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Silane Treatment in Polypropylene Composites: Adsorption and Coupling

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Abstract: The study of the effect of eight silane coupling agents on mechanical properties of PP/$CaCO_3$ composites showed that the application of certain compounds leads to the reactive coupling of the components. The adsorption of the silanes on the surface of the filler was studied by a dissolution method, while the structure of the adsorbed layer was determined by FTIR spectroscopy and GPC measurements. Model reactions and an FTIR study were carried out to reveal possible coupling reactions of PP and the active silanes. The results showed that amino-functional silane coupling agents adsorb on the surface of the filler, polycondensation taking place and a polysiloxane layer of high molecular weight forms as a result. The model reactions indicated that during processing, PP oxidizes even in the presence of stabilizers and oxygen-containing functional groups form on the polymer chains. These easily react with the amino functionality of the silane coupling agents strongly bonding the polymer to the treated filler.

INTRODUCTION

Organofunctional silanes are extensively used for the surface treatment of glass fibers and glass beads introduced into thermoset matrices (Refs. 1,2). These reactive coupling agents form chemical bonds with the active hydroxy groups of the filler and their functional group reacts with the resin during curing (Ref. 3). The strong covalent bonds formed in these reactions make possible efficient stress transfer and the utilization of the reinforcing effect of fibers. The success of these coupling agents in thermoset composites leads to extensive attempts to use them also in other polymers in spite of the fact that the proper conditions of reactive coupling do not always exist. Polypropylene is a nonpolar polymer without any reactive groups on the chain; thus, silanes can hardly be expected to act as efficient coupling agents in its composites. Nevertheless, occasionally reactive coupling and improvement of mechanical properties were observed even in particle-filled PP composites (Ref. 4), but an acceptable explanation has not been given for the phenomenon so far. Another difficulty is expected in PP/$CaCO_3$ composites since this filler does not contain active OH groups on its surface.

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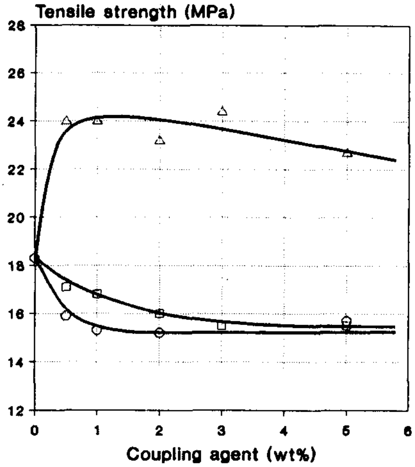


Fig. 1 *Effect of silane coupling agents on the strength of PP/$CaCO_3$ composites; (Δ) AMPTES, (□) SPTES, (O) STAC (for codes, see Table 1); filler content: 20 vol.-%*

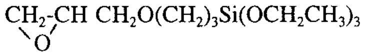
In an extended study (Refs. 5-8), a $CaCO_3$ filler was surface-treated with eight organofunctional silanes, both commercial and laboratory products, composites were prepared and their tensile properties determined. The efficiency of the silanes as coupling agents was checked and quantitatively evaluated by a simple semiempirical model developed earlier (Refs 9,10). In some cases, reactive coupling was observed in accordance with literature references (Ref. 4). This effect is well demonstrated by Fig. 1 where tensile strength of the composites is plotted against the surface coverage of the filler. It is apparent that the aminosilane has a strong reactive coupling effect, while stearic acid, used as a reference, and the other silane coupling agents act as nonreactive treating agents, surfactants. These apparently contradictory results initiated a detailed study of the interactions between the filler and coupling agents on the one hand, and between the silanes and the polymer on the other. This paper contains the most important results of this study and attempts to give a tentative explanation both for the different behaviour of the coupling agents and the mechanism of reactive coupling in PP/$CaCO_3$ composites.

EXPERIMENTAL

The $CaCO_3$ filler used (Omyacarb 2GU, Omya, Switzerland) had an average diameter of 2.5 μm and specific surface area of 3.59 m^2/g. The silane coupling agents used are listed in Table 1. The chemical structure of the original and adsorbed silanes was characterized by FTIR spectroscopy. A Mattson Galaxy 3020 apparatus was used for the registration of transmittance spectra, while DRIFT spectra were taken by a Bio-Rad FTS 65A/896 apparatus.

