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^{13}C and ^{29}Si NMR Investigations of Glass-Filled Polymer Composites

T. L. Weeding and W. S. Veeman*

Department of Molecular Spectroscopy, Faculty of Science, University of Nijmegen, Toerhooiveld, 6525 ED Nijmegen, The Netherlands

L. W. Jenneskens, H. Angad Gaur, H. E. C. Schuurs, and W. G. B. Huysmans

AKZO Corporate Research Arnhem, P.O. Box 60, 6800 AB Arnhem, The Netherlands.

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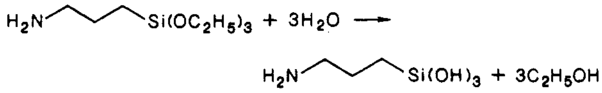
ABSTRACT: ^{13}C and ^{29}Si CP/MAS NMR have been employed to characterize the filler, the matrix, and the interfacial regions of microcomposite samples. As the interfacial region is the most important in determining the properties of a composite, we have focused our attention on this region with the goal of gaining insight into the adhesive mechanism on a molecular level. Five samples have been studied: the pure matrix polymer, the polymer plus the coupling agent only, the polymer plus the filler only, and two "complete" composites, one prepared from the polymer plus filler pretreated with the coupling agent and a second prepared by integral blending of the three components. The microcomposites were prepared with glass microspheres, polyamide-6, and the coupling agent (γ-aminopropyl)triethoxysilane. The spectra demonstrate differences between the interfacial layers of the composites that depend upon both the components which are present and upon the method of preparation.

Introduction

Composites are widely used as high-performance structural materials. Composites which consist of a particle or mineral-filled reinforced polymer matrix belong to the major class of microcomposites. The adhesion mechanism between the filler and matrix controls the transfer of stress and consequently strongly influences the final properties of the composites. Usually adhesion can be considerably enhanced by the addition of an appropriate bifunctional coupling agent such as a silane reagent (ca. 0.1–1% w/w). Various theories have been proposed to explain this phenomenon. One of these is the chemical bonding theory, which states that the formation of covalent chemical bonds between the coupling agent and the filler, and between the coupling agent and the matrix, leads to increased adhesive stability.[1] However, this theory has been unable to rationalize some of the properties of composites. An extension of the chemical bonding theory is the interpenetrating network (IPN) theory, which states that the matrix can diffuse into the coupling agent interphase to form an entangled network,[2] this also leads to increased adhesive stability. However, the adhesion mechanism has not yet been elucidated at the molecular level. Clearly a detailed knowledge of chemical and structural changes that occur in the composite, especially in the interphase region, is of interest for the optimization of composite properties. Solid-state NMR is ideally suited to this task since it allows one to nondestructively examine the environments of specific nuclei (^{29}Si and ^{13}C) in the matrix and on the surface of the filler, i.e., in the interfacial region. The purpose of this study is to explore the details of the adhesive mechanism which are manifest in the NMR spectra of composite samples.

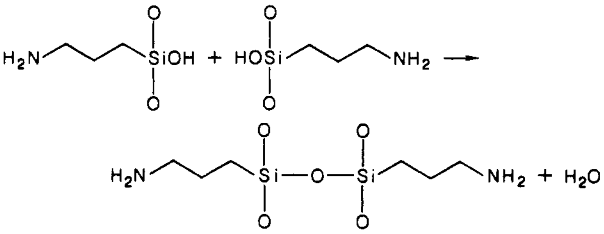
We report here on a detailed investigation of microcomposites made of polyamide-6 (PA6), glass microspheres, and the coupling agent (γ-aminopropyl)triethoxysilane (γ-APS). Five samples were examined: pure PA6, PA6 plus γ-APS, PA6 plus glass microspheres, and two samples containing all three components. The three-component composites were prepared in two different ways: (a) pretreated glass microspheres were added to the PA6 and (b) the coupling agent was added to the glass microsphere–matrix mix in the melt in the "integral blending" process.

The chemistry involved in the preparation of the composites comprises many reactions. It is well established that the ethoxy groups of γ-APS hydrolyze[3] to give silanol groups which can then react further.



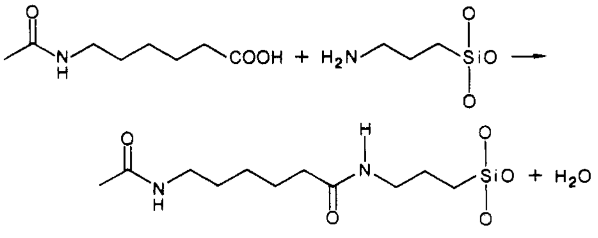
(1)

One of these reactions is the condensation reaction between molecules of hydrolyzed γ-APS to give a polysiloxane polymer.



(2)

Reaction of the amine of γ-APS with the carboxylic end groups of PA6 gives an amide bond, the desired covalent linkage between the polymer and the coupling agent.



(3)

Covalent bonds between the surface of the glass micro-

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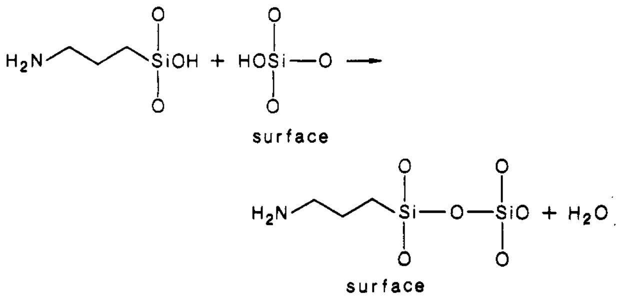
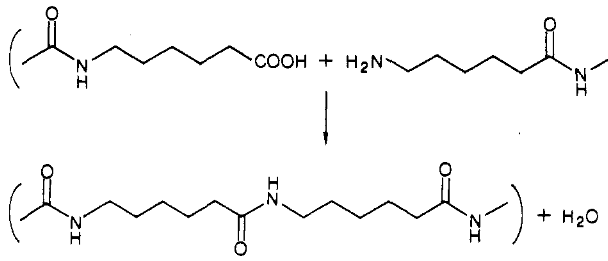
spheres and the coupling agent occur when silanols of the hydrolyzed γ-APS react with surface silanols on the glass microspheres to form siloxane linkages.



(4)

The condensation reaction between the carboxylic acid end group of one PA6 chain and an amine end group of another PA6 chain is also possible and results in an increase in the molecular weight of the polymer.



(5)

Naturally, the γ-APS moiety in reaction 2 may have already reacted with the carboxylic acid end group of PA6, or may react with PA6 in a subsequent reaction, to give PA6 polymer chains which are coupled by γ-APS. Similarly, the γ-APS of reaction 4 can also react with PA6 and thereby provide the optimal covalent bonding between the PA6 and the surface of the glass microspheres via the γ-APS coupling agent.

