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Infrared analysis and Izod impact testing of multicomponent polymer composites: polyethylene/EPDM/filler systems

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Various multicomponent polyethylene/rubber/filler composites have been characterized by diffuse reflectance infrared spectroscopy (DRIFT) and notched Izod impact testing. This work is part of a study which also included solid state and melt state dynamic mechanical testing of the same composites. The fillers used were an oxidized silicon powder and calcium carbonate. Fillers were also treated with coupling agents gamma-aminopropyltriethoxysilane (γ-APS) and gamma-methacryloxypropyltrimethoxysilane (γ-MPS). The rubbers were ethylene propylene diene (EPDM) rubber and a maleic anhydride grafted EPDM (EPDM-MA). DRIFT is useful for investigating the structure of these multicomponent composites on the molecular level. The DRIFT technique was used to confirm the presence of γ-MPS in the final composites treated with that coupling agent. The structure of the maleic anhydride functionality of a maleic anhydride grafted EPDM was also determined. The DRIFT analysis detected a reaction between the maleic anhydride modification of the EPDM and γ-APS during processing on the roll mill to form the cyclic imide structure. This is useful in interpreting a great deal of the dynamic mechanical results. The Izod impact testing shows that impact properties of both the oxidized silicon powder and calcium carbonate composites are improved by rubber addition. The use of EPDM-MA results in greater improvement than EPDM. This is likely due to greater filler–rubber interactions in the case of EPDM-MA which leads to encapsulation of the filler by the rubber due to favourable interfacial interactions. Comparison of the storage modulus G' at room temperature and Izod impact values was made for the PE/rubber/filler composites and the PE/filler and PE/rubber composites investigated in this study. Proper design of multicomponent PE/rubber/filler composites may clearly result in higher modulus and higher impact strength than that which is available with two phase PE/filler or PE/rubber systems.

1. Introduction

There has been recent interest in the use of multicomponent matrix/rubber/filler polymer composites because of the possibility of increasing both the modulus and impact strength of the material. The addition of a high modulus component to a plastic matrix enhances the composite modulus, but generally results in increased brittleness. On the other hand, addition of a rubber component often increases the impact strength but reduces the composite modulus. It is believed that careful incorporation of both high modulus and rubbery materials in a composite could result in an improvement of both the modulus and impact strength. Only a few publications have been concerned with such systems [1–4]. These composites are expected to exhibit complex behaviour because of the number of main components and the possible presence of matrix/filler, matrix/rubber, and rubber/filler interphases. Understanding of these systems may be further complicated by the use of coupling agents to modify the filler surface character.

Comitov *et al.* [2] studied multicomponent composites of calcium carbonate and SBR or BS-latex in polypropylene. They found that the impact strength was increased with the addition of the rubber modifier. Pukanszky *et al.* [3] studied systems of EPDM and calcium carbonate in polypropylene. They measured the stress–strain behaviour, shear modulus, impact strength, and dynamic mechanical properties of these composites. Dynamic mechanical spectra and scanning electron micrographs showed that in these systems the rubber partly covered the filler particles and/or filled in the voids in filler agglomerates. This morphology was critical in determining the properties of these composites. The addition of rubber was also found to restrain the deteriorating effect of the filler addition on composite impact strength. Pukanszky *et al.* [4] followed the torque and temperature against

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time curves during milling of PP/EPDM/$CaCO_3$ multicomponent composites.

The authors have conducted an exploratory study into the properties of these multicomponent systems [5–8]. The matrix used was high density polyethylene (PE). Fillers used were an oxidized silicon powder (model surface for siliceous materials) and calcium carbonate. EPDM rubber and a maleic anhydride grafted EPDM (EPDM-MA) were studied. The characterization techniques used were solid and melt state dynamic mechanical spectroscopy, Izod impact testing, and infrared spectroscopy. Dynamic mechanical results were compared with predictions based on the extended van der Poel model.

This paper reports the results of the infrared study and Izod impact testing. Descriptions of the roll milled composites are provided elsewhere [5]. Characterization of the oxidized silicon powder [5] and calcium carbonate [7] fillers have also been reported. The oxidized silicon powder is used as a model for fillers and reinforcements with siliceous surfaces. This powder has been used previously in model studies of silane coupling agents on such surfaces [9]. The weak infrared absorption of this powder makes it ideal for infrared studies of surface treatments or composites.

Diffuse reflectance spectra are generally plotted according to the Kubelka–Munk [6, 7] function as follows:

$$F(R_\infty) = (1 - R_\infty)^2/2R_\infty \qquad (1)$$

where $F(R_\infty)$ represents a ratio between constants related to absorption and scattering coefficients and R_∞ is the reflectance spectrum of a semi-infinite thickness media.

2. Experimental procedure

Details concerning materials used and composite preparation have been reported elsewhere [5, 7]. Fillers used were an oxidized silicon powder and calcium carbonate. The coupling agents gamma-aminopropyltriethoxysilane (γ-APS) and gamma-methacryloxypropyltrimethoxysilane (γ-MPS) were applied from aqueous methanol solution by evaporation of solvent.

The polyethylene used was DSM Stamylan HDPE 9089F; with a nominal melt index of 8 $dg\,min^{-1}$. This is a linear polyethylene with weight average molecular weight of 60 000 $g\,mol^{-1}$ and a density of 0.963 $g\,cm^{-3}$ at room temperature. The EPDM rubber used was DSM Keltan 312, with a nominal Mooney viscosity ML(1+4) 125° of 33. Maleic anhydride grafting was achieved in an extruder. Composites were roll milled at 170° C and pressed into plaques under standard conditions.

Model experiments were carried out in order to explore the possibility of reaction between silane coupling agents and the modified EPDM. These were carried out at room temperature in 1.0% solutions of the rubber in n-hexane (Riedel-dettaen, AG, chemically pure). EPDM solutions were also used as controls. To each of the solutions, 0.1 ml of a coupling agent (about 20 × the stoichiometric amount of coupling agent theoretically required to react with the EPDM-MA) was added. Coupling agents used were tetramethoxysilane (TMOS), gamma-aminopropyltriethoxysilane (γ-APS), and gamma-methacryloxypropyltrimethoxysilane (γ-MPS). All were purchased from Petrarch Systems and used as-received. The mixtures were stirred at room temperature for 15 h and then the polymer was precipitated by dropping into methanol (Merk, dried methanol, water content $< 0.01\%$). The polymer was then redissolved in n-hexane for casting onto films for infrared analysis.