Surface treatment was carried out by two different techniques, dry blending and adsorption from butan-1-ol solution. The first procedure was used for the determination of the adsorption of the silane on the filler surface (dissolution method; Refs 11,12). 200 g of $CaCO_3$ was

Table 1 Coupling agents used for surface treatment

Coupling agent	Formula	Grade	Source
SPTES	$CH_3(CH_2)_{16}COO(CH_2)_3Si(OCH_2CH_3)_3$	-	laboratory
PPTES	$CH_3(CH_2)_7COO(CH_2)_3Si(OCH_2CH_3)_3$	-	laboratory
ACPTES	$CH_3COO(CH_2)_3Si(OCH_2CH_3)_3$	-	laboratory
MPTMS	$CH_2=C(CH_3)COO(CH_2)_3Si(OCH_3)_3$	GF 31	Wacker
CVBS	$CH_2=CHC_6H_4CH_2NH(CH_2)_2NH(CH_2)_3Si(OCH_3)_3 . HCl$	Z 6032	Dow Corning
GPTES	 $\underset{\diagdown O \diagup}{CH_2\text{-}CH}\ CH_2O(CH_2)_3Si(OCH_2CH_3)_3$	SLM 50-882	Wacker
CHAPTMS	cyclohexyl-$NH(CH_2)_3Si(OCH_3)_3$	SLM 50-892	Wacker
AMPTES	$NH_2(CH_2)_3Si(OCH_2CH_3)_3$	GF 93	Wacker
STAC	$CH_3(CH_2)_{16}COOH$	-	-

dry-blended with various amounts of the silane coupling agents (0-5 wt.-%) and the filler was stored for two days under ambient conditions. 20 g of the treated filler was stirred in 100 ml of cyclohexane or methanol for 30 min and then left standing for a day. The suspension was centrifuged and the silane content of the solution was determined by FTIR or HPLC. The amount of adsorbed silane was calculated from the measured concentrations. The adsorption of aminosilanes was determined in methanol, while that of all other compounds in cyclohexane. In the other procedure, 700 g of $CaCO_3$ was stirred in 700 ml of butan-1-ol for 3 h, the slurry was left standing for 3 days and then the solvent was removed under vacuum. Prehydrolysis, usually recommended in the literature (Ref. 3), was not used in either procedure.

The structure of the adsorbed silane was characterized by DRIFT and FTIR before and after washing with THF. The molecular weight of the dissolved silanes was determined by GPC (Waters 510, Viscotek 200 detector).

Reactions between PP (Tipplen H 327, TVK, Hungary; MFI 10 g/10 min at 230 °C and 21.6 N) and the silanes were carried out in an internal mixer (Brabender W 50 EH) at 190 °C. 2 ml of a silane coupling agent was added to the melt of 35.9 g PP. Approximately 0.1-g samples were taken in 5- or 10-min intervals from the mixture. They were compression-moulded (Fontijne SRA 100) into 100-μm thin films, then extracted either in chloroform or methanol depending on the silane coupling agent used in the reaction. Extraction was carried out for 12 h in a Soxhlet extractor. FTIR spectra of the films were recorded before and after extraction. Various model reactions were also carried out. Oxidation of PP was accelerated by the introduction of O_2, while cumene hydroperoxide was added to increase the concentration of free radicals in the melt. The reactions were carried out both with neat PP and also in the presence of silanes.

RESULTS AND DISCUSSION

Principal condition of reactive coupling is chemical reaction, or at least a very strong interaction of both components with the coupling agent. As a consequence, we must study first the filler/coupling agent, then the coupling agent/polymer interaction in order to find a plausible explanation for the observed reactive coupling effect in the non-reactive system studied. The results of these investigations are reported in the following paragraphs.