Experimental Section

Samples. The components were carefully selected to minimize the effects of broad distributions of macromolecular and particle sizes. The PA6 which was used to prepare these composite samples was of low molecular weight ($M_w = 7000$, $M_n = 4650$, $M_z = 9900$, $M_w/M_n = 1.5$; $\epsilon_{COOH} = 266$ mequiv kg^{-1}, $\epsilon_{NH_2} = 298$ mequiv kg^{-1}). The polymer was extracted with methanol to remove residual monomer and oligomers. The glass microspheres were small, diameters 3–5 μm, to maximize surface area and number of reaction sites. If, as a first approximation, we assume smooth, spherical surfaces for the glass microspheres, they would have an area per gram of approximately 0.4 m^2. Further, if we take the value of 5/100 Å^2 reported for silica gel[5] as an estimate of the number of silanol groups on the surface of the glass microspheres, then there would be about 2×10^{18} silanols/g. If each of these silanols were to react with one molecule of γ-APS, then only about 0.1% (w/w) γ-APS would be required for complete reaction. However, it has been shown by FT-IR spectroscopy that in spite of the large excess of γ-APS available surface silanol groups are still observable at loading levels much higher than 0.1%. Preliminary scanning electron micrographs of these glass microspheres have shown that they have very rough surfaces. Therefore, the estimates of both the surface area and the amount of γ-APS required for monolayer coverage are lower limits. The actual values are probably 3–5 times larger. In these samples, the γ-APS is expected be present as an inhomogeneous polymeric layer on the surface of the glass microspheres when it is used for pretreatment.

The first group of samples was: (A) the original PA6 treated as for composite preparation but without the addition of either glass microspheres or γ-APS, (B) PA6 plus 10% γ-APS by weight, (C) PA6 plus 30% glass microspheres by weight, (D) PA6 plus 30% pretreated glass microspheres (8.4% γ-APS on glass microspheres by weight), and (E) PA6 plus 10% γ-APS and 30% glass microspheres, by weight, added together all at once (integral blending). The preparation of the composites were carried out on a 1-g scale according to the following procedure. The starting materials were placed in a sealed vessel which was then evacuated and flushed 3 or 4 times with N_2 before immersion in an oil bath at 220–230 °C. The starting material for samples A and B was PA6. For samples C and E, the starting materials were PA6 and glass microspheres, and for sample D, the vessel initially contained PA6 and pretreated glass microspheres. The contents of the reaction vessel were then heated with continuous stirring until the PA6 melted. The γ-APS was then injected, if necessary, and in all cases, the samples were stirred in their melted state for 5 min. After removal from the oil bath, the samples were allowed to cool to room temperature, removed from the vessel, ground in the presence of CO_2(s), and dried under vacuum at 100 °C for 8 h.

The pretreated glass microspheres used in composite D were prepared as follows. To a toluene solution (5 mL) of γ-APS (10% w/w) were added 0.5-g glass microspheres and 3 molar equiv of water, based on the γ-APS. After the mixture stirred for 1 h at room temperature, the glass microspheres were filtered off and dried under vacuum at 100 °C for 1 h. Since the γ-APS monomer and dimer are soluble in water, only γ-APS molecules which have reacted either with other γ-APS molecules at least twice or with the surface of the glass microspheres will be present after filtering. The amount of γ-APS present at the surface of the glass microspheres was assessed by thermogravimetry (TGA) and found to be 8.4% in the case of pretreatment. As mentioned above, this 8.4% level of γ-APS loading is higher than the 1% typically used in commercial applications. The high level of loading was chosen with the dual purpose of enhancing the sensitivity of our NMR experiments and maximizing coupling agent–filler and coupling agent–matrix reactions and interactions.

Although the interfacial region is structurally the most important part of the composite, it is also the most difficult to study spectroscopically because of the bulk material present. To examine the interfacial region more closely, the glass microspheres of samples C, D, and E (the PA6 composites containing glass microspheres only, γ-APS pretreated glass microspheres, and integrally blended γ-APS and glass microspheres, respectively), were isolated from the composites by dissolving the PA6 matrix in trifluoroethanol (TFE), a potent solvent for PA6. The insoluble fraction was isolated by filtration and was extracted twice with TFE in order to insure complete solution of organic material. Next, the insoluble fraction was dried under vacuum at 100 °C for 1 h. The combined filtrates were concentrated, and the solid residue was ground in the presence of CO_2(s) and dried under vacuum at 100 °C for 8 h. Both the soluble and insoluble fractions were examined with ^{13}C and ^{29}Si CP/MAS NMR spectroscopy. The second group of samples was comprised of (C′) the microspheres isolated from composite C (the composite containing glass microspheres only), (D′) the microspheres isolated from composite D (the composite containing pretreated glass microspheres) (E′) the microspheres isolated from composite E (the composite prepared by integral blending of PA6, γ-APS, and glass microspheres), (C″) the soluble polymer fraction of composite C, (D″) the soluble polymer fraction of composite D, and (E″) the soluble polymer fraction of composite E. All samples were stored under ambient conditions.

NMR Spectroscopy. The NMR spectra were measured at room temperature on a Bruker CXP 300 spectrometer equipped with an Aspect 3000 computer and a Bruker double-bearing CP/MAS probe. The 90° pulse lengths were 3.4–3.8 μs in length for ^{13}C, ^{29}Si, and ^{1}H nuclei. The majority of the data presented here were collected with cross-polarization (CP), which allows selective detection of those nuclei (^{13}C or ^{29}Si) near protons. In addition to this selectivity, CP enhances the sensitivity of the NMR experiment and shortens the necessary delay between acquisitions of successive transients. The mixing times used for cross-polarization were 1 ms for ^{13}C and 2 ms for ^{29}Si. Recycle delays were 2 s long, and the magic angle spinning (MAS) frequency was 3.7 or 4.0 kHz. Phase cycling and spin temperature alternation were used to minimize artifacts.[6] The ^{13}C cross-polarization spectra of the composites contain contributions from both amorphous and crystalline fractions. To measure the spectra from the fast-relaxing amorphous fractions alone, 90° pulses, high-power proton decoupling, magic angle spinning, short recycle

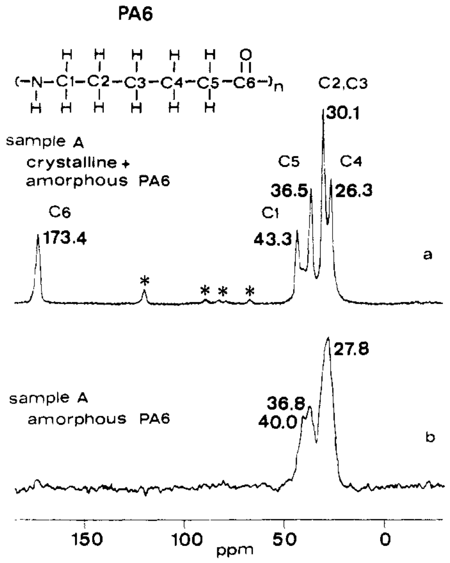


Figure 1. ^{13}C CP/MAS spectra of sample A (melted only PA6). (a) CP/MAS spectrum, 17 450 FIDs without Lorentzian broadening (FID = Free Induction Decay). Spectrum contains contributions from both crystalline and amorphous fractions. (b) MAS spectrum of amorphous fraction of PA6, 1850 FIDs collected at 1-s intervals. 50-Hz Lorentzian broadening.

delays, and a modification of the DEPTH pulse sequence, which eliminates background from the probe,[7] were used. Adamantane and the mineral thaumasite were used to optimize experimental parameters and as external secondary chemical shift references for ^{13}C (38.56 ppm for the methylene resonance relative to TMS[8]) and ^{29}Si (−179.5 ppm[9] relative to TMS), respectively.