Infrared spectra were obtained on a Bruker IF585 Fourier transform single beam instrument with liquid nitrogen cooled MCT detector. Spectral manipulation was carried out with software provided by the manufacturer.

Transmission spectra for the pure materials and model experiments were obtained from samples cast from n-hexane solution onto NaCl plates. The solvent was evaporated in air for approximately 1 h and then under vacuum at room temperature for at least 15 h. The transmission spectra were taken at 2 cm^{-1} resolution with 100 coadded scans.

Diffuse reflectance (DRIFT) spectra were taken using a Harrick Corporation DRA-PMN attachment with hemispherical mirrors. In order to obtain powdered samples for infrared measurement, material was carefully filed from the composite plaques. The samples were analysed neat and ratioed against a KBr powder reference. DRIFT spectra were taken at a resolution of 2 cm^{-1} with 200 coadded scans. No smoothing of the spectra was used. Unless otherwise noted, the spectra given in this paper are presented as collected with no baseline correction or other manipulation. All DRIFT spectra are plotted according to the Kubelka–Munk function.

Izod impact testing was done at room temperature with a notched specimen with specifications of ISO R180. The specimens were machined from the composite plaques and a 0.03 cm notch was carved into them by machine. The samples were approximately 5.0 cm long, 1.0 cm wide, and 3 mm thick. Five samples were tested from each composite.

3. Results and discussion

In the course of this investigation [5–8] a total of 50 composites were produced by roll milling and pressing. A summary of the composites produced is presented in Table I. All of these were analysed by solid state and melt state dynamic mechanical spectroscopy, Fourier transform infrared spectroscopy (FT-IR), and Izod impact testing. In the descriptions of the composites below "rubber" refers to both EPDM and EPDM-MA and "filler" refers to both the oxidized silicon powder and calcium carbonate.

3.1. Fourier transform infrared spectroscopy

The maleic anhydride modification of the EPDM rubber is depicted schematically in Fig. 1. The modification may exist in the anhydride or acid form. These two forms may be interchanged reversibly by the addition or removal of water. Experience has shown that the anhydride form will slowly convert to the acid form by absorbing water from the atmosphere if the

TABLE I Summary of sample compositions

ϕ_f (volume fraction of filler)	Rubber	ϕ_r (volume fraction of rubber)	Method of rubber addition	Coupling agent	CPA coverage (equiv. mon.)
PE only	–	–	–	–	–
Blends					
–	EPDM	0.1	–	–	–
–	EPDM	0.3	–	–	–
–	EPDM-MA	0.1	–	–	–
–	EPDM-MA	0.3	–	–	–
SiO_2 filled					
0.1	–	–	–	–	–
0.2	–	–	–	–	–
0.3	–	–	–	–	–
0.2	–	–	–	γ-APS	1,5
0.2	–	–	–	γ-MPS	1,5
0.5	EPDM	0.5	–	–	–
0.5	EPDM-MA	0.5	–	–	–
0.2	EPDM	0.001	Soln.[a]	–	–
0.2	EPDM	0.01	Soln.	–	–
0.2	EPDM	0.03	Soln.	–	–
0.2	EPDM	0.10	Soln.	–	–
0.2	EPDM	0.10	Mill[b]	–	–
0.2	EPDM	0.10	Mill	γ-APS	1,5
0.2	EPDM	0.10	Mill	γ-MPS	1,5
0.2	EPDM-MA	0.001	Soln.	–	–
0.2	EPDM-MA	0.01	Soln.	–	–
0.2	EPDM-MA	0.03	Soln.	–	–
0.2	EPDM-MA	0.10	Soln.	–	–
0.2	EPDM-MA	0.10	Mill	–	–
0.2	EPDM-MA	0.10	Mill	γ-APS	1,5
0.2	EPDM-MA	0.10	Mill	γ-MPS	1,5
$CaCO_3$ filled					
0.1	–	–	–	–	–
0.2	–	–	–	–	–
0.3	–	–	–	–	–
0.2	–	–	–	γ-APS	1
0.2	–	–	–	γ-MPS	1
0.2	EPDM	0.001	Soln.	–	–
0.2	EPDM	0.01	Soln.	–	–
0.2	EPDM	0.03	Soln.	–	–
0.2	EPDM	0.10	Soln.	–	–
0.2	EPDM	0.10	Mill	–	–
0.2	EPDM	0.10	Mill	γ-APS	1
0.2	EPDM	0.10	Mill	γ-MPS	1
0.2	EPDM-MA	0.001	Soln.	–	–
0.2	EPDM-MA	0.01	Soln.	–	–
0.2	EPDM-MA	0.03	Soln.	–	–
0.2	EPDM-MA	0.10	Soln.	–	–
0.2	EPDM-MA	0.10	Mill	–	–
0.2	EPDM-MA	0.10	Mill	γ-APS	1
0.2	EPDM-MA	0.10	Mill	γ-MPS	1

[a] Rubber deposited on filler from n-hexane solution before milling.
[b] Rubber and filler added separately during roll milling.

material is left in the laboratory environment. The acid may be converted to the anhydride by drying at high temperatures or roll-milling.

The infrared spectra obtained in transmission from cast films of the EPDM and EPDM-MA starting materials are given in Fig. 2 over the spectral range 2000 to 1300 cm^{-1}. The large peaks at approximately 1460 and 1370 cm^{-1} are due to C–C bonds in the rubber and are not shown in their full absorbance here. The small peaks at 1689 and 1611 cm^{-1} which appear in both spectra, but are more clearly evident in the EPDM due to the lack of overlapping bands, are due to C=C bonds in the third monomer of the EPDM terpolymer. In the EPDM-MA, the acid peak of the modification appears at 1714 cm^{-1}. The shoulder at 1736 cm^{-1} is due to the stabilizer which is added during the modification process. The anhydride form of the modification appears as two peaks, one at 1864 cm^{-1} and a larger one at 1789 cm^{-1}. The spectrum of the EPDM-MA clearly shows that both the anhydride and acid forms are present in the material as-received.

