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Possible coupling reactions of functional silanes and polypropylene

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Abstract

Apparent reactive coupling of $CaCO_3$ to polypropylene (PP) was achieved with the application of aminofunctional silane coupling agents. The strong coupling effect could be attributed to increased $CaCO_3$/silane and PP/silane interaction. A detailed study has shown that aminofunctional silanes bond strongly to the surface of the filler, but in the case of multilayer coverage also to the previous layers. Experiments were carried out to determine the mechanism of interaction between the silane coupling agents and the apolar polypropylene, which does not contain reactive groups. Model reactions followed by (Fourier Transform Infrared Spectroscopy) FTIR analysis demonstrated that during processing at elevated temperatures, oxidation of the polymer takes place in spite of the presence of stabilizers. Reactive carbonyl groups form as a result, which enter into chemical reactions with the amino functionality of the silane, resulting in strong amide bonds.

Keywords: Reactive coupling; Particulate-filled composites; Silanes

1. Introduction

Surface treatment of fillers and reinforcements is a well-known way to modify the interfacial interaction in polymer composites [1–5]. Non-reactive treatment results in a decrease in the surface tension of the filler leading to a decrease in particle/particle and particle/polymer interaction [6,7]. As a result, aggregation of the filler decreases, homogeneity, surface quality and processability improve, but the yield stress and tensile strength of the composite decrease. Reactive treatment assumes the presence of reactive groups both on the surface of the filler and in the polymer matrix [8–13]. $CaCO_3$ does not have active -OH groups on its surface which could react with silanes. Thermoplastic polymers, especially the apolar polyolefines, are also inactive, since their polymer chain does not contain any reactive groups, reactive coupling is not expected in such systems.

Trialkoxy functional silane coupling agents containing reactive organofunctional groups have been successfully applied for the treatment of glass fibres embedded in thermoset resin matrices [11–13]. In such systems, the coupling agent can react with the active surface of the fibre and the reactive groups of the resin [13]. Because of the high efficiency of silanes in advanced composites, they are often also used in experiments in polyolefines filled with mica, $CaCO_3$ or other mineral fillers [14–17]. Although occasionally their successful application is reported in polypropylene filled with various fillers [14,15,18], neither the reason for this success or the mechanism of the interaction are clear.

In a previous study, the reactive coupling effect of two aminofunctional silanes [(3-aminopropyl)triethoxysilane, AMPTES and *N*-(4-vinylbenzyl)-*N*′-(3-trimethoxysilylpropyl)-ethylenediamine hydrochloride, CVBS] was demonstrated in PP/$CaCO_3$ composites, resulting in enhanced tensile strength and decreased deformability compared to the non-treated system [19,20]. Analysis of the interaction between the silane coupling agents and $CaCO_3$ showed that aminofunctional silanes adhere to the surface of the filler much stronger than other silane coupling agents [21]. Dissolution experiments [7,22] proved that the adhesion between subsequent silane layers is as strong as the adhesion between the surface and the first layer, while in the absence of amino group, the silane coupling agents could easily be dissolved from the surface of the filler.

This paper focuses on the mechanism of interaction between the silane coupling agents and the polypropylene matrix. The results of model experiments are reported, the possible reactions analysed and a tentative explanation developed to explain reactive coupling in an apparently inert system.

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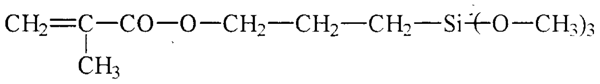
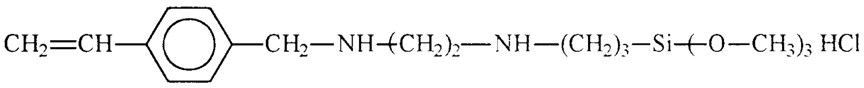
Table 1
Silane coupling agents used in the model reactions

Abbr.	Formula	Grade	Producer
MPTMS	 $CH_2{=}C(CH_3){-}CO{-}O{-}CH_2{-}CH_2{-}CH_2{-}Si{(O{-}CH_3)}_3$ (3-methacryloxypropyl)trimethoxysilane	GF31	Wacker
CVBS	 N-(4-vinylbenzyl)-N'-(3-trimethoxysilylpropylethyl)enediamine, hydrochloride	Z6032	Dow Corning
AMPTES	$NH_2{-}CH_2{-}CH_2{-}CH_2{-}Si{(O{-}CH_2{-}CH_3)}_3$ (3-aminopropyl)triethoxysilane	GF93	Wacker

2. Experimental

The effects of the coupling agents on PP/$CaCO_3$ interaction were checked in a series of experiments. A PP homopolymer (Tipplen H 327, TVK, Hungary) MFI = 10 g/10 min(230°C/21.6 N) was used, the $CaCO_3$ filler applied (Omyacarb 2 GU, Omya, Switzerland) had an average particle diameter of 2.5 μm and a specific surface area 3.59 m^2/g (BET, N_2 at 77K). A series of composites was prepared from the filler treated with each coupling agent. The volume fraction of the filler was changed from 0 to 0.3 volume fraction in steps of 0.05. Homogenization of the composites was carried out in an internal mixer (Brabender W 50 EH) at 43 ml charge volume, 190°C, 50 rpm for 10 min in air. The homogenized material was compression-moulded into 1-mm-thick plates at 190°C (Fontijne SRA 100). Specimens for tensile testing were cut from the compression-moulded plates. Young's modulus (E) was determined at 0.5 mm/min cross-head speed and 50 mm gauge length, while yield (σ_y, ϵ_y) and ultimate properties (σ, ϵ) were determined at 5 mm/min and 55 mm gauge length. Further details and the results of these experiments are discussed in detail elsewhere [20].