Results and Discussion

^{13}C CP/MAS Spectra. Figure 1a shows the ^{13}C CP/MAS spectrum of the melted only PA6 sample, sample A. This spectrum is typical of a sample containing both the α crystalline polymorph of PA6 and amorphous PA6.[10] The crystalline fraction has narrow resonances at 43.3, 30.1, 26.3, 36.5, and 173.4 ppm corresponding to C1, C2 and C3, C4, C5, and C6, respectively. These chemical shift values are the averages measured for the five samples; the largest standard deviation was 0.2 ppm. The aliphatic carbons in the amorphous fraction of the bulk PA6 have spin–lattice relaxation times (T_1) of less than 2 s, which are much shorter than those in the crystalline fraction (which are longer than 60 s). Closely spaced (1-ms) 90° pulses to the carbons saturate the nuclei in the crystalline fraction and allow measurement of the spectrum of the amorphous fraction alone. The spectrum of the amorphous fraction is shown in Figure 1b. The NMR peaks are broader than in the crystalline fraction, and there are changes in the chemical shifts of some of the aliphatic carbons. In amorphous PA6, C1 is found at 40.0 ppm, C2, C3, and C4 resonances are unresolved and located in the region 32–26 ppm with a maximum at 27.8 ppm, C5 is at 36.8 ppm, and C6 is at 173.8 ppm. Estimated error in the amorphous chemical shift values is ±0.3 ppm. These chemical shift assignments in both fractions are based upon additivity rules found in the literature and comparison with our earlier work on high molecular weight PA6 polymers.

In a separate study of composites prepared by extrusion of high molecular weight PA6 with 50-μm glass microspheres, both α-PA6 and γ-PA6 polymorphs were found to be present.[10] The ^{13}C CP/MAS spectrum of γ-PA6 is different from that of α-PA6. In the γ polymorph, C1 resonates at 39.9 ppm and C5 at 33.9 ppm rather than 43.3 and 36.5 ppm, respectively, seen in the α polymorph. Spectra measured after a delay in an inversion recovery experiment allow one to examine the carbons which have long spin–lattice relaxation times, i.e., the carbons in the crystalline PA6 fraction. Figure 2a shows a spectrum of the crystalline fraction measured after a delay of 7 s; as a comparison, Figure 2b shows the spectrum of both components measured after a short, 5-ms delay. The spectra in Figure 2 are of sample E. Careful inspection of the spectrum in Figure 2a shows that there is no intensity at 34 and 40 ppm, the chemical shift values characteristic of γ-PA6. For the composites reported on here, prepared with low molecular weight PA6 in the manner described above, no detectable amount of the γ-PA6 polymorph was found in any of the samples.

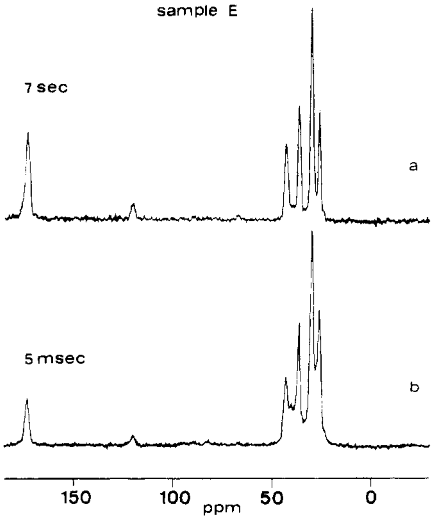


Figure 2. ^{13}C CP/MAS spectra of sample E taken after a relaxation delay; 710 FIDs without Lorentzian broadening. (a) 7-s delay; only crystalline PA6 is visible. (b) 5-ms delay, both crystalline and amorphous PA6 are visible.

Two model systems were prepared to provide insight into possible effects on the ^{13}C CP/MAS spectrum due to chemical and physical interactions between the γ-APS molecules and between the γ-APS and the matrix. These model systems were the polymer of γ-APS (poly(γ-APS)) and the polymer prepared from the reaction product of γ-APS and hexanoic acid, a model for PA6. Three peaks are present in the ^{13}C CP/MAS spectrum of poly(γ-APS), shown in Figure 3a, and correspond to the three carbons in the propyl group. The carbon α to the silicon, C1(γ-APS), at 12.7 ppm is the broadest (350 Hz); the center carbon, C2(γ-APS), at 28 ppm is of intermediate width (275 Hz), and the carbon adjacent to the nitrogen, C3(γ-APS), at 45.8 ppm is the narrowest (225 Hz). The differences in linewidth may reflect greater mobility at the ends of the chains and/or a broader distribution of environments near the siloxane network. The ^{13}C CP/MAS spectrum of the polymerized product of γ-APS and hexanoic acid (not shown) has peaks originating in the γ-APS at 42.7, 26.7, and 11.3 ppm. This spectrum suggests that the peaks at 42.7 and 26.7 ppm will be buried under the peaks of the bulk PA6 and that only the peak around 11 ppm might be observed in the composite samples containing polymerized γ-APS.

The first composite to be considered is sample B, prepared by the addition of γ-APS to PA6. The spectrum of this sample, in Figure 4a, shows no evidence of any of the γ-APS resonances, even the one at 11 ppm. This is explained by the low silicon content of sample B, which was determined by elemental analysis and found to be only 50% of the amount added to the melt. Apparently, the γ-APS partially evaporates (BP 217 °C) and/or reacts with the vessel when added separately to the PA6 melt. Con-

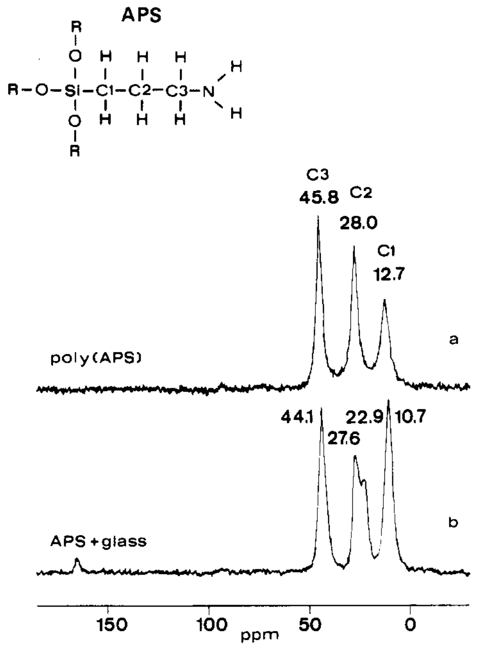


Figure 3. ^{13}C CP/MAS spectra. (a) Poly(γ-APS), 5325 FIDs with 10-Hz Lorentzian broadening. (b) Pretreated glass, 32600 FIDs with 10-Hz Lorentzian broadening.

sequently, the absence of a ^{13}C signal from C1(γ-APS) is not surprising. This explanation is corroborated by another experiment in which 10% (w/w) poly(γ-APS) was mixed with PA6 and investigated with ^{13}C CP/MAS NMR. Besides the high-intensity ^{13}C signals assigned to PA6, a low-intensity signal in the 10–12 ppm region was indeed observed. The γ-APS in sample B will be present not only as poly(γ-APS) but possibly also coupled to PA6. This means a broader distribution of chemical environments and therefore a broader C1(γ-APS) resonance. The ^{13}C CP/MAS spectrum of composite C, PA6 + glass microspheres only, shown in Figure 4b is basically the same as those of sample B (Figure 4a) and the melted only PA6 sample A (Figure 1a). There is no apparent influence on the spectra due to the presence of either the γ-APS or the glass microspheres.