Adsorption of coupling agents

As mentioned before, the interaction of the filler and the polymer can be characterized by a dissolution technique developed earlier (Refs. 11,12). Dissolution curve characteristics of nonreactive coupling are presented in Fig. 2. The amount of the bonded coupling agent is plotted against the coupling agent concentration used for the treatment. At low amounts, all the coupling agent is bonded to the surface, but at higher concentrations, equilibrium adsorption is reached. Two characteristic quantities can be derived from the dissolution curve: the concentration of the proportionally bonded coupling agent (c_{100}) and the value of maximum adsorption (c_{max}). c_{100} approximately corresponds to the monolayer coverage of the filler by the coupling agent and its value depends on the specific surface area of the filler, on the surface requirement and orientation of the low-molecular-weight compound, and on other conditions of

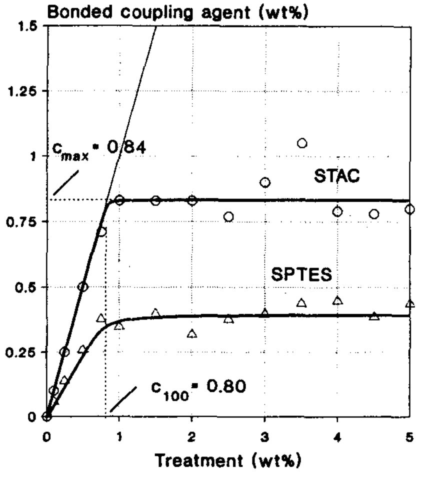


Fig. 2 *Dissolution curves of STAC and SPTES*

the dissolution measurement (solvent, temperature, concentration). According to the figure, the silane containing a long alkyl chain (SPTES) behaves very similarly to stearic acid, the surfactant most often used for the non-reactive treatment of $CaCO_3$. The only difference is found in the first, proportionally bonded region of the dissolution curve, the slope being here smaller than unity. The decreased slope is probably the result of the complex competitive processes of adsorption and dissolution taking place during the measurement (adsorption of silane and solvent, dissolution of silane). Since PPTES has a structure similar to SPTES, its dissolution is also very similar to the one presented in Fig. 2.

The type and size of the organofunctional group play an important role in the adsorption of the coupling agent on the filler surface. As Fig. 3 shows, MPTMS adsorbs in larger amounts and the adsorption continues up to the largest concentration used. A further increase in the amount of adsorbed coupling agent is shown by amino-functional silanes, virtually the total amount of AMPTES being bonded to the filler surface. These results prove that silane coupling agents adsorb on the surface of $CaCO_3$. The amount and strength of the adsorption depend on the structure of the silane and primarily on the size and character of the organofunctional group. Aminosilanes bond especially strongly to the surface, probably due to the catalytic effect of the amino group which increases the rate of polycondensation of the silane.

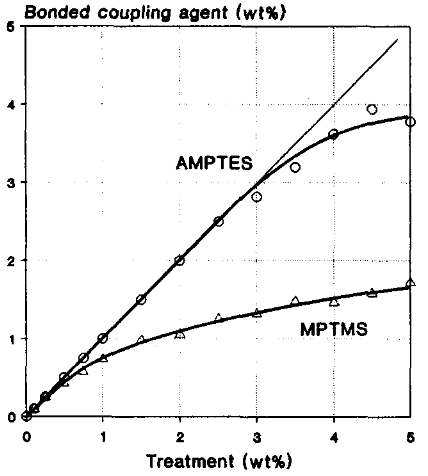


Fig. 3 *Dissolution curves of MPTMS and AMPTES*

The FTIR spectrum of SPTES and the DRIFT spectrum of $CaCO_3$ treated with this coupling agent are presented in Fig. 4. The figure clearly shows that profound changes take place in the structure of the silane due to adsorption. Analysis of the spectra and comparison with literature data show that polycondensation of the silane takes place during treatment and the following storage. The spectrum indicates that a polysiloxane with cage-like polycyclic structure forms