For the model experiments, 35.9 g PP was introduced into an internal mixer (Brabender W 50 EH) at 190°C. Two millilitres of the silane coupling agents, listed in Table 1, was added to the melt. Approximately 0.1 g samples were taken at 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 agents used in the reaction. Extraction was carried out for 12 h in a Soxhlet-extractor. FT*ir* spectra (Mattson Galaxy 3020) of the films were recorded before and after extraction. The spectrum of the virgin PP was subtracted from all spectra recorded, thus only difference spectra are presented in this paper, with the exception of the reference spectra of virgin materials, of course.

Various model reactions were carried out. Oxidation of PP was accelerated by the introduction of O_2, while cumene hydroperoxide (CHPO) 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. The model reactions were carried out and their conditions are summarized in Table 2.

Table 2
Model reactions and their conditions

Silane	Silane amount (g)	(wt%)	Additive Type	Amount	Reaction time (min)	Extraction solvent
—	—	—	—	—	120	—
—	—	—	CHPO	0.044 g	60	—
—	—	—	O_2	cont. flow	45	—
MPTMS	2.10	5.9	—	—	120	$CHCl_3$
MPTMS	2.10	5.9	CHPO	0.044 g	60	$CHCl_3$
MPTMS	2.10	5.9	O_2	cont. flow	60	$CHCl_3$
CVBS	1.80	2.0	—	—	120	CH_3OH
AMPTES	1.89	5.3	—	—	120	CH_3OH

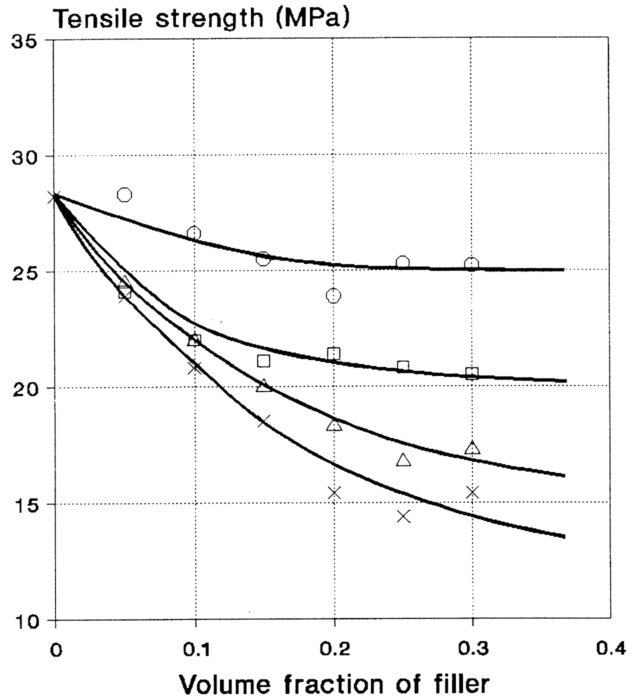


Fig. 1. Composition dependence of the tensile strength of PP/$CaCO_3$ composites. Treatment: (△) 0, (x) 1.3% MPTMS, (□) 0.7% CVBS, (○) 0.8% AMPTES [20].

3. Results and discussion

The tensile strength of PP/$CaCO_3$ composites is plotted against their filler content in Fig. 1. AMPTES and CVBS have a clear reactive coupling effect, their composite strength increases. (3-Methacryloxy-propyl)-trimethoxy-silane (MPTMS), on the other hand, exerts only a non-reactive, surfactant effect, in spite of the reactive double bond in its organofunctional ligament. This group should take part in radical reactions which might occur during the homogenization of the composite. An attempt was made to explain the inefficiency of MPTMS as a coupling agent, on the one hand, and the strong coupling effect of the aminofunctional silanes, on the other [20].

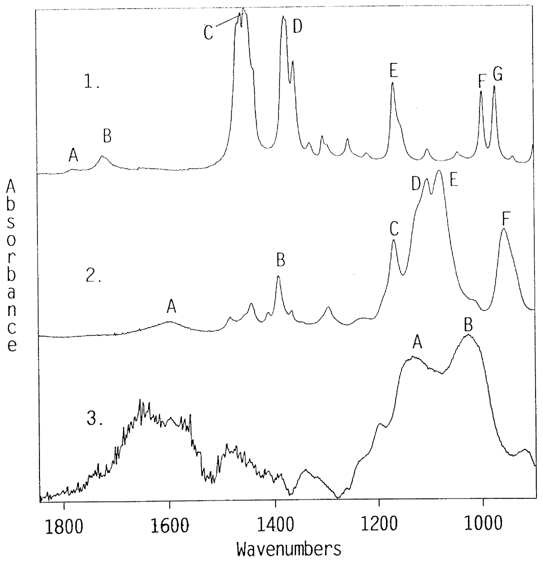


Fig. 2. Assignment of vibrations used for the detection of chemical reactions in model experiments. Spectra: (1) PP oxidized in air for 120 min, (2) neat AMPTES, (3) AMPTES hydrolysed in air (see Table 3).

Model reactions and FTIR analyses were used for the detection of chemical reactions leading to chemical coupling of the polymer and filler. To facilitate the understanding of the following discussion, the relevant sections of three spectra are presented in Fig. 2, while the assignment of the characteristic vibrations can be found in Table 3. As was indicated in the Experimental, difference spectra were used for the evaluation almost exclusively, the spectrum of

Table 3

Assignment of characteristic bands in the FTIR spectra of oxidized PP (spectrum 1), neat AMPTES (spectrum 2) and its hydrolysed form (spectrum 3) in Figure 2. Notation by Ref. [38].