The ^{13}C CP/MAS spectrum of the pretreated glass microspheres alone (Figure 3b) indicates what the coated glass microspheres might contribute to the spectrum of sample D, the next composite to be considered. At first sight, the spectrum of the pretreated glass microspheres is surprisingly different from that of poly(γ-APS) shown in Figure 3a. There are five peaks instead of only three. The peak of the central carbon in the propyl group has a shoulder, and the line widths of the three carbon resonances are approximately equal to one another. There is also a downfield peak in the spectrum at about 165 ppm which we assign to carbon in the ammonium bicarbonate salt formed when CO_2 and H_2O are absorbed from the atmosphere and react with the amine groups of the poly(γ-APS). Our peak assignment was confirmed by synthesizing the ammonium bicarbonate salt of poly(γ-APS) in the absence of glass microspheres. For this model compound the HCO_3^- resonance is located at 165 ppm, and C2(γ-APS) showed a shoulder due to molecules which participated in salt formation just as in the case of the pretreated glass microspheres sample. Thus, the apparent splitting of the C2(γ-APS) peak and the 165 ppm peak is most likely caused by bicarbonate salt formation and not by conformational effects. The formation of the bicarbonate salt of γ-APS in the presence of water and carbon dioxide under atmospheric conditions has been previously reported in a study with FT-IR spectroscopy.[11,12]

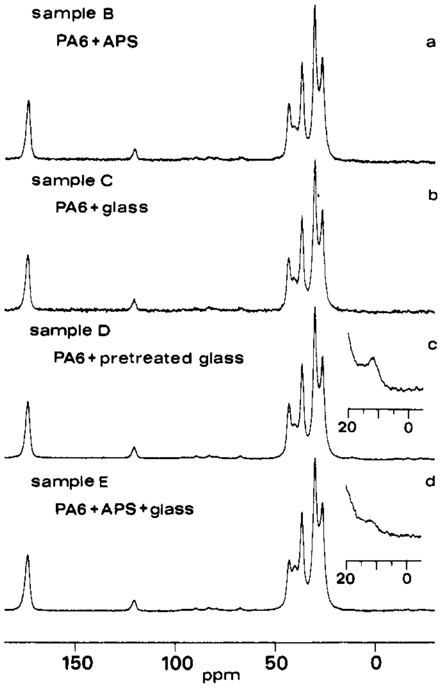


Figure 4. ^{13}C CP/MAS spectra of composites with 10-Hz Lorentzian broadening. (a) Sample B (PA6 + γ-APS), 3125 FIDs. (b) Sample C (PA6 + glass), 7100 FIDs. (c) Sample D (PA6 + glass pretreated with γ-APS), 3190 FIDs. The insert shows expansion of the region from 20 to −5 ppm. (d) Sample E (PA6 + glass + γ-APS), 8400 FIDs. The insert shows expansion of the region from 20 to −5 ppm.

Another change in the spectrum of the pretreated glass microspheres is that the C3(γ-APS) peak at 45.8 ppm in poly(γ-APS) is broadened and shifted 1.7 ppm upfield to 44.1 ppm while the 12.7 ppm peak is narrowed and shifted to 10.7 ppm, 2 ppm upfield. The change in line widths suggests mobilities at the different sites are more similar and/or the range of chemical shift environments is narrower than in the poly(γ-APS). Reaction with the surface of the glass microspheres has had effects upon the spectrum which are similar to those caused by reaction of γ-APS with hexanoic acid in terms of the direction and approximate magnitude of the changes in the C1(γ-APS) and C3(γ-APS) ^{13}C chemical shifts; in both cases the peaks are shifted upfield by about 2 ppm. These changes may be due in part to differences in magnetic susceptibility between the samples.

The spectrum of composite D (PA6 + pretreated glass microspheres), given in Figure 4c, shows only one peak from the polysiloxane layer on the pretreated glass microspheres, the C1(γ-APS) peak at 11.3 ppm. The rest are buried or, in the case of the 165 ppm peak, absent. Except for the 11.3 ppm peak, the spectrum is indistinguishable from those of samples A, B, and C.

The spectrum of the final composite, sample E, made by adding all three components together all at once in the integral blending procedure is shown in Figure 4d and is distinct from the spectra of composites B, C, and D. In this spectrum, the relative intensity at 43 ppm is decreased and at 40 ppm increased, and the resolution of the peaks at 26 and 30 ppm is worse than in the spectra of the other composites. It is possible to envisage the effects of a relatively greater amorphous contribution by considering the sum of the spectra shown in a and b of Figure 1. The source of these differences is a larger amorphous PA6 fraction in this microcomposite than in microcomposites B, C, and D. Although the amorphous fraction makes a larger contribution to the CP/MAS spectrum of sample E, the spectrum of the amorphous fraction, measured with 90° pulses, is unchanged. The spectra of the amorphous parts of the composites are all the same as that shown in Figure 1b except that the C1(γ-APS) peak at 11 ppm is observed for samples B and D and a small 165 ppm peak (from the bicarbonate salt) is observed for sample B. The peak at about 11 ppm is very weak in the spectrum of sample E, see Figure 4d.

The main reason for the relatively greater amount of amorphous polymer in composite E is autocondensation of the PA6 chains in the melt and possible coupling of the PA6 by γ-APS. Gel permeation chromatography (GPC) analysis of the soluble polymer fractions of samples A, B, C, D, and E indicated an increase in molecular weight when composites were prepared. The starting PA6 polymer had a MW of 7000, and the melting and stirring procedure (sample A) increased this to 11 000. Approximately the same increase, to 12 000, was seen for samples C and D. However, sample B (the composite prepared by adding only γ-APS) showed a bimodal distribution with maxima at 9500 and 42 000. Thus, a consequence of adding γ-APS to the PA6 melt is a molecular weight which is higher than that which results from PA6 condensation reactions alone. Sample E (the composite prepared by integral blending) gave a distribution with a maximum at 27 000. This is an increase which, as in the case of sample B, cannot be easily attributed to only condensation of PA6 molecules; it must also include a contribution from coupling of PA6 by γ-APS. Longer PA6 chains are less mobile and crystallize with greater difficulty than shorter chains, so condensation results in a larger amorphous fraction. Coupling of PA6 chains by γ-APS prevents crystallization near the ends of the chains. Since there is no well-defined peak at the C1(γ-APS) position (10–12 ppm) in the ^{13}C CP/MAS spectrum of E (Figure 4d), it appears that apart from evaporation of the γ-APS, multiple environments for C1(γ-APS) must be present which broaden the peak and make it difficult to detect.

