions on component interactions and composite structure would have been the detection of the same changes in a PP/OMMT/MAPP composite. However, the small, 1–5 wt% filler content used in these composites and the corresponding amount of surfactant makes the detection of chemical changes impossible, because they are below the sensitivity of the techniques used. On the other hand, the introduction of MAPP is claimed to extend gallery distances considerably and result in an intercalated or exfoliated structure. If the reactions discussed above do not take place and the interactions are not acting, we can expect the formation of microcomposites with unaltered gallery distances. Obviously exfoliated or intercalated structure should form when HDA modified montmorillonite is used for composite preparation and microcomposite formation when a silicate organophilized with CPCI is applied.

The XRD pattern of the Nanofil 848 silicate is compared to that of composites prepared with and without 20 wt% maleinated polypropylene (Fig. 11). A well defined reflection appears on the XRD pattern of the filler at about 5° corresponding to 1.8 nm gallery distance. The peak shifts somewhat towards smaller angles, to about 4.0° corresponding to 2.2 nm gallery distance, when a composite is prepared with 2 wt% of the N848 silicate, but without functionalized polymer. The shift of the silicate reflection might be interpreted as the diffusion of the PP chains into the galleries of the filler, but the change is small and XRD patterns are influenced by several factors (gallery distance, orientation, layer stacking), thus far reaching conclusions cannot be drawn from the observed change. However, the pattern changes drastically upon the addition of MAPP, the silicate reflection completely disappears or shifts outside the detection range of XRD. This clearly proves that the

components of the composite strongly interact with each other and MAPP molecules diffuse into the galleries of the silicate. Composites containing the silicate, which was treated with CPCI behave completely differently (Fig. 12). The silicate reflection shifts partially to larger 2θ angles (from 4.5° to about 5.8°), which indicates the collapse of some galleries. Decreased gallery distance may result from the rearrangement of the surfactant among the layers [55] or from the evaporation of some water [56]. The presence of MAPP basically does not change the gallery structure of the silicate, obviously microcomposite was prepared, as expected. The behavior of the two organophilized silicates in real composites is in complete agreement with our expectations and with the results presented above. CPCI does not contain an active hydrogen atom, thus cannot react with MAPP, and the filler organophilized with it cannot form intercalated or exfoliated composites like the silicate modified by HDA. This fact also emphasizes the importance of chemical reactions compared to direct dipole like or hydrogen bridge interactions.

4. Conclusions

Model reactions carried out with components frequently used for the preparation of intercalated or exfoliated PP nanocomposites proved that maleinated polypropylene can react chemically with the surfactant applied for the organophilization of the filler if this latter contains active hydrogen groups. The reaction of hexadecylamine and MAPP was detected by MALDI-TOF spectroscopy, DSC measurements and FTIR spectroscopy. Anhydride groups were consumed and mainly amide groups formed in the reaction. The formation of cyclic imides could not be proved by the techniques used. MAPP reacted also with the surfactant adsorbed on the surface of the silicate in ionic form. On the other hand, CPCI not containing active hydrogen atoms did not react with maleinated PP. Intercalated or exfoliated composite could be prepared from the silicate organophilized with HDA, while microcomposite formed from the filler treated with CPCI. Chemical reactions remove the surfactant from the surface of MMT and hydrogenated silicate sites are left behind. The high energy surface interacts either with the anhydride or the amide groups by dipole–dipole interactions. Even the unmodified polypropylene chains may be attached much stronger to the surface by London dispersion forces than to the silicate covered by aliphatic chains. Although the effect of competitive adsorption (MAPP, HDA) and mutual solubility of the components (PP, MAPP, surfactant, reaction products) cannot be neglected, chemical reactions play a crucial role in structure formation in PP nanocomposites containing a functionalized polymer. Direct interaction of the silicate surface and the functionalized polymer as well as the formation of hydrogen bridges seem to play a lesser role, but the relative influence of processes may change with

the type of surfactant, functionalized polymer, surface coverage and processing conditions.

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