Identification		Group, bond	Vibration	Wavelength (cm^{-1})	Ref.
Spectrum	Band				
1	A	γ-lactone	νC=O	1779	[39,40]
	B	aldehyde, ketone, acid	νC=O	1723	[27]
	C	C–H in -CH_3	δ_{as}C–H	1446–1466	[27]
	C	C–H in -CH_2-	β_sC–H	1446–1466	[27]
	D	C–H in -CH_3	δ_sC–H	1375	[27]
	E		νC–CH_3	1166	[32]
	F		$\gamma CH_3 + \nu$C–C	997	[39]
	G		$\gamma CH_3 + \nu$C–C	973	[39]
2	A	primary amine	$\beta_s NH_2$	1596	[27]
	B	C–H in -CH_3	$\beta_s CH_3$	1390	[27]
	C	ethoxy in silyl ester	Si-O-C	1166	[27]
	D		ν_{as}Si–O—C	1103	[27]
	E		ν_{as}Si–O—C	1080	[27]
	F		ν_sSi-O-C	957	[27]
3	A	polysiloxane	ν_{as}Si–O—Si	1133	[34], [35]
	B	polysiloxane	ν_{as}Si–O—Si	1125	[34], [35]

Table 4
Formation of functional groups in PP at various processing conditions [23]

Functional group	Relative amount (%) at conditions 2 h/138°C	1 h/210°C
γ-Lactone	17	7
Aldehyde	21	21
Ketone	21	21
Acid	25	25
Ester	16	0
Vinyl-alkene	—	26

the neat polymer was subtracted from all spectra recorded on the reaction mixtures.

3.1. Oxidation of PP

A large number of papers was published on the thermo-oxidative degradation of polymers including PP [23–26]. During the processing of the polymer under atmospheric conditions [24], hydroperoxides form and β-scission of the polymer takes place leading to the formation of various oxygen-containing groups on the chain. Rabek [23] analysed the reaction products and determined their relative amounts at different processing conditions (Table 4).

Carbonyl groups were also detected in the PP-matrix used for the preparation of our composites [19,20]. Two new absorption bands appeared at 1779 and 1723 cm^{-1} in the FT*ir* spectrum of the PP processed in the internal mixer: the first can be assigned to the stretching vibration of the C=O group of γ-lactone, while the second to the carbonyl group of saturated ketones, aldehydes and acids [27]. CHPO accelerates the formation of carbonyl groups already at the beginning of the homogenization (Fig. 3). Oxygen exerts its effect after 20–30 min mixing, after this interval the carbonyl group content of the polymer increases sharply. The presence of CHPO and oxygen induces the same changes in the concentration of γ-lactone (Fig. 4), although in oxygen its amount increases only after an induction period of about 25 min. Introduction of CHPO decreases this induction period to 5–10 min. Although these induction periods and the exact effect of oxygen and CHPO, as well as the related chemical reactions are difficult to explain, the above presented experiments clearly show that during homogenization reactive carbonyl groups form in our commercial PP in spite of the presence of stabilizers.

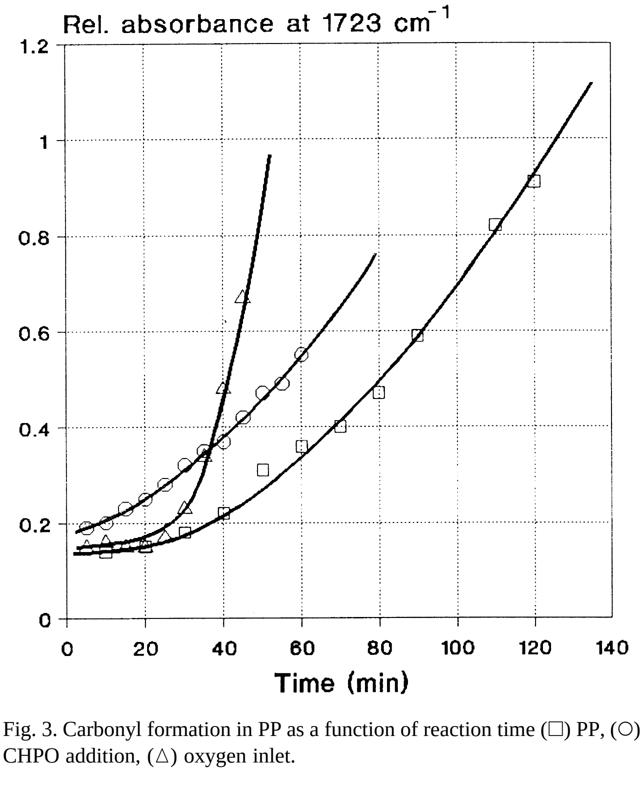


Fig. 3. Carbonyl formation in PP as a function of reaction time (□) PP, (○) CHPO addition, (△) oxygen inlet.

3.2. Reaction of MPTMS and PP

The introduction of MPTMS into PP leads to the appearance of two new absorptions at 1722 cm^{-1} and 1639 cm^{-1} corresponding to the vibration of the carbonyl group and the double bond of MPTMS, respectively. In Fig. 5, the changes in carbonyl group content are presented as a function of homogenization time. Mixing was carried out in the presence of oxygen. As homogenization proceeds, the MPTMS content of the polymer seems to approach each other before and after extraction, but never reaches the same level till the end of the mixing. The effect of extraction indicates that the total amount of MPTMS does not react with the polymer, a certain part can always be extracted. The maximum in MPTMS content detected at around 10 min mixing time is a result of the relative slow introduction of the silane into the mixer. Although the continuous decrease of carbonyl content before extraction can be explained by the lack of reaction and evaporation of MPTMS during mixing, the presence of the maximum after

