Bifunctional Coupling Agents for Improved Mechanical Properties in Fiberglass/Polyethylene Composites

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ABSTRACT: Two bifunctional compounds, 12-azido-1-diazo-2-dodecanone (**A**) and 1-diazo-17-octadecene-2-one (**B**), show an ability to act as coupling agents in fiberglass/ polyethylene composites. Under appropriate conditions the diazoketone functional groups in both **A** and **B** react with hydroxyl groups on a fiberglass surface, whereas the azide group in **A** and the alkene group in **B** form bonds with the plastic matrix during processing. FTIR and NMR spectroscopy were used to study the decomposition of each of these compounds under heat and UV light. Each treatment resulted in a relatively fast decomposition of the diazoketone functional group, along with a slower reaction of the azide and alkene groups. Thus it was possible to react the diazoketone end of these compounds with a fiberglass surface, without affecting the azide or alkene functional groups on the other ends of the molecules. In samples of treated fiberglass containing compounds **A** or **B** and mixed by extrusion with polyethylene, the mechanical properties of the composites had improved properties over composites containing untreated samples of fiberglass. With **A** as the coupling agent, both the tensile properties and Izod impact showed changes that indicated that a bifunctional bridge was formed between the fiberglass and polyethylene phases. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2562–2578, 2002

Key words: bifunctional bridge; fiberglass; coupling agent; organosilanes; fiberglass/ polyethylene composites

INTRODUCTION

Hard glassy fillers such as fiberglass can be added to various thermoplastic materials such as polyethylene to develop new composites with a range of properties that extend beyond those exhibited by unaltered polyethylene. In particular, fiberglass can be added to increase both the hardness and tensile modulus of these compounds. Polyethylene, however, is a nonpolar hydrophobic material, whereas glass is polar and hydrophilic. The resulting chemical dissimilarity causes voids to develop at both the molecular and the microscopic levels in these composites, and maximum benefit from the mixing of these two materials is often not achieved. This is usually addressed by the addition of commercial additives (commonly organosilane structures), which act as wetting and bonding agents between the two phases.

Organosilanes have been thoroughly studied in polyethylene/glass composites. Ishida[1] and Singh et al.[2] have shown that alkoxysilanes react with glass or fibrous materials that contain surface

hydroxyl groups. Azzopardi and Arribart[3] have demonstrated a similar reaction between hydroxysilanes and glass. These reactions have been proven by dynamic mechanical measurements, IR measurements,[2–4] and electron microscopy of fractured blends.[5,6] Malik et al.[7] have shown that surface treatment of mica, TiO_2, and carbon black fillers in HDPE composites with silane and titanate coupling agents decreases the particle–particle interactions, and increases the polymer–particle interactions in these composites. Mieck et al.[8] used bifunctional silanes to improve the adhesion in flax fiber containing composites with polypropylene. Maurer and Welander[9] have shown that an increase in silane coupling agent in glass/polyethylene composites reduces the free volume in the interphase region between glass and polyethylene. It is also known that an increase in the compatibility and penetration of the organic portion in an aminofunctional silane strengthens the adhesion between a polymer and a silane-treated glass surface.[10] Evidence is now available that aminosilanes react not only with the glass surface but also with polypropylene, polyamide, and polycarbonate matrix polymers.[11] It has also been shown that acryloxy-substituted silanes[12] and trimethoxysilanes[13] bind silica and fiberglass, respectively, to polymethyl methacrylate. A vinyl benzylamino-substituted silane binds a hard clay filler with epoxidized rubber.[14]

Despite their utility in glass/polyethylene composites, organosilanes as a group of compounds suffer from premature hydrolysis during storage, producing oligomers and other by-products that are not very reactive with a glass surface. The result can be poor chemical bonding between filler and polymer.[15] When silanes are used as additives in rubber compounding, the additive often leaches out of the polymer and reacts on the surface of the steel mold, causing considerable fouling of the mold. Pleuddemann[16] has shown that organosilanes are easily hydrolyzable. An Si–O–glass bridge in polyethylene/silane/glass composites is hydrolyzed to form an organosilane triol, with release of the bond between the coupling agent and the glass.