The three samples of glass microspheres (samples C′, D′, and E′ isolated from composites C, D, and E, respectively) gave strong ^{13}C CP/MAS signals in stark contrast to the pure glass microspheres, which gave no ^{13}C signal at all. Clearly all three samples contain organic material at the surface of the glass microspheres. Apparently there are strong chemical and/or physical interactions between the glass microspheres and the organic components which prevent the solution of the organic material by TFE. An estimate of the amount of organic material present at the surface of the glass microspheres was obtained with thermal gravimetric analysis (TGA), which showed a 6.2% weight loss for sample C′, a 34.4% weight loss for D′, and a 17.2% weight loss for sample E′. This is in agreement with the signal to noise (S/N) ratios observed in the ^{13}C NMR spectra, see Figure 5. Since the glass microspheres used in the preparation of composite D received a 8.4% loading with γ-APS, the net weight gained by the microspheres due to interaction with the PA6 is greater in the case of pretreatment of the glass microspheres (sample D) then when all components are integrally blended (sample E). There appears to be a qualitative relation between the amount of γ-APS present at the surface and the amount of PA6 adhering to the microspheres; i.e., with increased loading of γ-APS, more organic material adheres, resulting in a thicker interfacial layer. However, on the basis of these spectra we are unable to determine whether chemical bonding or interpenetration of the networks is the mechanism responsible for the increased interaction with PA6; it is likely that both mechanisms contribute.

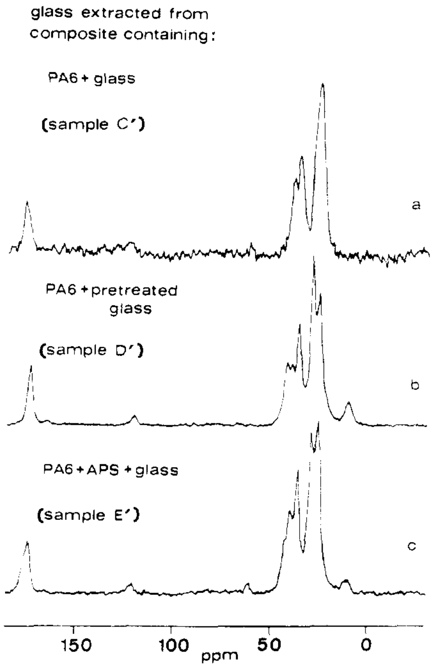


Figure 5. ^{13}C CP/MAS spectra of microspheres isolated from the composite samples, with 25-Hz Lorentzian broadening. (a) Sample C′ (from composite C), 8100 FIDs. (b) Sample D′ (from composite D), 7500 FIDs. (c) Sample E′ (from composite E), 8150 FIDs.

The CP/MAS spectrum of C′ (the glass microspheres removed from the composite containing only PA6 and glass microspheres) in Figure 5a is similar to the spectra of the amorphous fractions of the original sample (Figure 1b) except for the enhancement of the carbonyl intensity caused by cross-polarization. The carbonyl peak (C6 of the PA6) is shifted downfield from 173.4 to 176.8 ppm. There is also a small peak at 61 ppm from the TFE solvent used to dissolve the PA6 matrix. In a FT-IR analysis of chemical and hydrogen bonding between metal oxide surfaces and an aminosilane reagent,[13] it was suggested that the amine group hydrogen bonded directly to a silica surface. Therefore, it is possible that part of the interaction between the PA6 and the glass microspheres is hydrogen bonding between NH_2 groups and acid sites on the glass microspheres. However, this interaction remains a matter of controversy.[14]

The ^{13}C CP/MAS spectrum of D′ (glass microspheres removed from the composite made by combining pretreated glass microspheres and PA6) in Figure 5b contains evidence of both amorphous and crystalline regions of PA6. It is obvious that this thick layer of organic material contains crystallites in addition to the amorphous layer observed on the surface of the glass microspheres in the first sample, sample C′ in Figure 5a. There is also a strong peak at 11 ppm from C1(γ-APS) and, once again, a weak signal at 165 ppm from the bicarbonate salt. Apparently the relative contribution of this 165 ppm peak to the spectrum of sample D (Figure 4c) is too small for it to be seen, but when the bulk of the PA6 is removed, it becomes visible as in the case of the pretreated balls, Figure 2b. It is also possible that when PA6 is present it shields unreacted amine groups of the γ-APS so that formation of the bicarbonate salt does not occur.

The ^{13}C CP/MAS spectrum of the glass microspheres isolated from the composite prepared by adding PA6, γ-APS, and glass microspheres together all at once, sample E′, is different from those of both C′ and D′ as shown in Figure 5c. Both the amorphous and crystalline peaks are present, but the crystalline fraction is relatively smaller than in sample D′ as shown by the lower intensity of the 43 ppm peak relative to the 40 ppm peak and the increase in the 26.5 ppm peak intensity relative to the 30 ppm peak. The thinness of the polymer layer is probably responsible for the lower crystallinity of sample E′ compared with sample D′. Disruption of the PA6 crystallization by partial coupling of the polyamide chains by γ-APS during composite preparation may also contribute to the formation of large amorphous regions. The C1(γ-APS) peak at about 11 ppm is visible in the spectrum of E′, unlike the spectrum of its intact parent, composite E. The presence of the C1(γ-APS) peak shows that a large fraction of the γ-APS has diffused to the glass microsphere surface and is therefore concentrated in the interfacial layer of this composite when prepared by integral blending.

Unfortunately, it is once again not possible to make any definitive statement about the presence or absence of an interpenetrating network based upon these spectra. If they were entangled in a poly(γ-APS) layer, PA6 chains could not crystallize. However, the purely amorphous PA6 layer on the surface of the glass microspheres in the composite containing no silane, Figure 5a, shows that even without hindrance by the polysiloxane the PA6 adopts a highly disordered configuration. Thus, no conclusions about interpenetration may be drawn based upon the relative crystallinity of the PA6 on the surface of these glass microspheres. The relatively larger amount of PA6 present when the surface of the glass microspheres is pretreated with the coupling agent strongly indicates that some entanglement of PA6 chains in the γ-APS layer is responsible for adhesion in these composites. The larger amount of γ-APS at the interface of sample D′ relative to sample E′ also provides more amine groups for reaction with PA6 carboxylic acid end groups. This amide formation may also contribute to the presence of a thicker PA6 layer. The spectra of the PA6 in the intact composites C, D, and E are quite similar to one another (Figure 4b–d) but different from the spectra of C′, D′, and E′ (Figure 5a–c). This shows that the PA6 in the interfacial layer in a given composite is clearly different from the bulk PA6 in the same composite.

The ^{13}C CP/MAS spectra (not shown) of the polymer fractions of the composites, C″, D″, and E″ are very similar to one another and to those of the composites C and D. There is no evidence of either the C1(γ-APS) peak or the ammonium bicarbonate peak at 165 ppm in any of these spectra. The absence of the 11 ppm peak in these data shows that in composites D and E all of the γ-APS which is detectable with ^{13}C NMR (at 11 ppm) is at the surface of the glass microspheres. However, as discussed below, ^{29}Si CP/MAS NMR does show the presence of a small amount of γ-APS in the polymer matrix of composite E.