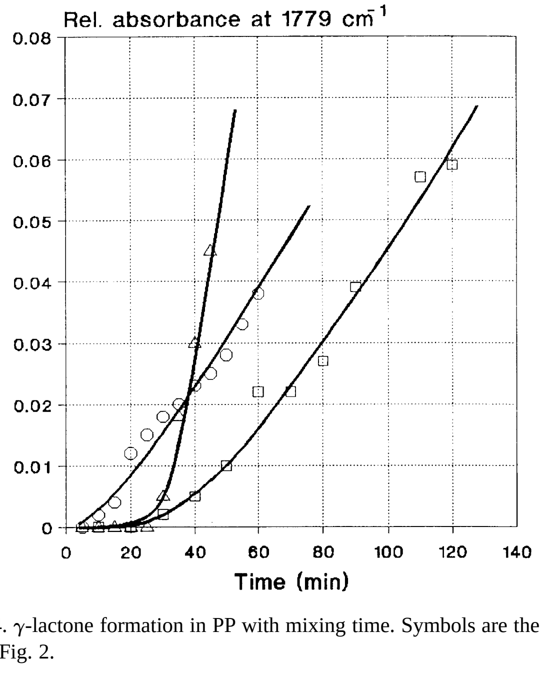


Fig. 4. γ-lactone formation in PP with mixing time. Symbols are the same as in Fig. 2.

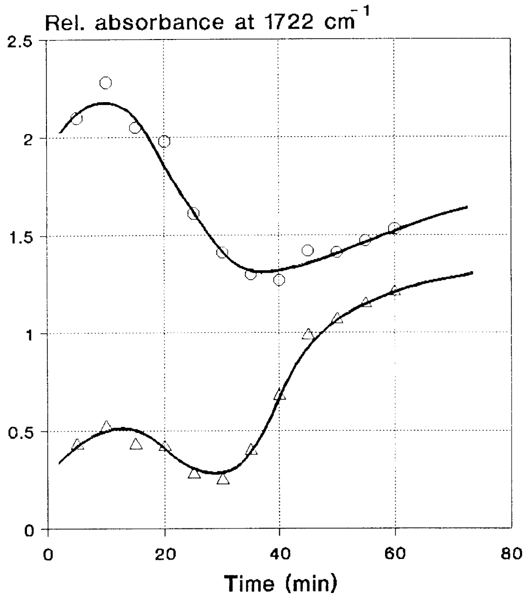


Fig. 5. Changes in the carbonyl content of PP in the presence of MPTMS and O_2 as a function of reaction time; (○) before extraction, (△) after extraction.

extraction is difficult to explain. Incomplete extraction, further reaction or decomposition might be the reason for the decrease in carbonyl content. The subsequent increase is caused by the oxidation of the polymer and not by the bonding of MPTMS, a fact which becomes obvious if we compare Figs 3 and 4.

MPTMS reacts more readily with PP in the presence of CHPO (Fig. 6), the maximum observed in Fig. 5 is absent here. The large difference between the carbonyl contents measured before and after extraction, however, clearly shows that only a relatively small portion of the silane reacts with the polymer. The continuous increase of carbonyl content, which is a combined effect of MPTMS addition and oxidation, does not make a more accurate analysis possible, and a separation of the processes taking place during mixing.

The double bond content of PP is influenced less by oxidation, although disproportionation and secondary reactions may lead to the formation and/or consumption of double bonds. The intensity of the double bond absorption at 1639 cm^{-1} is plotted against reaction time in Fig. 7. The results clearly show that the amount of unreacted MPTMS decreases with the time of mixing. The decrease may be the result of reaction, i.e. bonding to the polymer, or simply evaporation. The rate of decrease depends on processing conditions, i.e. on the presence of oxygen or peroxide. These differences indicate that the reaction of the silane and polymer is influenced by the presence of these components. However, the final double bond content of PP is the same, irrespectively of reaction conditions.

Unfortunately, this kinetic study and the analysis of the functional groups do not make the exact determination of the reactions of the silane and polymer possible. The slow decrease of double bond content indicates that even if MPTMS bonds into the polymer through its double bond, the reaction is rather slow. The total consumption of double bonds requires 50–60 min even in the fastest case. Chemical coupling through the double bond is supported by the effect of CHPO, its addition leads to the fastest reaction.

The 2000–1000 cm^{-1} wavenumber range of the difference spectra of PP reacted with MPTMS in air is presented in Fig. 8. The spectra of the virgin PP mixed for 120 min and that of the MPTMS are also included (spectra 1 and 2). The scale of absorbance is different in each case. After 10 min, a significant difference can be observed between the spectra

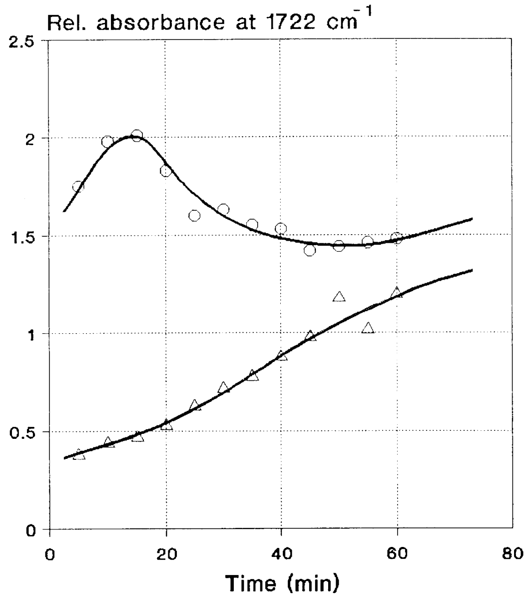


Fig. 6. Effect of CHPO on the carbonyl group content of PP containing MPTMS; (○) before extraction, (△) after extraction.