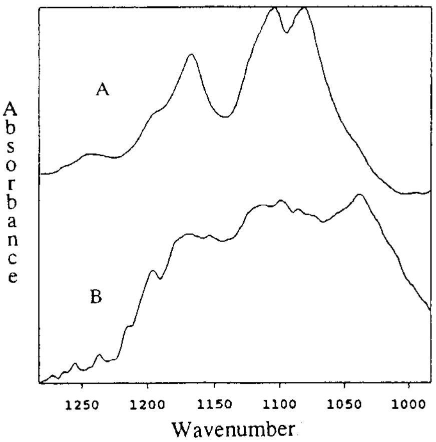


Fig. 4 *(A) FTIR spectrum of neat SPTES, (B) DRIFT spectrum of adsorbed SPTES*

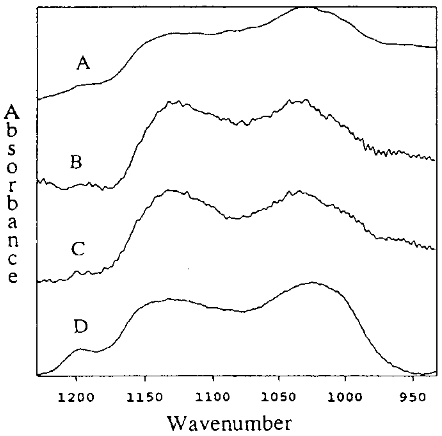


Fig. 5 *Spectra of polysiloxane formed from AMPTES: (A) butan-1-ol treatment, (B) dry-blending, (C) after washing with THF, (D) neat AMPTES film*

from SPTES (Refs. 13,14). This result verifies our procedure and proves that prehydrolysis of the silane before treatment is not necessary. The cage-like structure leads to poor resistance to solvents; the polysiloxane can be completely removed from the surface by washing with THF.

Also AMPTES forms a polysiloxane layer on the surface of the filler, but the structure and properties of the polymer are completely different. Parts of four spectra are compared in Fig. 5. Spectrum A was obtained on the filler treated with butan-1-ol. Virtually the same spectrum is obtained when the treatment was carried out by dry blending (B). The spectrum does not change on washing the filler with THF (C) and completely corresponds to that of a polysiloxane film prepared by polycondensation of neat AMPTES (D). The spectrum of the hard, transparent film obtained by simple storage of AMPTES in a crystallization dish under laboratory conditions was recorded by transmittance FTIR. The results unambiguously prove several points: (i) Polymerization of the silane takes place on the surface of the filler. (ii) The structure of the polysiloxane is the same in all cases. (iii) The treatment technology does not influence the structure of the adsorbed layer. (iv) The structure of the film formed from AMPTES is different from that of SPTES, an open, ladder-type polysiloxane network being formed in the former case. (v) The structure of the adsorbed layer depends mainly on the size and type of the organofunctional group of the silane.

Table 2 Fraction of bonded silane, relative amount and molecular weight of the polysiloxane fractions dissolved from the filler surface by THF

Coupling agent	Bonded silane (%)	Molecular weight					
		1 000 - 4 000		4 000 - 50 000		> 50 000	
		M_w	amount	M_w	amount	M_w	amount
SPTES	0	3 080	1.00	4 140	1.04	131 300	0.08
PPTES	12	2 330	1.00	5 070	2.30	166 170	0.40
ACPTES	43	1 290	1.00	5 580	2.90	169 400	3.70
MPTMS	0	-	-	-	-	-	-
GPTES	89	1 660	1.00	-	-	149 000	0.80
CVBS	45	-	-	37 400	1.00	142 800	3.10
CHAPTMS	56	-	-	-	-	136 900	1.00
AMPTES	93	-	-	-	-	139 500	1.00

Both the molecular weight of the polysiloxane layer and its resistance to THF depend on the chemical structure of the silane. Molecular weights of different fractions and the amount of the adsorbed polymer determined from the FTIR spectra after washing with THF are presented in Table 2. The molecular weight distribution of the polysiloxane was usually bimodal, sometimes even more than two peaks being observed (Fig. 6). The heights of the peaks were always related to the smallest one, which gives an estimate of the relative amount of different fractions. As Table 2 and Fig. 6 show, the molecular weight and the amount dissolved change strongly from one silane to the other. The silanes with long chains give polymers of low molecular weights which can be dissolved from the surface of the filler with THF easier than those formed from silanes with smaller organofunctional groups. Aminosilanes invariably transform to high-molecular-

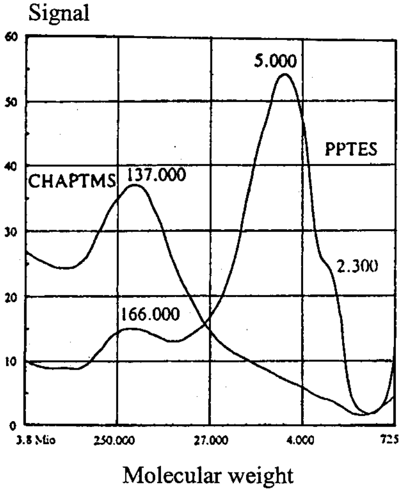


Fig. 6 *Molecular weight distribution of polysiloxanes dissolved from the surface of $CaCO_3$ treated with PPTES and CHAPTMS*

weight polysiloxanes, which strongly resist dissolution with THF.