Diffuse reflectance infrared spectroscopy (DRIFT) was used to obtain spectra of all the composites in this study except those of 0.30 rubber volume fraction in PE. Material was carefully filed from each of the

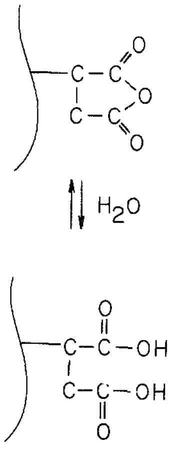

Figure 1 Schematic depiction of maleic anhydride modification of the EPDM rubber.

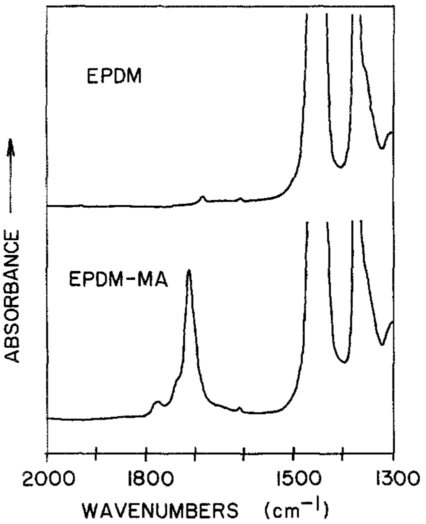

Figure 2 Transmission spectra of the rubbers used in the region 2000 to 1300 cm^{-1}.

composites to obtain powdered samples. Some representative spectra are presented in Figs 3 to 5 and 8. Fig. 3 gives the spectrum of PE over the range 2000 to 700 cm^{-1}.

The spectrum of a composite of 0.20 volume fraction (ϕ) SiO_2 is given in Fig. 4 between 2000 and 700 cm^{-1}. The sloping baseline (uncorrected) is characteristic of composites incorporating the SiO_2 filler. Note that the absorbtion of the oxidized silicon powder is quite weak over the whole wavenumber range shown. The most prominent band is at 1220 cm^{-1} due to Si–O–Si bonds. The use of the SiO_2 filler as a model surface for siliceous materials was excellent for the infrared study. The weak absorbtion of this powder makes it ideal for infrared studies. The spectrum of a composite of 0.20 volume fraction $CaCO_3$ in PE is given in Fig. 5 from 4000 to 700 cm^{-1}. The $CaCO_3$ absorbs very strongly in the regions 1810–1790, 1600–1400, and 900–850 cm^{-1}. The spectrometer was often saturated in these regions, making quantitative analysis impossible in these regions.

The presence of γ-MPS in the composites with treated fillers was confirmed by FT-IR. The technique of digital subtraction was used to obtain Fig. 6, which presents a difference spectra over the region 2000 to 1500 cm^{-1} showing the carbonyl band of the γ-MPS at 1722 cm^{-1} in composites of SiO_2 treated with one and five equivalent monolayers of γ-MPS. Fig. 7 shows the difference spectrum for a composite of $CaCO_3$ with one equivalent monolayer treatment of γ-MPS. A residual band due to the $CaCO_3$ appears at 1800 cm^{-1}.

Particular attention was paid to the 1900 to 1600 cm^{-1} region in composites including EPDM-MA in order to investigate the structure of the maleic anhydride modification in the composites. In order to better resolve the bands due to the EPDM-MA the technique of digital subtraction was used to isolate the spectrum of the EPDM-MA in each composite. Fig. 8 presents the spectra of PE and a blend of 0.1 volume fraction EPDM-MA in PE. The difference spectrum isolating the EPDM-MA component is given in Fig. 9 over the region 1900 to 1600 cm^{-1}. The anhydride form of the modification is evident at 1863 cm^{-1} and more strongly at 1787 cm^{-1}. The acid form is apparent at 1710 cm^{-1} along with a shoulder due to the stabilizer. Compared to the spectrum of the original EPDM-MA, it is clear that there has been some transformation to the anhydride form during processing on the roll mill. This transformation was observed to a certain extent in all of the composites containing EPDM-MA.

In the cases of the two composites with five equivalent monolayers of γ-APS on SiO_2 and one equivalent monolayer of γ-APS on $CaCO_3$ with EPDM-MA as the rubber component, a new band was detected at 1742 cm^{-1} which was not found in any of the other composites. The spectra obtained by digital subtraction are presented in Fig. 10 for the SiO_2 composite and Fig. 11 for the $CaCO_3$ composite. The acid form

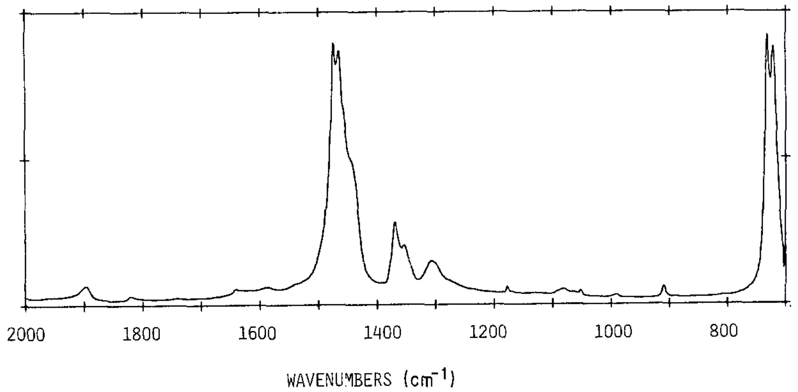

Figure 3 DRIFT spectrum of PE used, DSM Stamylan HDPE 9089F. $\Delta R_\infty = 0.47$.

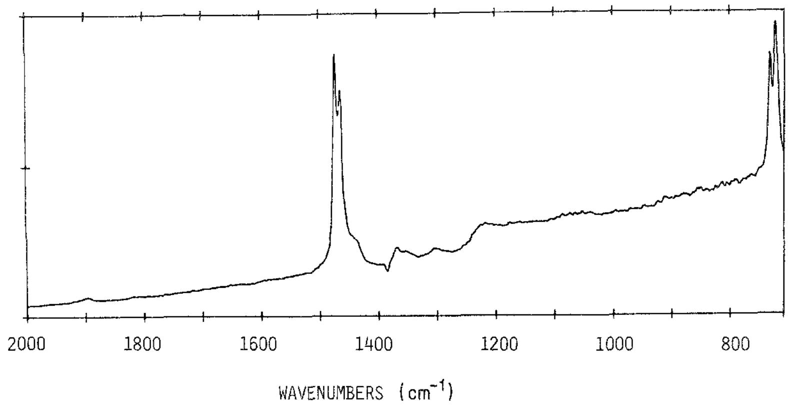

Figure 4 DRIFT spectrum of composite with $\phi_{PE} = 0.80$ and $\phi_{SiO_2} = 0.20$. $\Delta R_\infty = 4.0$.