Ultimately, a surface-active agent is needed that can provide a better chemical bond between polymer and filler. Preferably this will involve the use of bifunctional coupling agents that are not easily hydrolyzed after reaction with the two phases. Perez-Camacho et al.[17] used 3-amino-1-propanol to bridge maleated SEBS rubber and styrene–maleic anhydride copolymers. This principle can be easily extended to polymer composites containing glass and polymeric phases when the appropriate functionalization is present in the coupling agent to cause reaction with each phase.

In the early 1990s Holden et al.[18,19] synthesized and tested a series of bifunctional compounds containing diazoketone, azide, and alkene functional groups. Several compounds in this series containing the diazoketone group were able to react with the hydroxylated surfaces of alumina and silica gel. This was demonstrated by the fact that compounds containing this group could not be extracted from the surface of the glass after UV irradiation. Some of the compounds studied by McGarvey and Holden also contained the thermally reactive azide group at the other end of the molecule. This functional group can decompose to a nitrene upon heating or irradiation by UV, providing a possible route for the reaction of azide groups with thermoplastic polymers during mixing at elevated temperatures. Aroyl azide compounds have been studied by Bohme et al.,[20] and shown to react with the surface of a polyacrylonitrile polymer by a photochemically initiated insertion reaction involving intermediate nitrene formation. A number of other compounds in the McGarvey/Holden series contained the alkene group, which is vulnerable to free-radical attack at elevated temperatures during the processing of thermoplastic polymers.

Two bifunctional compounds, 12-azido-1-diazo-2-dodecanone (**A**) and 1-diazo-17-octadecene-2-one (**B**), were chosen for study as potential coupling agents in polyethylene/fiberglass composites. Both compounds contained the diazoketone group, whereas **A** also contained an azide group and **B** an alkene group on the opposite ends of the molecules. The structures of these compounds and their potential as coupling agents are illustrated in Figure 1.

Laboratory investigations by FTIR and NMR were undertaken on compounds **A** and **B** to determine the rates of decomposition under heat and UV light. Under similar experimental conditions their reaction with the surface of a fiberglass filler was also determined, by measurement of the amount of unreacted compound that could be extracted from the surface of treated glass samples.

Composites of polyethylene and treated fiberglass with **A** and **B** were made by extrusion, and the properties of several blends made with these compounds were compared with each other. The properties were also compared to a composite pre-

Compound A

12-Azido-1-diazo-2-dodecanone

Compound B

1-Diazo-17-octadecen-2-one
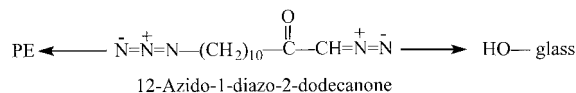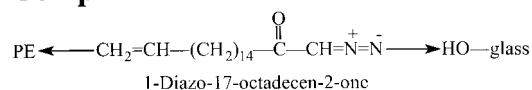
Figure 1   Structures of compounds **A** and **B**.

pared with a commercially recommended silane-based coupling agent. Early studies indicated the greatest promise for compound **A.** Thus optimization of the blending process and the conditions under which the bifunctional agent would bond to the polyethylene matrix was undertaken primarily on this coupling agent. A variety of extrusion conditions were investigated, including variation of the temperature and residence time in the extruder, use of an N_2 blanket on the extruder, and addition of benzoyl peroxide (BPO) or azobisisobutyronitrile (AIBN) during the extrusion process.

EXPERIMENTAL

Fiberglass 739DD, floccular glass fiber with no sizing, was obtained from Fiberglass Canada. This is a milled glass product with average length of $\frac{1}{32}$ in. (0.8 mm), average filament diameter of 15.8 μm, and nominal bulk density of 0.8 g/cm^3, yielding an *L/D* for these fibers of 50. High-density polyethylene (HDPE; Sclair 2710) was obtained from Dupont (Wilmington, DE) and linear low-density polyethylene (LLDPE; Novapol GI-2024-A) was obtained from Novapol Industries.