The results clearly prove that polycondensation of silane coupling agents occurs always on the surface of an inorganic filler and, in spite of the absence of chemical coupling, the polymer formed may be attached strongly to the surface. The possibility of a strong coupling agent/filler interaction having thus been proved, the chemical coupling of the polysiloxane layer and polypropylene must be now verified.

Coupling reactions

A great number of papers were published on the thermooxidative degradation of polymers including PP (e.g., Refs. 15,16). During the processing of the polymer under atmospheric conditions, hydroperoxides form and β-scission of the polymer takes place leading to the formation of oxygen-containing groups on the chain (Ref. 16). Rabek (Ref. 15) analyzed the reaction products and determined their relative amounts under various processing conditions showing that a considerable amount (~25 %) of carboxylic acids forms in the polymer.

Model reactions were carried out in order to check the possibility of carbonyl formation under the condition of sample preparation. Carbonyl groups were detected in the PP matrix used for the preparation of our composites in spite of the presence of stabilizers (Fig. 7). The new absorption band detected at 1723 cm^{-1} was assigned to the carbonyl group of saturated ketones, aldehydes and acids (Ref. 17). The presence of cumene hydroperoxide, i.e. an increase in the concentration of free radicals, accelerates the formation of carbonyl groups as it is shown in Fig. 7. Oxygen exerts its effect after 20-30 min of mixing, when the

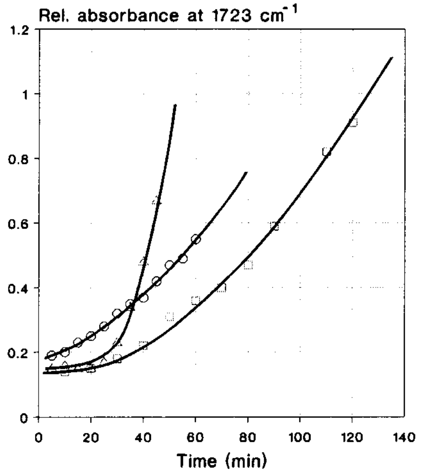


Fig. 7 *Carbonyl formation in PP as a function of homogenization time at 190 °C, (□) neat PP, (○) cumene hydroperoxide added, (Δ) oxygen presence*

carbonyl group content in the polymer sharply increases. Although the exact chemical reactions leading to these changes are not known, it is clear that functional groups form during the processing of PP even in the presence of stabilizers. One might object that the reaction times used here are long compared with the time of homogenization. However, we must bear in mind that the sensitivity of IR spectroscopy is not exceptionally high and that a few bonds are sufficient to increase interaction significantly. According to the results, the carbonyl groups and in particular the acid groups are the only candidates which can react with the coupling agents forming covalent bonds.

Possible reactions of three silane coupling agents were studied in further model reactions. Because of limited space, only the results obtained on AMPTES are presented here. Extraction of the films used for the monitoring of chemical changes in the polymer gave unambiguous proof of the coupling of the silane and the polymer. Only a limited extent of such coupling occurred between PP and MPTMS, but AMPTES was already totally bonded to the polymer after a short mixing time. The spectra of the samples taken after 10 min of mixing are virtually identical before and after extraction (Fig. 8, spectra 2 and 3). The same conclusion can be drawn from Fig. 9 showing the changes in the concentration of various functional groups as a function of mixing time.