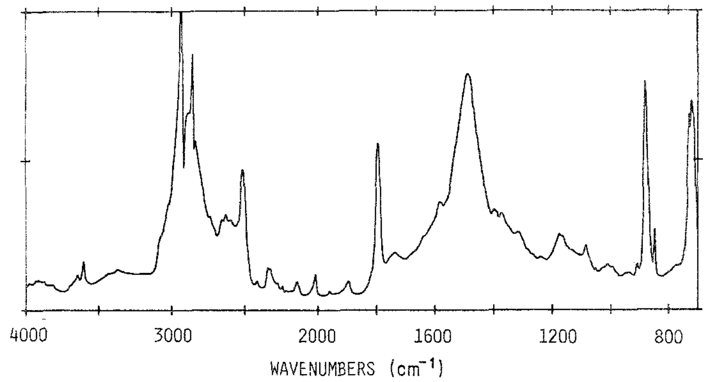

Figure 5 DRIFT spectrum of composite with $\phi_{PE} = 0.80$ and $\phi_{CaCO_3} = 0.20$. $\Delta R_\infty = 10.0$.

of the modification also appears in each of these spectra at 1710 cm^{-1}. The anhydride form appears in the spectrum from the SiO_2 composite but cannot be distinguished in the $CaCO_3$ composite because of the presence of a strongly absorbing filler band near that region. In Fig. 11 the peaks and negative bands between 1850 and 1770 cm^{-1} are residuals from the subtraction of this strongly absorbing band. The 1742 cm^{-1} band has been assigned to the cyclic imide structure indicated in Fig. 12 which is believed to have been formed due to a reaction between the EPDM-MA and γ-APS during processing on the roll mill. The chemical natures of the two moieties indicate that some interaction of these groups may be possible. This interaction could be simple hydrogen bonding, salt formation, acid-base interactions, or chemical reaction. It is conceivable that reaction could take place on the roll mill during processing. The most evident possibilities for reaction are the formation of amic acid or cyclic imide structures illustrated in Fig. 12. Under the conditions of roll milling at 170° C, the formation of the amic acid is expected to be the rate-limiting step for the aliphatic diacid. The imid formation will occur quickly once the amide is formed. Hence, very little or no amic acid would be expected in the final composite.

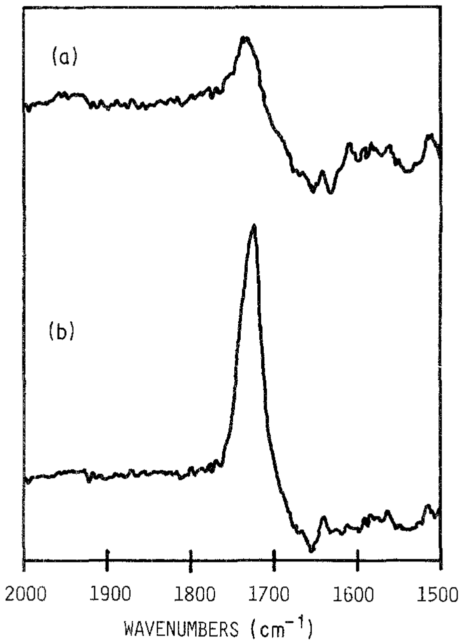

Figure 6 DRIFT difference spectra showing γ-MPS carbonyl band in composites with $\phi_{SiO_2} = 0.20$: (a) one equivalent monolayer $\Delta R_\infty = 0.15$; (b) five equivalent monolayers $\Delta R_\infty = 0.45$.

The infrared spectra obtained from the composites

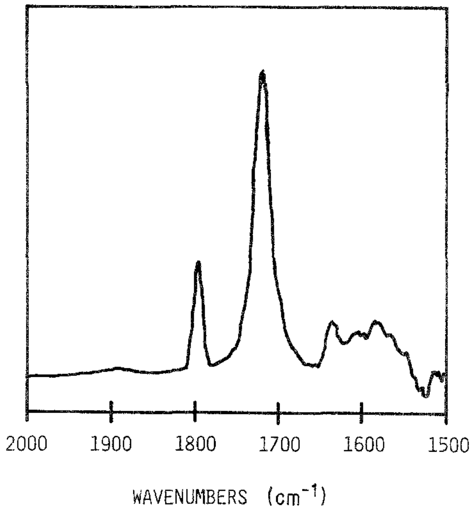

Figure 7 DRIFT difference spectrum showing γ-MPS carbonyl band in a composite with $\phi_{CaCO_3} = 0.20$ at one equivalent monolayer treatment. $\Delta R_\infty = 0.6$.