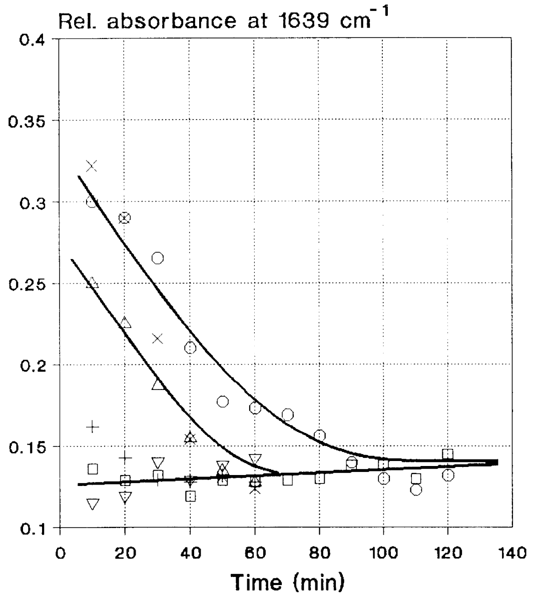


Fig. 7. Change in the double bond content of PP containing MPTMS as a function of reaction time and conditions. Before extraction: (○) air, (x) oxygen, (△) CHPO. After extraction: (□) air, (+) oxygen, (▽) CHPO.

recorded on the films before and after extraction in the region of the Si–O–Si vibration at 1200–1000 cm^{-1}. Before extraction, the spectrum (spectrum 3) corresponds to that of the neat MPTMS, the Si-O-CH_3 vibration dominates (spectrum 2), indicating that only a small part of the trimethoxy-silyl group hydrolyses and condenses to polysiloxane. During extraction (spectrum 4), the unreacted silane is removed, only that part of MPTMS remains in the matrix which is bonded to it. This part hydrolyses and converts to polysiloxane (disappearance of the strong ν_{as} Si-O-CH_3 band of the monomer at 1092 cm^{-1}, A in spectrum 3).

After 120 min mixing time, a considerable amount of MPTMS reacts with the polymer, all of which condenses, a combination of vibrations characteristic for the Si-O-Si bonds of a polysiloxane appears in this region. Spectra recorded before and after extraction are basically identical (spectra 5 and 6). In accordance with the results of Fig. 7, the vibration of the double bond at 1639 cm^{-1} (spectrum 3, B) completely disappears. Reaction of MPTMS with the polymer and the conversion of the trimethoxy-silyl group to polysiloxane continuously increases during mixing.

The analysis of the complete spectra indicates that chemical coupling of MPTMS and the polymer takes place in the melt. This is indicated by the disappearance of the double bond and the appearance of characteristic groups in the extracted polymer. The bonded silane condenses to polysiloxane. At longer reaction times, oxidation of PP takes place, absorption of the carbonyl groups formed overlaps with that of the bonded MPTMS (see Fig. 8). The coupling reaction is relatively slow, hardly any silane is bonded into the polymer in the first 10 min. Since homogenization of the composite does not exceed this time, the slow rate and the chemical reactions of the silane (condensation) unambiguously explain the inefficiency of MPTMS as a coupling agent in PP/$CaCO_3$ composites.

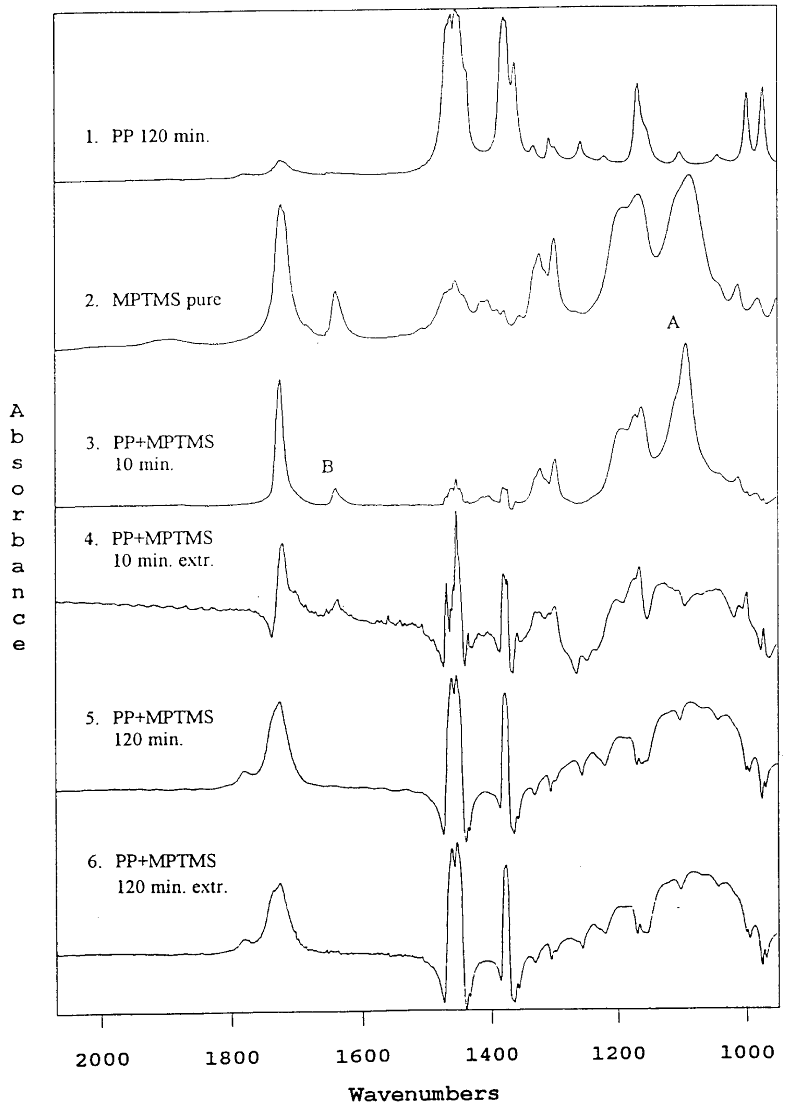
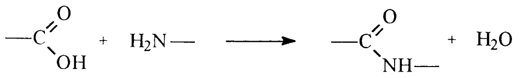


Fig. 8. FTIR difference spectra of PP films reacted with MPTMS.