^{29}Si CP/MAS Spectra. The ^{29}Si data presented here were collected with cross-polarization; therefore, only ^{29}Si nuclei which are near protons will be observed, and silicon nuclei in the bulk of the glass microspheres will not be observed. Indeed, when the ^{29}Si NMR spectrum of the composite containing pretreated glass microspheres is measured without CP, the ^{29}Si resonances from the polysiloxane layer are not visible beneath the broad wings of the peak from ^{29}Si nuclei in the bulk of the glass microspheres.

The ^{29}Si CP/MAS spectrum of the pure glass microspheres is given in Figure 6a. One intense central line at −98.6 ppm (Q^3) has two side peaks at −89.9 (Q^2) and −109.6 ppm (Q^4). In analogy with the ^{29}Si CP/MAS spectra of silica gel and other well-characterized silicates,[15] these lines may be assigned to the three species indicated in the spectrum.

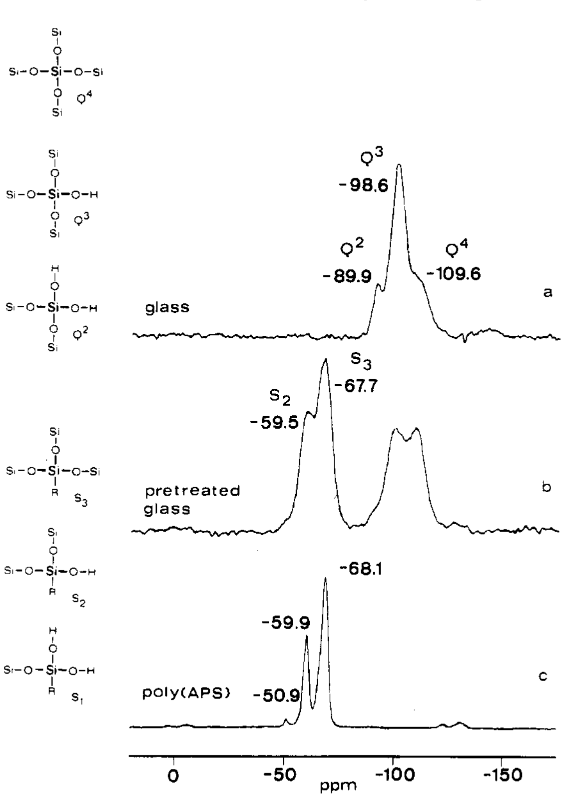


Figure 6. ^{29}Si CP/MAS spectra. (a) Pure glass microspheres, 12 800 FIDs with 75-Hz Lorentzian broadening. (b) Glass microspheres pretreated with 8.4% γ-APS, 6240 FIDs with 75-Hz Lorentzian broadening. (c) Poly(γ-APS), 28 250 FIDs with 25-Hz Lorentzian broadening.

After these balls are reacted with 8.4% γ-APS, new lines appear in the ^{29}Si CP/MAS spectrum as shown in Figure 6b. These are due to the Si nuclei of the γ-APS in the interfacial layer. (A single line is observed in the ^{29}Si spectrum of pure γ-APS at −45 ppm.[16]) The −67.7 ppm peak, denoted S_3, is assigned to ^{29}Si nuclei bonded to three other Si atoms (either on the surface or in a poly(γ-APS) polymer layer) via oxygen bridges, and via a fourth bond to the aminopropyl substituent. The −59.5 ppm peak is due to Si bonded via oxygens to two other Si atoms, one hydroxyl group, and the aminopropyl group, denoted S_2. Since the S_3 peak is dominant in the poly(γ-APS) layer, it is clear that the polysiloxane is highly cross-linked. The shoulder due to the Q^2 surface species which is present in Figure 6a is less pronounced in the spectrum of pretreated glass microspheres; apparently the Q^2 sites on the surface of the glass microspheres react readily with the γ-APS. The Q^3 peak is the most intense for the pure glass microspheres, whereas the intensities of Q^3 and Q^4 are equal in Figure 6b. The change in relative intensities is due to a combination of factors including a decrease in the amount of Q^3 sites through reaction with γ-APS and an increase in the amount of Q^4 sites when the coupling agent reacts with the surface.

A variable mixing time experiment on the pretreated glass microspheres was used to determine the optimal length of time for cross-polarization from the protons to the silicons.[17] There is no single optimum mixing time for all the Si peaks because of differences in the environments of the two pairs of Si nuclei, Q^3 and Q^4, S_2 and S_3. The Q^3 and Q^4 sites both have longer cross-relaxation times, $T_{\mathrm{Si-H}}$, and a longer proton $T_{1\rho}$ while the sites in the siloxane show shorter $T_{\mathrm{Si-H}}$ and a shorter proton $T_{1\rho}$. Two mseconds, optimum for the S_2 peak, was selected as the mixing

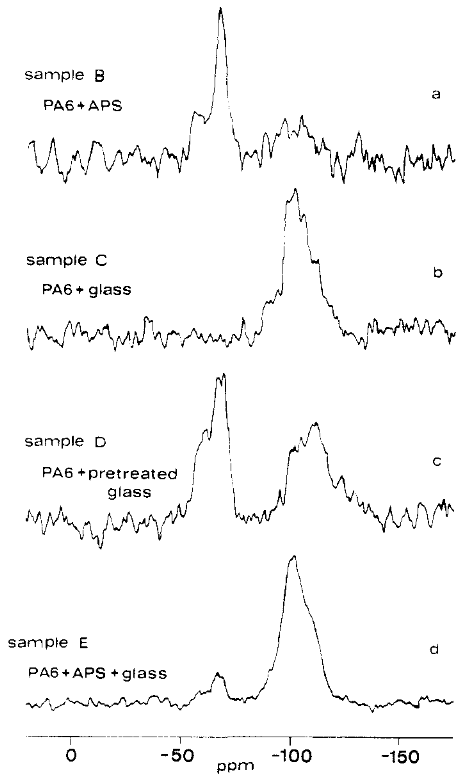


Figure 7. ^{29}Si CP/MAS spectra of composite samples with 75-Hz Lorentzian broadening. (a) Sample B, 13 325 FIDs. (b) Sample C, 21 500 FIDs. (c) Sample D, 28 925 FIDs. (d) Sample E, 24 100 FIDs.

time in the ^{29}Si CP/MAS measurements. However, as the intensity of the surface sites would be enhanced with longer mixing times, these data are presented as qualitative evidence for the chemical species which are present. A quantitative study is in progress.

Before we discuss the ^{29}Si CP/MAS spectrum of sample B (PA6 + γ-APS), Figure 6c shows the CP/MAS spectrum of the polysiloxane polymer derived from γ-APS. The S_2 and S_3 peaks are the same as those seen on the pretreated glass microspheres although they are better resolved in the pure poly(γ-APS). There is an additional line at −50.9 ppm which is assigned to Si bonded to one other silicon, two hydroxyls, and the aminopropyl group, denoted S_1. In passing, we note that the polymer of hexanoic acid and γ-APS also has the S_2 and S_3 lines at −57.1 and −69.3 ppm, respectively, but the S_2 line is very weak.