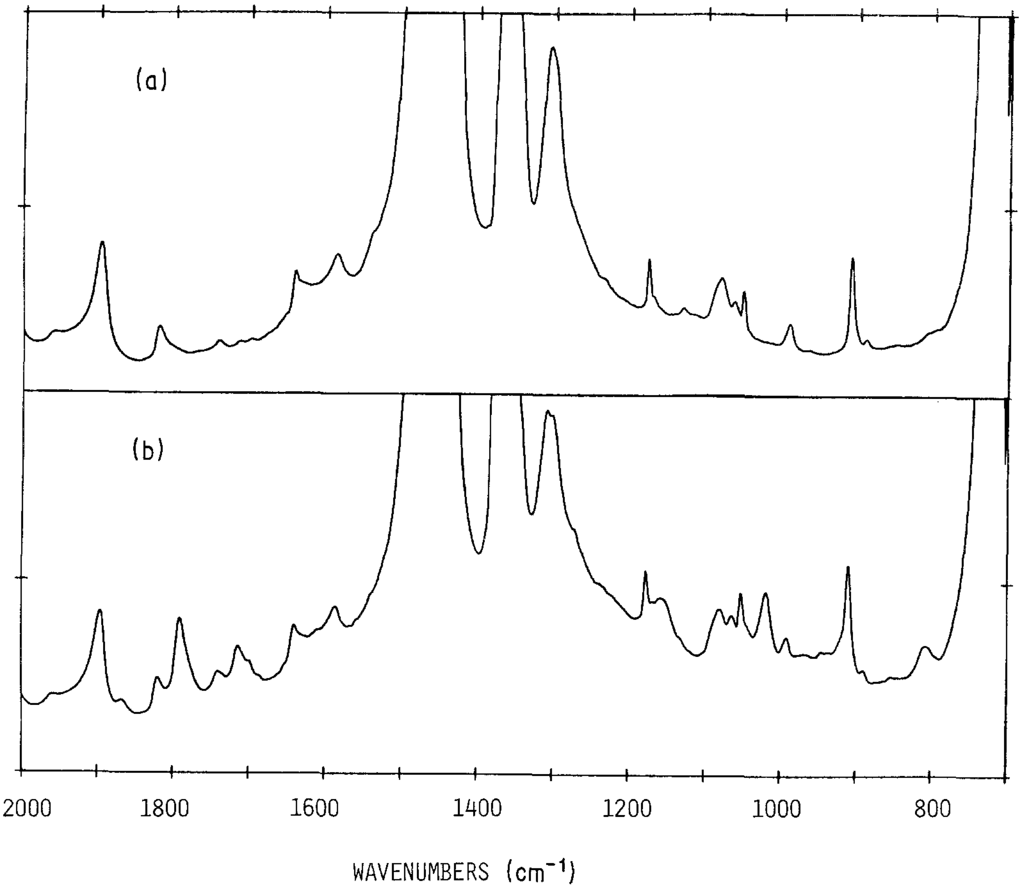

Figure 8 DRIFT spectra of (a) PE and (b) blend of $\phi_{\text{EPDM-MA}} = 0.10$ in PE.

in Figs 10 and 11 show that the cyclic imide was actually formed. Dynamic mechanical experiments from this study have suggested the presence of some strong interaction between the γ-APS surface treatment and EPDM-MA [5, 6, 8]. The chemical reaction discussed here is critical in explaining these dynamic mechanical results.

Model experiments were done in n-hexane solution to further explore the possibility of reaction of the EPDM-MA with various coupling agents. Coupling agents used were tetramethoxy silane (TMOS), (γ-APS), and (γ-MPS). The coupling agents were added to a 1.0% solution of rubber and stirred at room temperature for 15 h. The use of EPDM solution controls demonstrated that the separation technique employed ensured the removal of unreacted coupling agent from the final polymer product. The resulting polymer was analysed by infrared transmission spectroscopy.

Reaction of EPDM-MA with γ-APS under these conditions produces a salt. The changes due to reaction with γ-APS are presented in Fig. 13 over the spectral range 2000 to 700 cm^{-1}. Note that the peaks

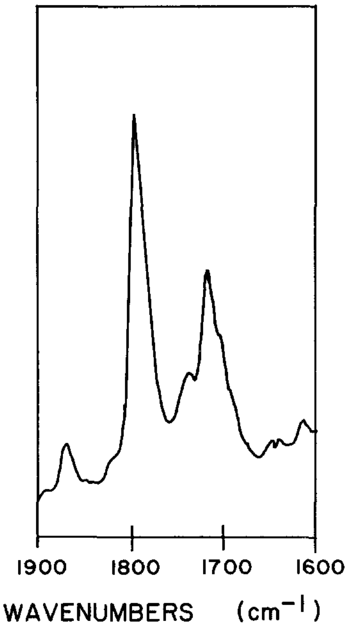

Figure 9 DRIFT difference spectrum of maleic anhydride modification in blend with $\phi_{\text{PE}} = 0.90$ and $\phi_{\text{EPDM-MA}} = 0.10$. $\Delta R_{\infty} = 0.15$.

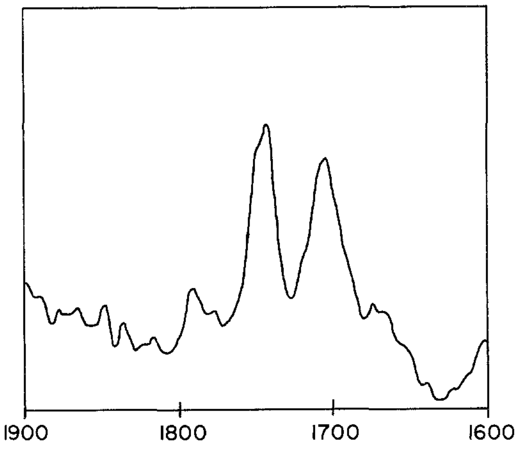

Figure 10 DRIFT difference spectrum of maleic anhydride modification in composite with $\phi_{\text{PE}} = 0.70$, $\phi_{\text{SiO2}} = 0.20$, and $\phi_{\text{EPDM-MA}} = 0.10$ with a filler treatment of five equivalent monolayers γ-APS. $\Delta R_{\infty} = 0.04$.

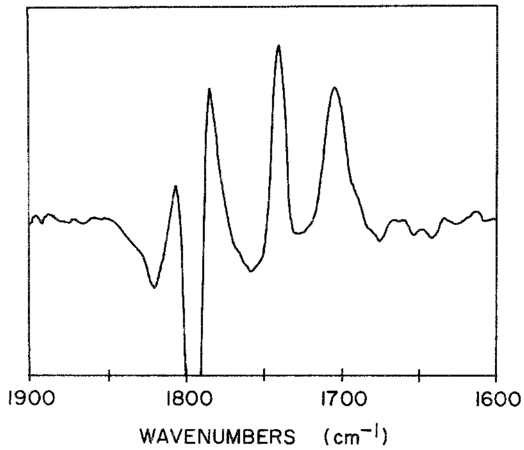

Figure 11 DRIFT difference spectrum of maleic anhydride modification in composite with $\phi_{PE} = 0.70$, $\phi_{CaCO_3} = 0.20$, and $\phi_{EPDM\text{-}MA} = 0.10$ with a filler treatment of one equivalent monolayer γ-APS. $\Delta R_\infty = 0.07$.

due to the acid at 1714 cm^{-1} and the anhydride at 1864 and 1789 cm^{-1} forms of the modification have disappeared. A peak at 1568 cm^{-1} and a shoulder at 1390 cm^{-1} due to the CO_2^- salt have appeared. Several new peaks have also appeared in the region 1200 to 1000 cm^{-1}. The peaks at 1146 and 1053 cm^{-1} have been assigned to Si–O–Si bonds; that at 1095 cm^{-1} to $Si\text{–}OCH_2CH_3$.