Compounds **A** and **B** were synthesized according to the method outlined in McGarvey and Holden.[18] The effect of heat on the decomposition of the diazoketone group over a range of temperatures was determined by depositing samples of **A** and **B** onto IR disks, heating the coated disks for various times at a prescribed temperature, and measuring the FTIR spectra on the cooled disks. NMR and FTIR studies at 150°C were undertaken by depositing these compounds onto watch glasses from solutions in CHCl$_3$, and heat-

ing them in an oven controlled at this temperature. At specified intervals a sample was removed from the oven, dissolved into CDCl$_3$, and the 400-MHz NMR spectrum measured. Then a portion of this solution was deposited onto an NaCl disk, and the FTIR spectrum measured. In general as the compounds were heated, they became less soluble in CDCl$_3$, because of chemical changes that took place with heat.

All UV treatments were conducted using a Hanova utility UV quartz lamp, which is able to deliver the full range of wavelengths in the UV–vis spectrum. The effect of UV light on **A** and **B** was tested by coating IR disks with the compound being studied and exposing them for various times to UV light, after which the IR spectra were determined.

To determine the percentage recovery of **A** and **B** from the surface of fiberglass after treatment by UV light or heat, a sample of the compound was first deposited onto the surface of the fiberglass. For heat treatments, the samples were placed into round-bottom flasks, immersed in a bath adjusted to the specified temperature, and shaken regularly. For UV treatments the samples were placed into quartz round-bottom flasks and exposed to UV light while rotating on a rotary evaporator. The atmosphere in the flasks could be adjusted to contain air or N_2. After treatment, a 10-g sample of the treated fiberglass was slurried in hexane, and UV spectroscopy was used to measure the amount of **A** or **B** that could be extracted from the surface of the fiberglass sample. In each case the percentage recovered compound was plotted against time of exposure.

To undertake extrusion studies, 200-g samples of treated fiberglass were prepared by depositing **A** or **B** from solution onto the surface of the glass, followed by a heat treatment. The standard application rate for both compounds was 0.1% w/w, approximately four times the calculated amount needed to form a monolayer, to allow for evaporation from the surface of the fiberglass during heat or UV treatment. The treated samples of fiberglass were dry-mixed at a 20% w/w level with HDPE or LLDPE, which had been first ground into a powder. This mixture was extruded in a single-screw extruder (zones adjusted to 220, 270, 270, and 180°C, 70-s residence time), and injection-molded (zones adjusted to 210, 230, 225°C and nozzle temperature at maximum). Tensile and impact properties were tested on an average of five
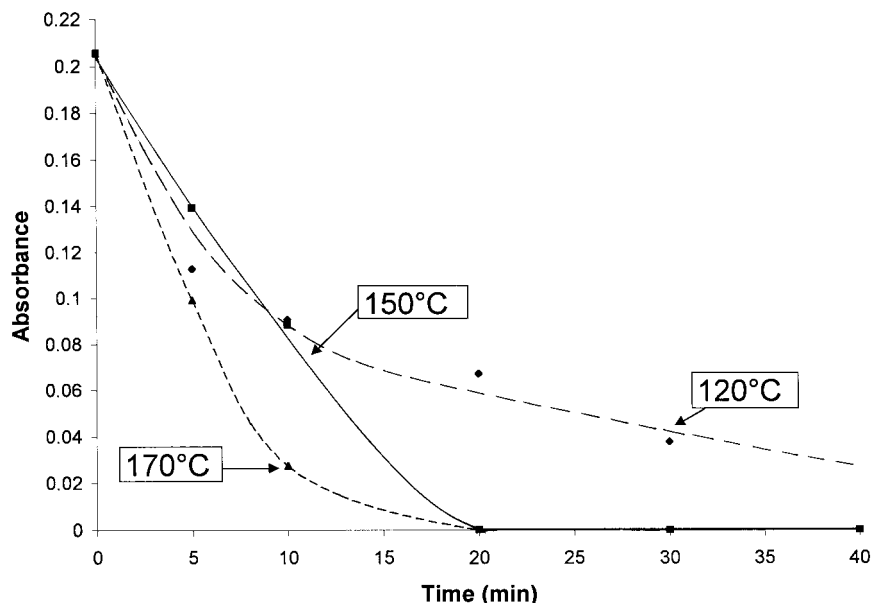
Figure 2 Decomposition rates by IR of the diazoketone group at various temperatures obtained by loss of C—H peak at 3091 cm^{-1} for compounds **A** and **B**.

samples. Tensile strength, tensile modulus, and elongation at yield were determined at 100 mm/min crosshead speed by ASTM D638M (type 1 specimen). Notched impact strength was tested using a 2-lb hammer according to ASTM D256 Type A with notch backward.