Reactions of the coupling agent with the surface silanols change the relative intensities of Q^2, Q^3, and Q^4 sites. When a Q^2 silanol reacts with γ-APS, the silicon becomes a Q^3 site and the silicon of the γ-APS becomes a S_1 site. Correspondingly, a surface Q^3 becomes Q^4 when it reacts with γ-APS. The S_1 sites become S_2 sites by condensation reactions or by reaction with a second surface site. Similarly, S_2 sites become S_3 sites by further reaction. The relative intensities of the ^{29}Si CP/MAS NMR peaks originating in the polysiloxane layer are therefore expected to be sensitive to the history of the sample. For example, if the samples were heated, further condensation is possible with the result that the S_3 peak would grow at the expense of the S_2 peak.

The ^{29}Si CP/MAS spectra from composites B and C are given in a and b of Figure 7, respectively. In the spectrum of composite B (PA6 + γ-APS), Figure 7a, the S_2 and S_3 lines are present with a low S/N ratio. Unlike the ^{13}C CP/MAS spectrum of sample B, which showed no evidence of the 11 ppm γ-APS resonance, the ^{29}Si CP/MAS spectrum clearly shows the presence of the coupling agent. The S_2 and S_3 silicon resonances appear at about the same field whether the final product is a layer on the surface of the glass microspheres, a pure γ-APS polymer, or γ-APS reacted with PA6. The spectrum of the composite made by adding microspheres to PA6, sample C, is shown in Figure 7b. It is very much like that of the pure glass microspheres with a reduced S/N due to the effective dilution of the silicon in the sample. There seems to be little enhancement of the cross-polarization due to the presence of the PA6, which indicates only weak coupling between the polymer matrix and the glass microspheres.

The ^{29}Si CP/MAS spectra of composites D and E are presented in parts c and d of Figure 7. Except for the reduced S/N, the spectrum of D looks very much like the spectrum of the pretreated glass microspheres which it contains. The two lines characteristic of the silicons from the interfacial layer, S_2 and S_3, are present as are the poorly resolved, equally intense Q^3 and Q^4 lines. The presence of the PA6 and the possible reaction between carboxylic acid end groups of the PA6 and the NH_2 of the aminopropyl moiety have had no noticeable effect on the spectrum. However, the appearance of the ^{29}Si CP/MAS spectrum of E (PA6 + γ-APS + glass microspheres all at once) in Figure 7d is rather different from that of sample D. The ^{29}Si nuclei at the surface of the glass microspheres are like those of the pure glass microspheres: Q^2, Q^3, and Q^4 are all present, with Q^3 as the dominant peak. Very little of the silicon from the γ-APS is visible. S_2 and S_3 lines are present, but they are weaker than those in the spectrum of composite D. The smaller contribution of γ-APS to the spectrum is caused by evaporation during preparation and side reactions of the γ-APS with the surface of the reaction vessel, as mentioned above. When this spectrum of sample E is compared with that of sample C (Figure 7b), the improved S/N of the Q^3 and Q^4 peaks shows more protons near the surface available for cross-polarization and therefore better bonding between the glass microspheres and the organic layer. However, the relative intensities of the Q^3 and Q^4 peaks in Figure 7d are little changed compared to the glass microspheres in Figure 6a; only the S/N is improved. This shows that the enhanced cross-polarization affects the surface sites similarly. From this we can conclude that the dominant mechanism responsible for the change in relative intensities of the Q^3 and Q^4 sites in the spectrum of sample D (Figure 6c) is reaction with γ-APS and not a change in relative cross-polarization efficiencies.

The ^{13}C spectra of the glass microspheres extracted from the composites were quite different from the ^{13}C spectra of the intact composite from which they were removed. In contrast, the ^{29}Si CP/MAS spectra of the isolated glass microspheres from composites C, D, and E are essentially the same as those obtained for the parent composites. However, as shown in Figure 8, the S/N ratios are strongly enhanced due to the much larger amount of glass microspheres in the sample, approximately 3 times as much. The spectrum of sample C′ in Figure 8a contains only the Q^2, Q^3, and Q^4 sites typical of an unmodified glass surface. The CP/MAS spectrum of sample D′ in Figure 8b is very much like that of the pretreated glass microspheres except for lower resolution of the S_2 and S_3 peaks. From this spectrum it appears that inclusion in the PA6 and subsequent solution of the polymer matrix have little affected the underlying polysiloxane layer on the surface of the glass microspheres. The CP/MAS spectrum of sample E′ in Figure 8c shows surface sites on the glass microspheres with only slight changes in relative intensities compared to sample C′. Most interesting are the weak S_2 and S_3

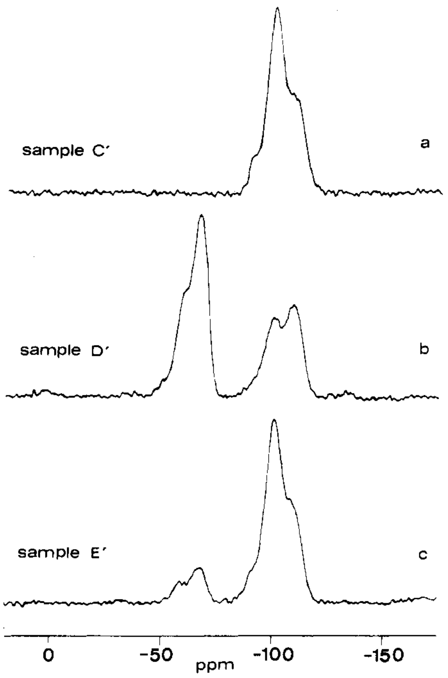


Figure 8. ^{29}Si CP/MAS spectra of isolated glass microspheres, with 25-Hz Lorentzian broadening. (a) Sample C′, 27 600 FIDs. (b) Sample D′, 24 925 FIDs. (c) Sample E′, 25 750 FIDs.

peaks which are clear evidence of the presence of γ-APS at the surface. However, the amount of γ-APS at the surface is clearly less than that present in the case of sample D′. One can therefore conclude that some of the γ-APS does diffuse to the surface of the glass microspheres, and reacts, when it is added to the mixture of melted PA6 and glass microspheres.

A significant difference between composites D and E was revealed by the ^{29}Si spectra of their isolated polymer fractions, samples D″ and E″, respectively. Only in the case of sample E″ was a signal observed (not shown). Part of the γ-APS polymerizes in the melt before siloxane formation can occur at the glass microsphere surface. The single peak was at −67.7 ppm and assigned to S_3 of poly(γ-APS). The weakness of this signal relative to the S_2 and S_3 sites on the glass microspheres isolated from sample E, sample E′, shows that most of the γ-APS in the composite is near the surface and not in the matrix. It is not clear whether there are also amide bonds formed between the coupling agent and the polymer. The presence of the silane in the polymer matrix will also modify the behavior of the matrix and thereby the composite properties. These data further show that no detectable amount of the polysiloxane layer on the pretreated glass microspheres comes loose during either the composite preparation or the glass microsphere isolation procedure.