In the case of γ-MPS, there was no detectable change in the infrared spectrum of EPDM-MA. In the case of TMOS, there was a slight conversion of the acid form of the modification to the anhydride form. This indicates dehydration of the acid modification and is not unexpected since it is well known that the silane methoxy groups are hydrolysable. No other spectral changes were observed. Therefore, no reaction or salt formation similar to that observed for γ-APS was seen with either TMOS or γ-MPS under the conditions studied. The absence of a reaction between γ-MPS and EPDM-MA under the conditions of the model experiment does not preclude a reaction under processing conditions; however, it does indicate that such a reaction may be less likely than in the case of γ-APS.

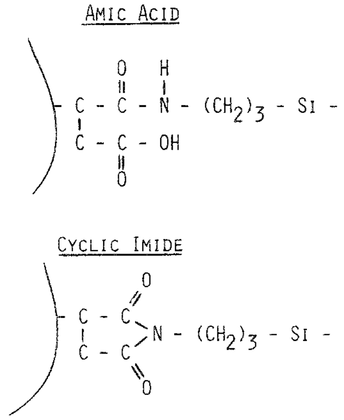

Figure 12 Possible products for reaction between γ-APS and EPDM-MA during processing on the roll mill.

3.2. Izod impact testing of composites

The effect of filler addition on the impact strength of PE/filler composites is given in Fig. 14. The impact strength decreases with filler addition, as expected.

The influence of the solution deposited rubbers on the impact strengths of PE/rubber/filler composites

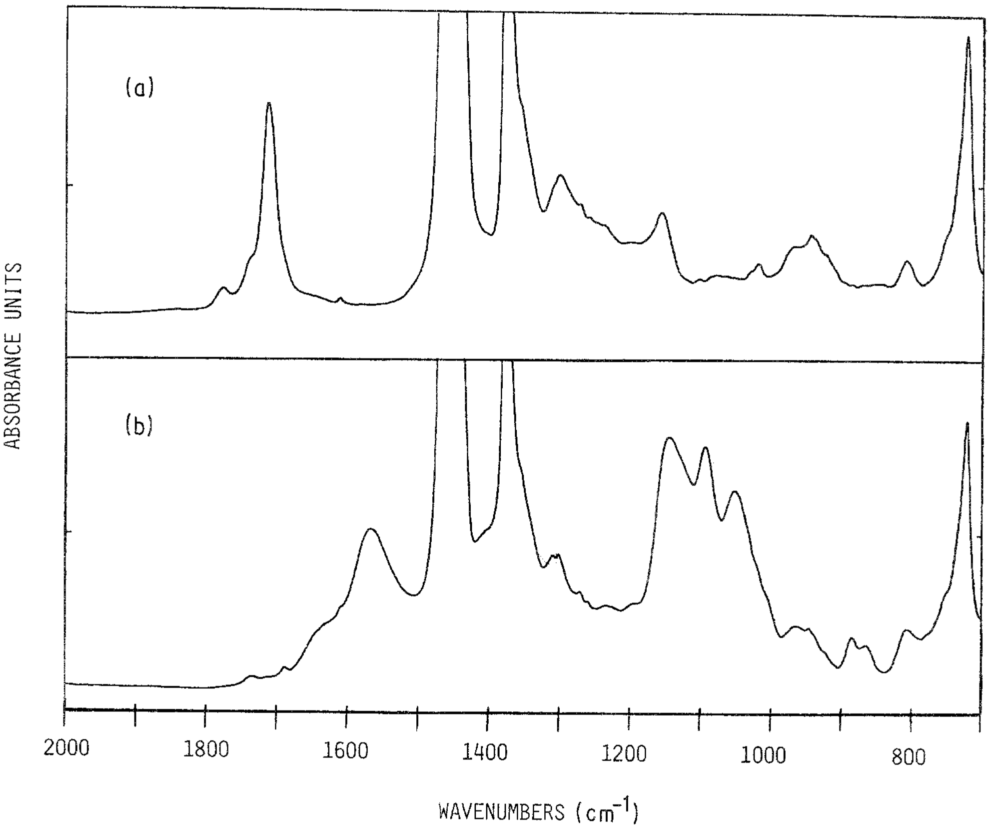

Figure 13 Model experiment reaction of EPDM-MA and γ-APS in n-hexane solution. (a) EPDM-MA, (b) salt of EPDM-MA and γ-APS.

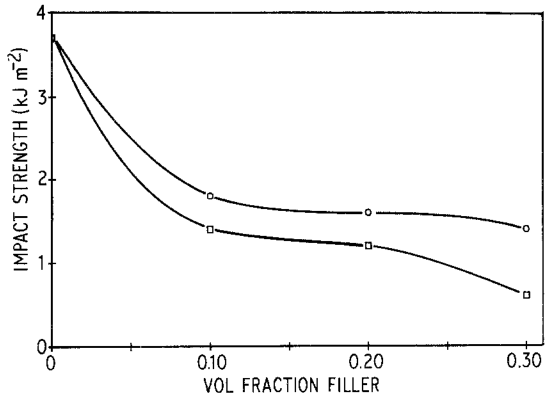

Figure 14 Izod impact strength plotted against filler volume fraction for PE/filler composites: (○) SiO_2 filled and (□) $CaCO_3$ filled.

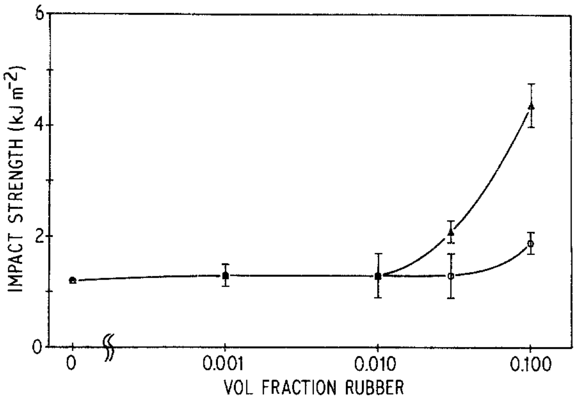

Figure 16 Izod impact strength plotted against rubber volume fraction for multicomponent composites with $\phi_{C\text{-}CO_3}$ = 0.20 and the different rubbers: (○) EPDM and (△) EPDM-MA.

are given for SiO_2 in Fig. 15 and $CaCO_3$ in Fig. 16. In both cases the EPDM-MA provides significantly better impact strength than the EPDM.