3.3. Reaction of AMPTES with PP

Model experiments with aminofunctional silane coupling agents yielded completely different results. AMPTES binds totally into the polymer already after 10 min. The spectra of the samples taken after 10 min mixing are practically identical before and after extraction (spectra 2 and 3 in Fig. 9). The same conclusion can be drawn from Fig. 10, showing the changes in the concentration of the various functional groups as a function of mixing time. The spectra measured before and after extraction practically overlap each other.

The absorbance at 1596 cm^{-1} appearing in the spectrum of AMPTES (spectrum 1, A, in Fig. 9) can be assigned to the deformational vibration of the N-H bond of the primary amine group [27]. After 10 min reaction time, this band disappears and two vibrations appear at lower and higher wavenumbers, i.e. at 1640 (B) and 1563 cm^{-1} (C). According to Refs. [28–31], in the solid state the amide-I (C=O) vibration of secondary amides appears between 1680 and 1630 cm^{-1}. The deformational vibration of the N-H bond of a secondary amide absorbs in the range of 1581–1518 cm^{-1} (see Ref. [27]). Accordingly, we may assume that the above-mentioned vibrations at 1640 and 1563 cm^{-1} are the amide-I and amide-II bands of a secondary amide, respectively. Table 4 shows that a significant amount of carboxyl groups form during the processing of PP which can react with the amino functionality of AMPTES, i.e.(1)



$$\text{—C}(=\text{O})\text{OH} + \text{H}_2\text{N—} \longrightarrow \text{—C}(=\text{O})\text{NH—} + \text{H}_2\text{O} \qquad (1)$$

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 cm^{-1} (Fig. 9, spectrum 4, D). The double band

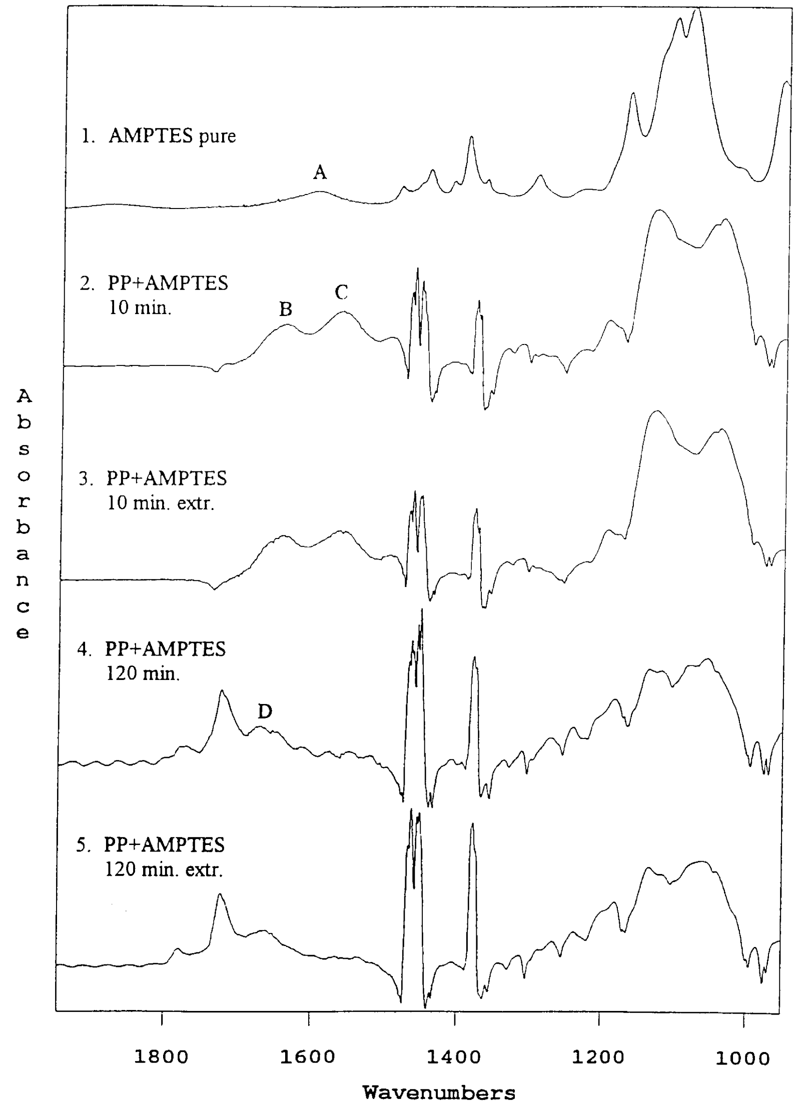
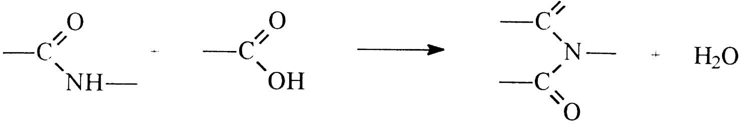


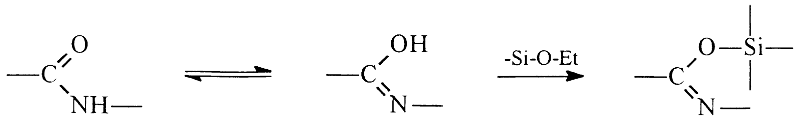
Fig. 9. FTIR difference spectra of PP films reacted with AMPTES.

appearing at 1790–1720 cm^{-1} and 1710–1670 cm^{-1} can be related to the symmetric and antisymmetric C=O vibration of imides [27,32,33]. This hints at the possibility that the secondary amide enters into a reaction with another acid group forming imides:(2)



(2)

Theoretically, the tautomeric conversion of the amide to unstable imidic acid is also possible, which may react further with the free, not hydrolysed -Si-O-Et groups, resulting in the stable silyl ester of imidic acid:(3)



(3)

The C=N vibration of the formed imidic acid ester appears at 1690–1645 cm^{-1} (see Ref. [32]). This may explain the appearance of vibration D at around 1670 cm^{-1} and the disappearance of the amide-II band, as well. However, the existence of free ethoxy-silyl groups in the melt at long reaction times is not likely.