The following variables were investigated to determine the optimum extrusion conditions for preparation of fiberglass/polyethylene composites:

1. A range of extruder temperatures and residence times to determine the best extruder profile to react chemically treated fiberglass with polyethylene. In addition, the use of a nitrogen blanket over the extruder.
2. Comparison of HDPE to LLDPE because of the greater degree of branching in the latter.
3. Use of lower quantities of coupling agent on treated fiberglass.
4. Use of benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) in the extruder, to increase the concentration of free radicals.
5. Comparison to a commercially recommended coupling agent for this application: Dow Z-6032 (N-β-(N-vinylbenzylamino)-ethyl-γ-aminopropyltrimethoxysilane).

RESULTS OF DECOMPOSITION STUDIES

Effect of Heat

IR Results

The temperature dependence of diazoketone decomposition in compounds **A** and **B** can be followed by plotting the C—H absorption (3091 cm^{-1}) of this group versus time at different temperatures. Figure 2 shows a comparison of decomposition rates at temperatures from 120 to 170°C, and it can be seen that the rate of decomposition increases dramatically as temperature increases. On the basis of these results a temperature of 150°C was chosen for most of the subsequent heat treatments involving **A** or **B**.

Figures 3 and 4 show the IR spectra of compounds **A** and **B** after heating at 150°C for selected time intervals up to 60 min. In Figure 3 the decomposition of the diazoketone group in compound **A** is