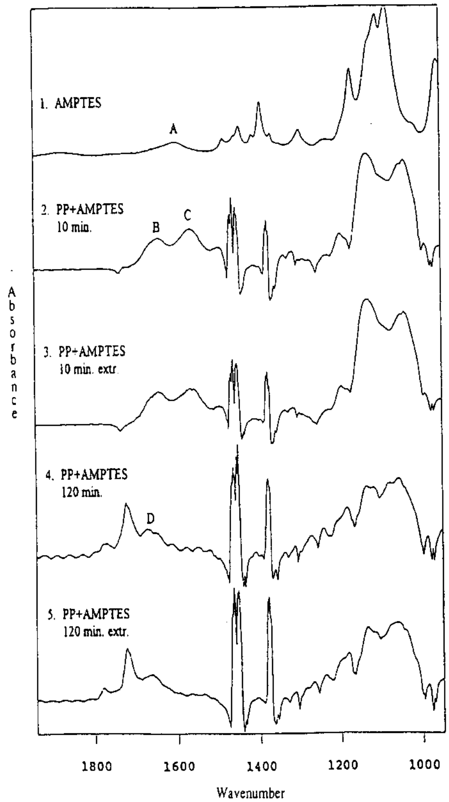
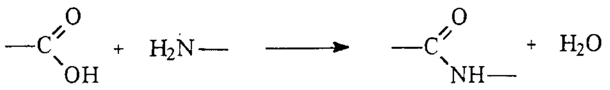


Fig. 8 *FTIR difference spectra of the reaction product of PP and AMPTES*

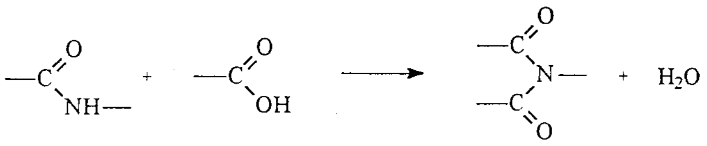
The absorbance at 1596 cm^{-1} appearing in the spectrum of AMPTES (Fig. 8, spectrum 1, A) can be assigned to the deformational vibration of the N-H bond in the primary amine group (Ref. 17). After 10-min reaction time, this band disappears and two bands appear at lower and higher wavenumbers, at 1640 (B) and 1563 $\mathrm{cm^{-1}}$ (C). According to Refs. 18-21, the amide I (C=O) vibration of secondary amides in the solid state appears between 1680-1630 $\mathrm{cm^{-1}}$.

The intensity of deformational vibration of the N-H bond of a secondary amide absorbs in the range of 1581-1518 $\mathrm{cm^{-1}}$ (see Ref. 17). Accordingly, we may assume that the above mentioned vibrations at 1640 and 1563 $\mathrm{cm^{-1}}$ are the amide I and amide II bands of a secondary amide, respectively. We showed above (see Fig. 7) that significant amount of carboxyl groups form during the processing of PP, which can react with the amino functionality of AMPTES.



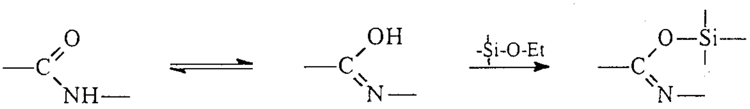
$$-\mathrm{C}(=\mathrm{O})\mathrm{OH} + \mathrm{H_2N}- \longrightarrow -\mathrm{C}(=\mathrm{O})\mathrm{NH}- + \mathrm{H_2O} \qquad (1)$$

The intensity of the deformational vibration of the N-H bond (amide II) gradually decreases with increasing reaction time, while the amide I absorption shifts to higher wavenumbers. After 120 min, an absorption band appears at 1670 $\mathrm{cm^{-1}}$ (Fig. 8, Spectrum 4, D). The double band appearing at 1790-1720 $\mathrm{cm^{-1}}$ and 1710-1670 $\mathrm{cm^{-1}}$ can be assigned to the symmetric and antisymmetric C=O vibration of imides (Refs. 17,22,23). This suggests the possibility that the secondary amide enters into reaction with another acid group forming imides:



$$-\mathrm{C}(=\mathrm{O})\mathrm{NH}- + -\mathrm{C}(=\mathrm{O})\mathrm{OH} \longrightarrow (-\mathrm{C}(=\mathrm{O}))_2\mathrm{N}- + \mathrm{H_2O} \qquad (2)$$

Theoretically, the tautomeric conversion of the amide to unstable imidic acid is also possible, which may react further with the free, not hydrolyzed -Si-O-Et groups resulting in the stable silyl ester of imidic acid:



$$-\mathrm{C}(=\mathrm{O})\mathrm{NH}- \rightleftharpoons -\mathrm{C}(\mathrm{OH})=\mathrm{N}- \xrightarrow{-\mathrm{Si-O-Et}} -\mathrm{C}(\mathrm{O{-}Si}{-})=\mathrm{N}- \qquad (3)$$

The C=N vibration of the formed imidate appears at 1690-1645 $\mathrm{cm^{-1}}$ (see Ref. 23). This may explain the appearance of band D around 1670 $\mathrm{cm^{-1}}$ and the disappearance of the amide II band as well. However, the existence of free ethoxysilyl groups in the melt at long reaction times is not probable.