Dynamic mechanical experiments have indicated that the nature of the rubber-filler interaction has a great influence on the resulting composite morphologies. Solid state dynamic mechanical spectra of composites of PE/EPDM-MA/$CaCO_3$ showed a much larger rubber glass transition peak than similar composites of PE/EPDM/$CaCO_3$ [7]. This was attributed to the presence of more rubber around the filler particles in the case of EPDM-MA. Melt state measurements on the PE/rubber/$CaCO_3$ composites indicated a greater interaction between EPDM-MA and $CaCO_3$ than between EPDM and $CaCO_3$ [8]. Solid state proton NMR relaxation model experiments also showed a significant immobilization of the EPDM-MA chains on the $CaCO_3$ surface [7], indicating some kind of interaction at the filler surface. This was attributed to the formation of salts between the EPDM-MA and $CaCO_3$ filler surface. Therefore, the superior impact strength of PE/EPDM-MA/$CaCO_3$ composites compared to PE/EPDM/$CaCO_3$ composites is most likely due to differences in rubber–filler interaction strengths and which result in different morphologies. Complete or partial encapsulation of the filler particles with rubber would be expected to have a drastic effect on the impact strength of the composites. Specifically, our results indicate that a morphology with more rubber around the filler particles instead of separate from the filler produces a composite with higher impact strength.

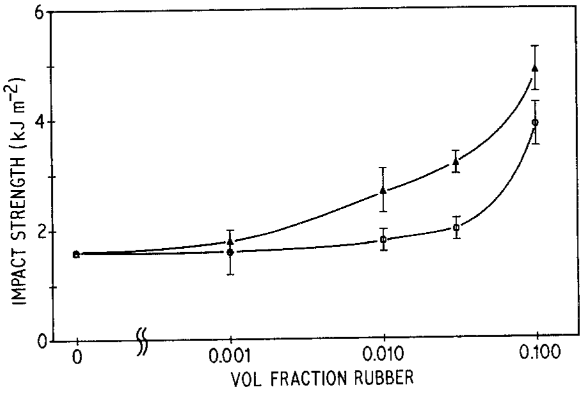

Figure 15 Izod impact strength plotted against rubber volume fraction for multicomponent composites with ϕ_{SiO_2} = 0.20 and the different rubbers: (○) EPDM and (△) EPDM-MA.

The reason for the differences in the SiO_2 composites is not as clear. Differences in morphology for composites of the two rubbers were not nearly as apparent in the dynamic mechanical properties as in the case of $CaCO_3$ composites. However, the SiO_2 surface has some polar groups such as silanols (Si-OH) [9] on the surface which could interact with the maleic anhydride functionality of the EPDM-MA. The alkaline nature of the $CaCO_3$ and acidic nature of the maleic anhydride modification leads to strong acid–base interactions. However, Si-OH is a weak acid and only hydrogen bonding and London forces would be present with the maleic anhydride modification.

Interpretation of Izod impact testing results on a fundamental level is very difficult. However, our experiments have shown a correlation between increased Izod impact values and the presence of more rubber around the filler particles as determined from dynamic mechanical spectroscopy. This is especially evident in the case of PE/rubber/$CaCO_3$ composites.

The presence of a rubber shell around the filler particles changes the stress distribution around the particles. For rigid spherical fillers in a polymer matrix with good interfacial adhesion, the stress concentration is at the poles of the particles, and this is where cracking will occur [10, 11]. For soft spherical particles such as rubber, the stress concentration is at the equator and this is where cracking or crazing will develop [12, 13]. This difference in the stress fields is believed to be at least partially responsible for the differences between the impact behaviours commonly observed for addition of the two types of particles: lower impact strength with the addition of rigid spherical fillers and higher impact strength with the addition of rubber [14]. The addition of a series of thicker rubbery layers to rigid fillers in a polymer matrix alters the stress concentration from the poles to the equator of the particles. Hence, the application of rubber layers to rigid fillers in a matrix is expected to improve the impact strength due to a change in the location of the stress concentrations. However, the systems in this study exhibit many complex features which complicate interpretation of the results, including: phase intermixing of the rubber and matrix

TABLE II Effect of coupling agents on impact strengths of PE/filler composites (volume fraction filler = 0.20)

Filler	Coupling agent	Amount of agent (equiv. mon.)	Impact strength (kJ m^{-2})	Standard deviation (kJ m^{-2})
SiO_2	none	–	1.6	0.0
	γ-APS	1	1.8	0.1
	γ-APS	5	2.1	0.0
	γ-MPS	1	3.5	0.2
	γ-MPS	5	2.2	0.3
$CaCO_3$	none	–	1.2	0.0
	γ-APS	1	1.6	0.2
	γ-MPS	1	1.7	0.1

[5], particle–particle interactions [5, 8], filler–matrix interactions [5, 7], non-spherical particle geometry, and rough filler surfaces.

The effects of the use of coupling agents on PE/filler composite Izod impact strengths are summarized in Table II. A few trends can be determined from the data presented. In the case of PE/filler composites, the coupling agents increased the impact strengths compared to the untreated composites. This type of behaviour has been observed in other systems as well [15, 16]. In the case of γ-APS, the impact strength increases monotonically with increased amount of coupling agent over the range studied. In the case of γ-MPS, the impact strength increased with the use of one equivalent monolayer and then decreases slightly with the use of five equivalent monolayers. There is probably some optimum which could be determined with additional experiments.

This improvement of impact properties with coupling agent treatment could be due to several possible effects including: (1) morphological differences in the composite due to the surface treatment, (2) surface energetic differences due to the treatments, and (3) a plasticizing effect due to the presence of a coupling agent. In fact, solid state dynamic mechanical measurements on the SiO_2 composites implied a decrease in particle–particle friction due to coupling agent treatment [5]. Solid state and melt state dynamic mechanical measurements on the $CaCO_3$ composites also showed a reduction in particle–particle interactions with treatment [7, 8]. In both cases, better dispersion of the filler was probably the dominant factor in these effects. Better dispersion could be the cause of improved impact strength in the composites studied here. The complexity of the system under study complicates interpretation of the impact strength data.

The effects of coupling agents on multicomponent composite Izod impact strengths are summarized in Table III. Again, both γ-APS and γ-MPS tend to improve the impact strengths of the composites. The results are especially good for composites including both γ-APS and EPDM-MA. This may be due to the chemical reaction between γ-APS and the EPDM-MA which was discussed above. Solid state dynamic mechanical spectroscopy shows that this reaction resulted in a morphology with more rubber around the filler particles [5]. This is more evidence which suggests that the presence of rubber around the filler particles instead of separate from the filler is favourable for better impact strength.