The time dependence of the changes in concentration of the various functional groups is presented in Fig. 10. The intensity of the carbonyl absorbance increases with reaction time (P in Fig. 10) similarly to the virgin PP (Fig. 3). In the AMPTES/PP reaction, however, carbonyl content increases only after an induction period of 30–40 min, up to this point its value is 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 vibration appears in the spectrum. After a slight initial decrease, the total amount of amide and imide (or imidic acid ester) groups seems (B, D) to remain constant up to the end of the reaction. The amide groups transform into imides according to (2) resulting in a continuous decrease of N-H content (Fig. 10, C). After 80 min, all the secondary amide is consumed, the total amount has been converted to imide (or imine).

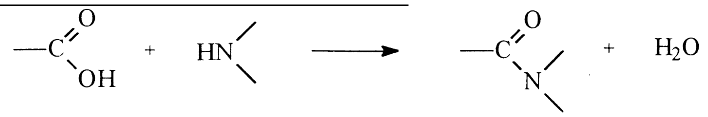
After 10 min reaction time, the antisymmetric stretching vibration of the triethoxy-silyl group of AMPTES at 1103 and 1080 cm^{-1} completely disappears and a new double band appears at 1128 and 1039 cm^{-1}. These absorption bands are characteristic of high molecular weight polysiloxane chains [34,35] (Fig. 9, spectrum 2). According to the spectrum, AMPTES reacts with some moisture present (see, e.g. reactions (1) and (2)), hydrolyses and condenses to polysiloxane even at the 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. FT*ir* 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. This conclusion is supported by the appearance of amide-I and -II (Fig. 9, B, C) vibrations and the disappearance of the deformational vibration band of primary amine (A). Since this reaction seems to proceed very fast, we can assume that it also takes place during the homogenization of PP/$CaCO_3$ composites. The above-presented results supply unambiguous proof that the enhanced interaction observed in these composites has a chemical nature, covalent bonds form between the components.

3.4. Reaction of CVBS and PP

The three absorption bands appearing in the spectrum of CVBS in the wavenumber range of 1750–1550 cm^{-1} (Fig. 11, spectrum 1) can be assigned to the stretching vibration of the Ar-C=C group (A, 1628 cm^{-1}), to the aromatic ring system (B, 1600 cm^{-1}), and to the deformational vibration of the NH_2^+ group (C, 1583 cm^{-1}) [27].

After 10 min mixing of CVBS with PP, these absorption bands disappear and a new set of vibrations can be observed (spectrum 2, Fig. 11). The carbonyl vibration at 1723 cm^{-1} (D) is the result of oxidation, and similarly to all previous systems its intensity gradually increases with reaction time. The intensity of the absorption band E at 1656 cm^{-1} is strongest after 10 min, but contrary to D its intensity decreases as a function of time. According to Refs. [36,37], the amide-I vibration of tertiary amides appears in the region of 1670–1630 cm^{-1}. If an aromatic ring is also attached to the nitrogen atom, the band shifts to higher wavenumbers within the range mentioned above. In the case of AMPTES, the amide-I absorption of the secondary amide was detected at 1640 cm^{-1}, thus the band observed in the spectrum of CVBS at 1656 cm^{-1} (Fig. 11, E) can be identified as the amide-I vibration of a tertiary amide. We can assume that the following reaction takes place between PP and CVBS:(4)



(4)

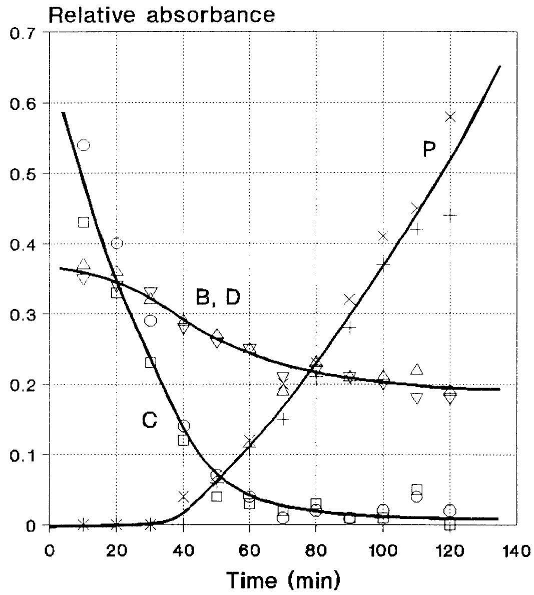


Fig. 10. Change of functional groups in the reaction of PP with AMPTES as a function of reaction time; (x, +) carbonyls, (○,□) amide-II, (△,▽) amide-I; (x,○,△) before extraction, (+ ,□,▽) after extraction.

The exact position of the amide-I vibration may be explained by the coupling of tertiary amide with the aromatic ring through a methylene group.

The third band appearing at 1606 cm^{-1} (F) may be assigned to the skeletal vibration of the aromatic ring [27]. The relative shift of 6 cm^{-1} compared to the same vibration of CVBS at 1600 cm^{-1} (B) may be explained by the interaction of the coupling agent and the PP matrix. The absorption band at 1628 cm^{-1} (A) assigned to the vinyl group of CVBS and the N-H deformational vibration in the NH$_2^+$ group at 1583 cm^{-1} (C) completely disappear after 10 min reaction time. The first overlaps with the amide-I band (E), while the second disappears due to the formation of the tertiary amide.