Time dependence of the changes in the concentration of various functional groups is presented in Fig. 9. The intensity of carbonyl absorbance increases with reaction time (P in Fig. 9) similarly to the virgin PP (Fig. 7). However, in the AMPTES/PP reaction, the carbonyl content increases only after an induction period of 30-40 min, its value up to this point being zero. The difference may be explained by the immediate reaction of the primary amino group of AMPTES with the forming carboxyl groups of the polymer. After approximately 40 min, all free NH_2 groups are consumed and carbonyl absorption appears in the spectrum. After a slight initial decrease, the total amount of amide and imide (or imine) groups (B, D) seems to remain constant up until the end of the reaction. The amide groups transform into imides according to (2) resulting in a continuous decrease in the NH content (Fig. 9, C). After 80 min, all the secondary amide is consumed, the total amount having been converted to imide (or imidate).

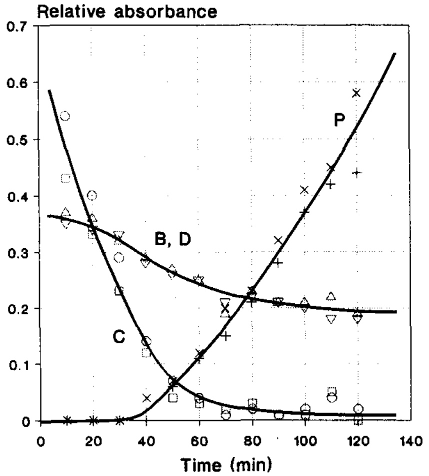


Fig. 9 *Reaction of PP with AMPTES, change in functional group content with reaction time; P: carbonyl, C: amide II, B,D: amide I and imide, (x, O, Δ) before extraction, (+, □, ▿) after extraction*

After 10-min reaction time, the anti symmetric stretching vibration of the triethoxysilyl group of AMPTES at 1103 and 1080 cm^{-1} completely disappears and a new double band appears at 1128 and 1039 cm^{-1}. These absorption bands are characteristic of high-molecular-weight polysiloxane chains (Refs. 13,14) (Fig. 8, spectrum 2). According to the spectrum, AMPTES reacts with some moisture present (see, e.g., reactions 1 and 2), hydrolysing and condensing to polysiloxane even at a high reaction temperature (190 °C).

The results show that AMPTES enters into chemical reactions with the polymer matrix immediately after melting. The chemical bonds formed are stable, they cannot be disrupted even by 12-h extraction. FTIR spectra indicate that secondary amide forms in the chemical reaction between the primary amino group of AMPTES and the carboxyl groups continuously forming in the PP. Since this reaction seems to proceed very fast, we can assume that it takes place also during the homogenization of PP/$CaCO_3$ composites.

CONCLUSIONS

The above presented results clearly show that reactive coupling of the components is possible in a relatively inert system like the PP/$CaCO_3$ composite if organofunctional silane coupling agents are used. Surface treatment of the filler with various silanes always leads to the polycondensation of the coupling agent. Polymerization takes place even in the absence of prehydrolysis and the structure of the polysiloxane layer is independent of the surface treatment technique. On the other hand, both the structure and molecular weight of the polysiloxane depend very much on the organofunctional group of the coupling agent. Large groups lead to a low- molecular-weight polymers, which can be easily dissolved from the surface of the filler. Small groups result in a high-molecular-weight product, which adheres more strongly to the filler. Polycondensation of aminosilanes is especially fast and also adhesion of the polymer is very strong, which might be explained by the catalytic effect of the amino group on the condensation reaction.

Model reactions proved that PP is oxidized during processing even in the presence of stabilizers leading to the formation of reactive groups on the polymer chain. These groups react with the amino functionality of the silane forming strong amide groups. The strong adhesion of the polysiloxane layer on the surface of the filler and the chemical reaction of this polymer layer with PP leads to the observed reactive coupling of the otherwise non-reactive components, PP and $CaCO_3$.

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