The overall performance for the multicomponent composites is summarized in Fig. 17 for SiO_2 composites and Fig. 18 for $CaCO_3$ composites. These figures show the storage modulus G' at 20° C and 0.2153 Hz as determined from the torsion pendulum experiments [5, 7] plotted against the notched Izod impact strength. The polyethylene matrix characteristic occurs at a G' of 7.3×10^8 Pa and impact strength of 3.7 kJ m^{-2}. The heavy solid in each plot line above PE connects the points for PE/filler composites. The

TABLE III Effect of coupling agents on impact strengths of multicomponent PE/rubber/filler/composites (Volume fraction filler = 0.20, volume fraction rubber = 10)

Filler	Rubber	Coupling agent	Amount of agent (equiv. monolayer)	Impact strength (kJ m^{-2})	Standard deviation (kJ m^{-2})
SiO_2	EPDM	none	–	2.9	0.1
		γ-APS	1	5.2	0.2
		γ-APS	5	3.4	0.3
		γ-MPS	1	7.5	0.2
		γ-MPS	5	6.0	0.2
	EPDM-MA	none	–	4.2	0.2
		γ-APS	1	7.0	0.2
		γ-APS	5	8.6	0.5
		γ-MPS	1	5.6	0.3
		γ-MPS	5	5.2	0.4
$CaCO_3$	EPDM	none	–	1.9	0.2
		γ-APS	1	3.1	0.2
		γ-MPS	1	3.1	0.3
	EPDM-MA	none	–	5.0	0.3
		γ-APS	1	7.5	0.5
		γ-MPS	1	6.3	0.4

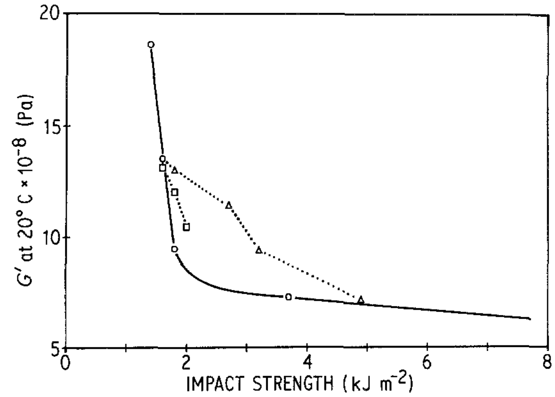

Figure 17 Storage modulus G' plotted against Izod impact strength for some SiO_2 composites. (○) PE and PE/SiO_2 composites; (□) multicomponent composites with $\phi_{SiO_2} = 0.20$ and EPDM volume fractions of 0.001, 0.01 and 0.03; and (△) multicomponent composites and $\phi_{SiO_2} = 0.20$ and EPDM-MA volume fractions of 0.001, 0.01, 0.03, and 0.10.

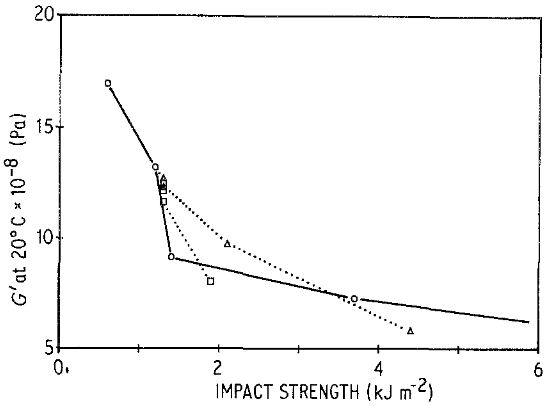

Figure 18 Storage modulus G' plotted against Izod impact strength for some $CaCO_3$ composites. (○) PE and PE/$CaCO_3$ composites; (□) multicomponent composites with $\phi_{CaCO_3} = 0.20$ and EPDM volume fractions of 0.001, 0.01, 0.03, and 0.10; and (△) multicomponent composites with $\phi_{CaCO_3} = 0.20$ and EPDM-MA volume fractions of 0.001, 0.01, 0.03, and 0.10.

solid line below PE connects the points for PE/filler composites. The solid line below PE connects the points for PE/rubber blends (none of these points are actually shown in this plot since they occur at very high impact strengths). Assuming that both high modulus and impact strength are desirable properties in terms of composite performance, any composite with a characteristic which falls to the upper right of the heavy line will be superior to what is available with the PE/filler or PE/rubber systems. Any composite with a characteristic which falls to the lower left of this line is inferior. On both of the plots, there are several multicomponent composites which show properties superior to the properties available with PE/filler or PE/rubber. These plots also show the advantage of EPDM-MA compared to EPDM composites. Further optimization of the composite composition and processing condition may be expected to further improve their properties.

4. Conclusions

Diffuse reflectance infrared spectroscopy (DRIFT) is useful for direct analysis of multicomponent composites. Specifically, in this study the DRIFT technique was used to detect γ-MPS in PE/SiO_2 and PE/$CaCO_3$ composites, to determine the form of the maleic anhydride modification of the EPDM-MA in blends, and to detect a reaction between γ-APS and EPDM-MA during processing on the roll mill at the interphase in PE/EPDM-MA/SiO_2 and PE/EPDM-MA/$CaCO_3$ composites.

The oxidized silicon powder is a useful model surface for infrared studies. Its low infrared absorbance is ideal for DRIFT studies of the composites. Composites incorporating $CaCO_3$ filler may also be effectively analysed by DRIFT in regions where strong absorptions due to the $CaCO_3$ are absent.

In multicomponent PE/rubber/filler composites, the EPDM-MA provided superior impact strengths compared to the EPDM rubber. This has been attributed to morphological differences between the composites made with the two different rubbers. Specifically, a morphology with more rubber around the filler particles results in better impact strength. Use of coupling agents improved the composite impact strengths both in PE/filler and PE/rubber/filler systems. Composites including EPDM-MA and γ-APS provided the best impact strengths, probably due to a chemical reaction between the two functionalities.

Many of the multicomponent composites investigated in this study exhibited higher room temperature storage modulus and impact strength than was found to be available for two component PE/filler or PE/rubber systems. Optimization of system composition and processing conditions is expected to result in even more improved composites.

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