Similarly to the reactions of AMPTES, the intensive absorption band of the trimethoxy-silyl group of CVBS at 1084 cm^{-1} disappears after 10 min reaction time and a wide band appears, indicating the formation of a polysiloxane structure (Fig. 12). The spectra recorded before and after extraction are identical, thus we may assume that CVBS already forms a strong bond with the polymer at the beginning of the reaction. The bond created resisted 12 h extraction with methanol.

IR spectroscopy undoubtedly indicates the formation of covalent tertiary amide bonds between CVBS and PP. The thin films used for i.r. analyses were extremely brittle compared to PP films without CVBS, which also shows that chemical reactions take place in the melt leading to cross-linking of the polymer treated with CVBS. The enhanced interaction between PP and CaCO$_3$ is a result of the covalent bonds formed during the homogenization of the composite.

4. Conclusions

Earlier studies have shown that application of aminofunctional silanes leads to reactive coupling in PP/CaCO$_3$ composites. This was rather surprising, since both PP and

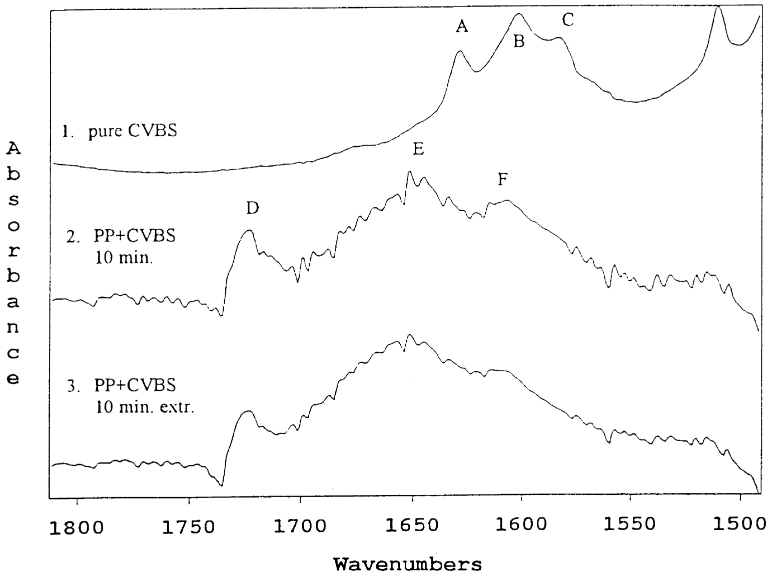


Fig. 11. FTIR difference spectra of PP films reacted with CVBS in the range of 1800–1500 cm^{-1}.

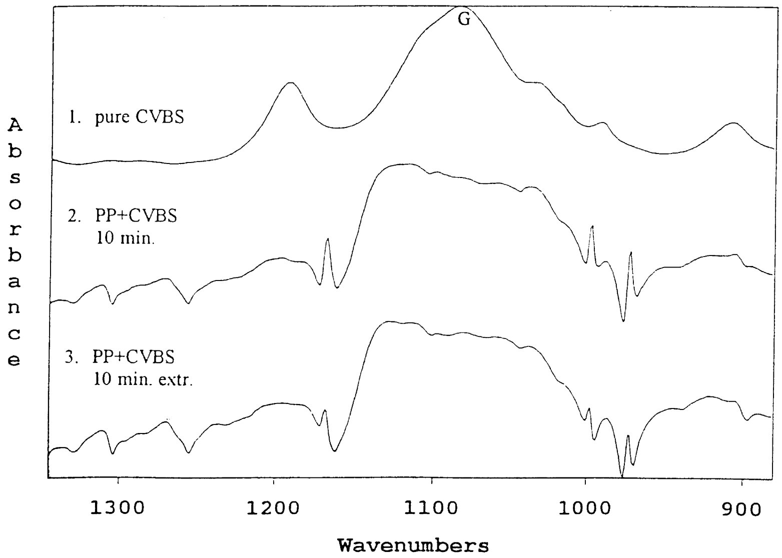


Fig. 12. FTIR difference spectra of PP films reacted with CVBS in the range of 1300–900 cm^{-1}.

$CaCO_3$ are inactive materials due to the lack of reactive groups on the polymer chain or on the surface of the filler, respectively. It was proven previously that aminofunctional silane coupling agents adhere strongly to the surface of $CaCO_3$ and form a polysiloxane layer probably due to the catalytic effect of the amino group in the polycondensation process.

Model experiments revealed that during processing, reactive carbonyl groups form on the PP chains in spite of the presence of stabilizers. The introduction of additional oxygen and peroxides promotes carbonyl formation, but oxidation of the polymer also takes place to a significant extent in air.

Since oxidation is a radical process, strong activity of the methacrylo functional MPTMS was expected. MPTMS reacts with PP through its double bond, indeed, but the reaction is slow, it takes longer than the homogenization of the PP/$CaCO_3$ composites. Although the reaction can be accelerated by the introduction of oxygen or peroxides, sufficient covalent bonds do not form during homogenization leading to the inefficiency of MPTMS as a coupling agent in this system.

AMPTES, a coupling agent containing primary amine as organofunctional group, reacts instantaneously with the carboxyl groups of the polymer forming secondary amide bonds. During processing, the secondary amide groups take part in further reactions with the continuously forming carboxyl groups, resulting in imide groups. Polycondensation of the triethoxy-silyl group also proceeds fast, it is already completed in the starting phase of the reaction. These fast reactions of the silane and polymer lead to the enhanced interaction between the components of PP/$CaCO_3$ composites.

Also, CVBS, another aminosilane coupling agent, reacts with the carboxyl groups of PP, forming tertiary amide groups. Reactions are also fast in this case, they are completed during the homogenization of the composite, leading to the reactive coupling effect observed.

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