Conclusions

^{13}C CP/MAS Data. The ^{13}C CP/MAS spectra of processed PA6 (sample A) and composites made from PA6 + γ-APS (sample B), PA6 + glass microspheres (sample C), and PA6 + pretreated glass microspheres (sample D) are all very similar to one another except for the presence of a peak at 11.3 ppm corresponding to C1 of the polymerized silane coupling agent, γ-APS, for sample D. There are no shifts of the ^{13}C resonances of the PA6 when the composites are made, and only the α crystalline polymorph of PA6 is observed. Sample E, integrally blended PA6 + glass microspheres + γ-APS, contains a larger amount of amorphous PA6 polymer than the other composites. The increase in amorphous PA6 is primarily due to condensation reactions between PA6 chains and coupling of PA6 by γ-APS, which increases the molecular weight and makes crystallization more difficult. No reaction between the amine and the carboxylic end groups of the PA6 can be observed directly in the ^{13}C CP/MAS spectra. However, formation of the ammonium bicarbonate salt of the NH_2 groups of the γ-APS is readily detectable with ^{13}C NMR.

The ^{13}C CP/MAS spectra of the three different samples of glass microspheres isolated from the composites show unique interfacial polymer layers. In sample C′, isolated from composite C, the glass microspheres *do* have a layer of PA6; however, it is only amorphous. Sample D′, isolated from the composite containing pretreated glass microspheres, has a PA6 layer which contains crystalline and amorphous PA6 fractions in approximately equal amounts. Sample E′, the filler isolated from composite E, has a predominantly amorphous layer with a small crystalline fraction. These results show that the interfacial PA6 is distinct from the bulk PA6 in the different intact composites in which the relative crystallinities of the (bulk) PA6 were found to be more similar to one another. Thermogravimetric analysis indicates that relative amounts of PA6 on the surface of the glass microspheres are approximately 1:4:2 for samples C′, D′, and E′, respectively. The bonding between the glass microspheres and the organic layer is therefore best when the γ-APS coupling agent is present. However, even in the absence of coupling agent, there are strong interactions between the surface of the glass microspheres and the polymer as evidenced by an organic layer on the surface. In addition to better bonding between the glass microspheres and the organic matrix, pretreating the glass microspheres with γ-APS appears to increase the amount of PA6 which is associated with the interfacial layer, thereby supporting crystallization of the PA6. It is not obvious from these ^{13}C data whether the increased interaction is due to chemical bonding or interpenetration of the PA6 and γ-APS networks.

^{29}Si CP/MAS Data. The ^{29}Si CP/MAS spectra of the composites show five different ^{29}Si environments. Three of these are surface sites, Q^2, Q^3, and Q^4, and two are in a siloxane layer, S_2 and S_3. From the spectra it is clear that γ-APS reacts with the Q^2 and Q^3 sites on the surface of the glass microspheres. When the composite is prepared by integral blending (sample E), much of the γ-APS diffuses to the surface of the glass microspheres and participates in the formation of siloxane linkages, primarily with other γ-APS molecules. The silicons originating in the γ-APS are found in two types of environments (at about −60 and −68 ppm), independent of the manner of composite preparation. However, the extents of reaction and, thus, the relative amounts of the different species are dependent upon the way in which the composite is prepared. There is no evidence of chemical bonding between the γ-APS and PA6 in these ^{29}Si spectra.

The results of ^{29}Si investigations of the microspheres isolated from the composites, samples C′, D′, and E′, support the results derived from the spectra of the intact composites: (a) the greatest amount of γ-APS is present at the surface when the glass microspheres are pretreated with the coupling agent, (b) γ-APS does diffuse to the surface when added to the melt containing glass microspheres (integral blending) (c) the structures present are independent of the method of preparation, and (d) there is no clear evidence which points to either chemical bonding or interpenetration as the unique mechanism responsible for enhanced adhesion in the composites.

^{29}Si CP/MAS NMR spectra of the soluble polymer fractions of the composites show that when a composite is prepared by adding the γ-APS to the melt containing PA6 and glass microspheres, some poly(γ-APS) is formed in the polymer matrix itself. In the spectrum of the polymer fraction of D, no ^{29}Si is visible, indicating that the layer of siloxane from pretreatment remains firmly attached to the glass microspheres.

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Registry No. PA6, 25038-54-4; γ-APS, 919-30-2.

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Relaxation Behavior of Linear Polymer Chains with Statistically Distributed Functional Groups

Reimund Stadler* and Liane de Lucca Freitas

Institut für Makromolekulare Chemie, Hermann Staudinger Haus, Stefan Meier Strasse 31, D-7800 Freiburg, West Germany. *Received September 17, 1987;*
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ABSTRACT: On the basis of the Doi–Edwards model of reptation, the terminal relaxation properties of a linear polymer melt in which the monodisperse polymer chains carry a certain number N of associating functional groups is described. The relaxation behavior is strongly influenced (i) by the mean lifetime of the complexes formed between two functional groups and (ii) by the mole fraction of complexed groups. Tube renewal processes are incorporated into the model. The theoretical relaxation curves are in qualitative agreement with corresponding experimental results obtained for a model system.

Introduction

The linear viscoelastic properties of polymer melts are strongly influenced by the presence of a few functional groups. Typical examples are ionomers like sulfonated EPDM rubbers or polystyrene sulfonates.[1,2] Considerable experimental work dealt with the influence of parameters like the polarity of the surrounding medium and counterion and degree of modification on the bulk and solution properties.[3,4] Recent work on ionomeric model systems (halatotelechelics) showed that the association behavior is governed by well-defined ionic clusters with 10–12 ionic dipoles associated to a multiplet.[5,6] To describe theoretically the behavior of polymers with associating groups, it is generally assumed that dimeric complexes between the ionic groups are formed.[7-9] The main focus of these investigations was the behavior in dilute solution; especially the coil collapse due to the interacting groups has been considered.[9] No theoretical description of the dynamic behavior of ionomers, which accounts for the detailed picture of the different levels of molecular organization, is available.

To elucidate the basic assumptions of the theoretical models, appropriate model systems must be chosen. We have reported on the formation and the rheological properties of thermoreversible networks, where the junctions are formed by a defined hydrogen-bond complex between two functional groups.[10,11] In such a system, IR spectroscopy of the hydrogen-bond complex[12] allows a direct relation between complex formation and the mechanical properties. It should be mentioned that Longworth and Morawetz[13] reported on the influence of hydrogen bonding on the melt viscosity in styrene–methacrylic acid copolymers as early as 1958. The experimental techniques now available allow a more detailed analysis. In addition, the interpretation of rheological data should be simplified by the use of polymers of narrow molecular weight distribution.

In this paper, a simple theoretical model that describes the flow behavior of polymers with a defined number of functional groups is presented based on an approach first introduced by González.[8] The model is based on the concept of relaxation by reptation,[14] and the effect of associating groups is introduced into the tube model of Doi and Edwards,[15] including extensions that take into account the tube renewal processes.[16-18]

Theoretical Model

The polymer melt consists of linear monodisperse polymer chains with degree of polymerization P_n. A small fraction u (=degree of modification <5%) of the repeating units carries the functional groups U, which are able to form dimeric complexes. Thus, the number of functional groups per chain N is given by $P_n u$. Complexation is described by the equilibrium reaction

$$\mathrm{U} + \mathrm{U} \xrightarrow{K_0} \mathrm{U}_2 \qquad (1)$$