evidenced by a rapid reduction in the peaks at 3091 and 1645 cm^{-1}, corresponding to the C—H and C=O stretching frequencies of this group, respectively. (See peaks labeled X and Z.) The new peaks that rise in the carbonyl region (1700–1780 cm^{-1}) are the result of new carbonyl species forming after breakdown of the diazoketone group. The decomposition of the azide group is observed at 2102 cm^{-1} (peak Y). In Figure 4 the decomposition of the diazoketone group follows a
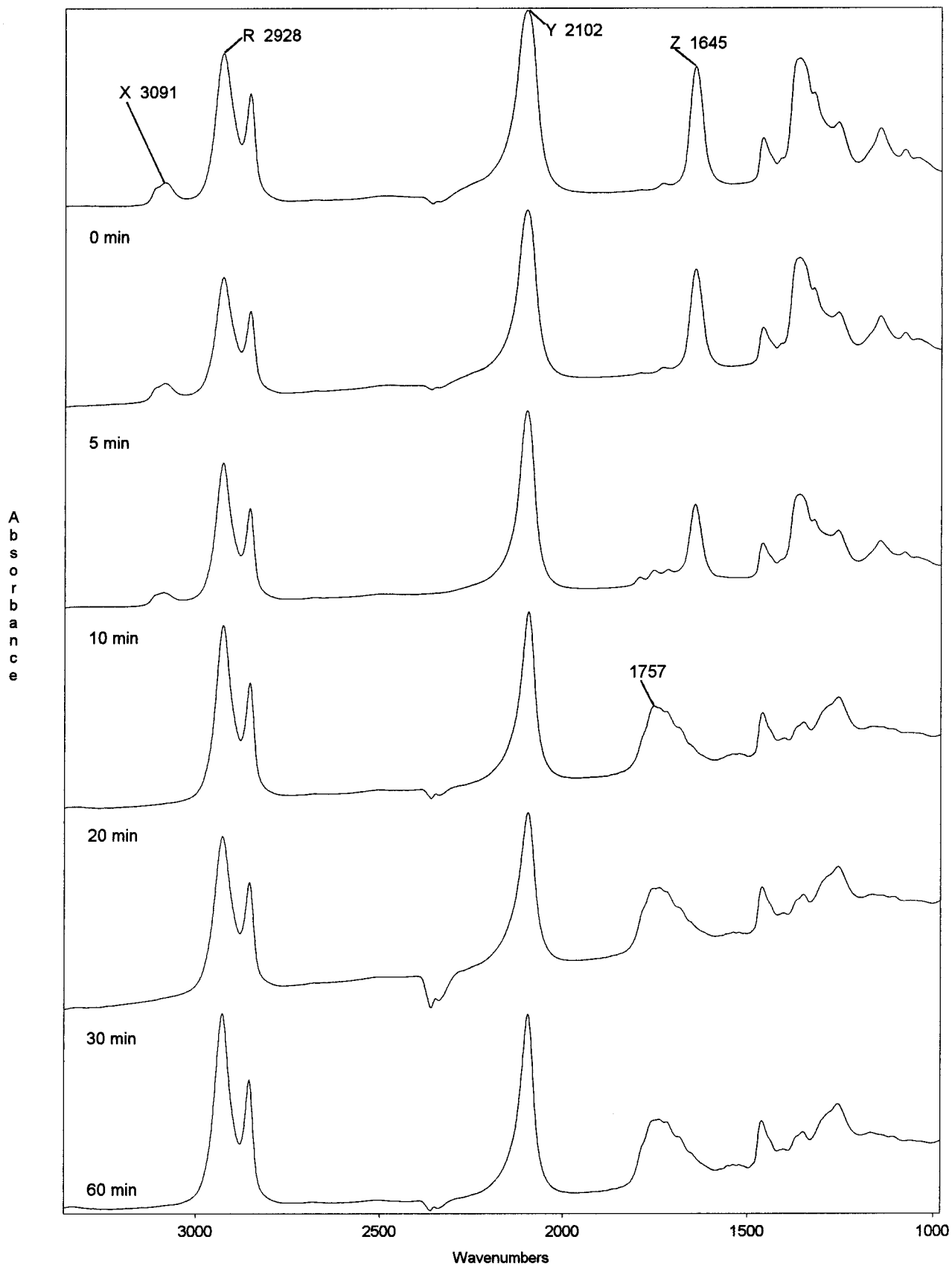
Figure 3   IR spectra of compound **A** heated at 150°C after 0, 5, 10, 20, 30, and 60 min.
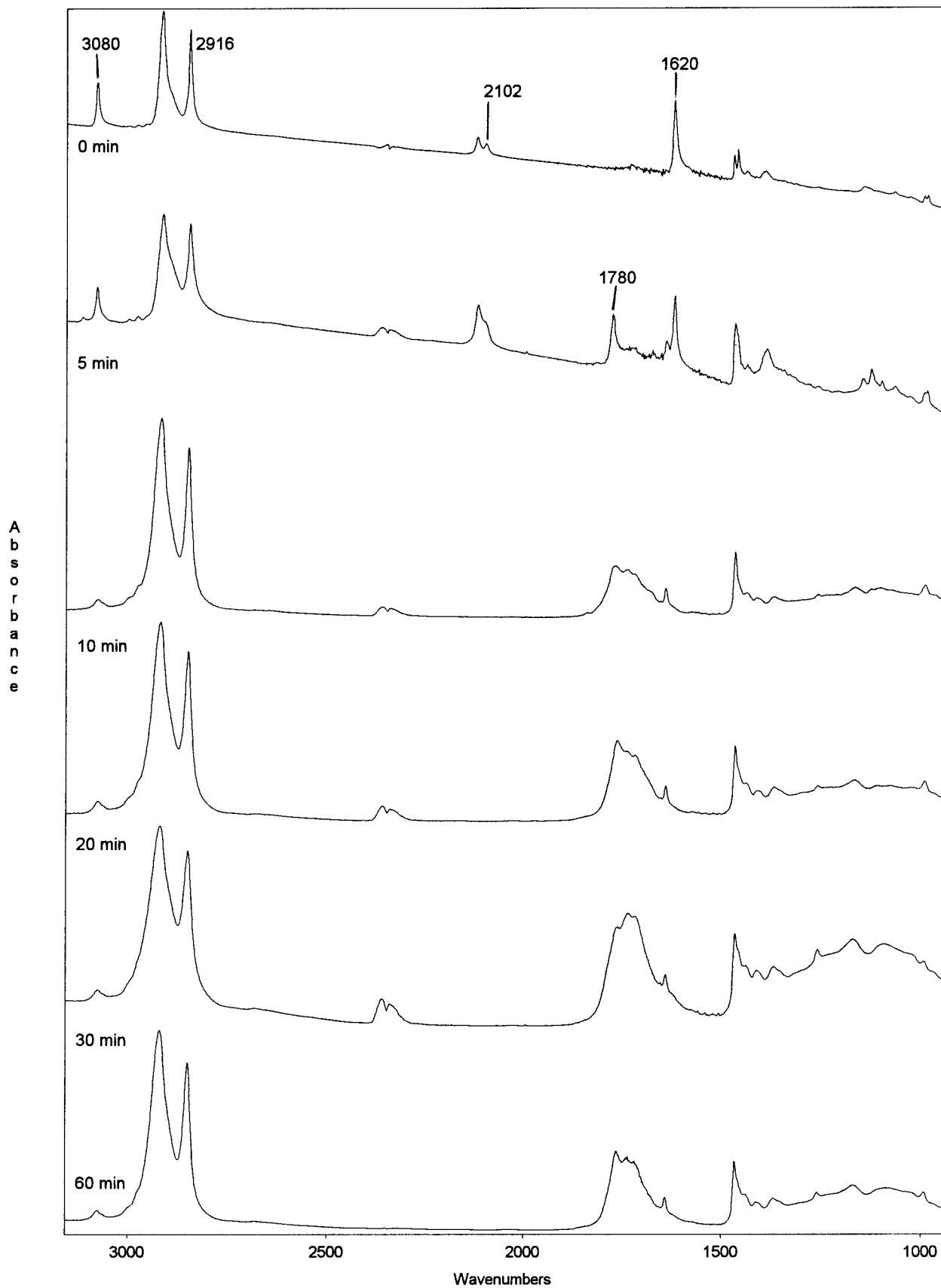
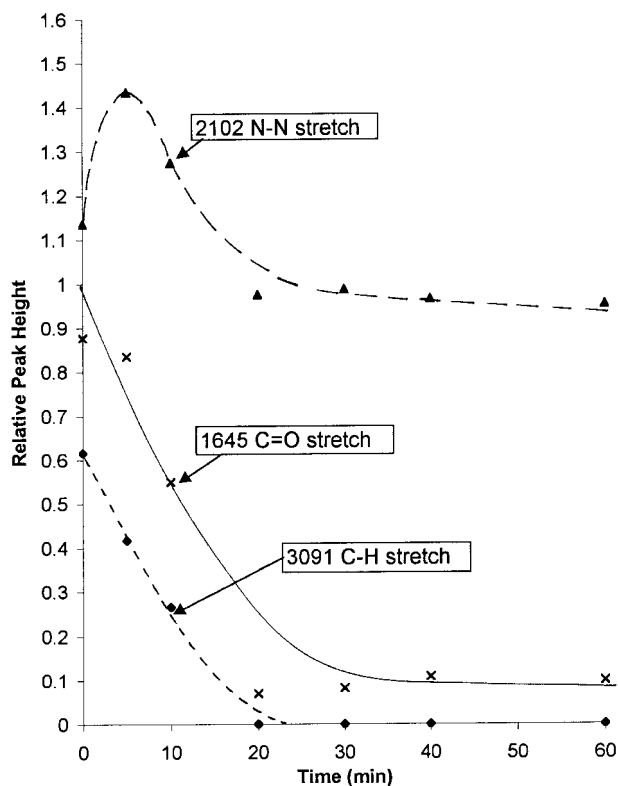**Figure 4**   IR spectra of compound **B** heated at 150°C after 0, 5, 10, 20, 30, and 60 min.

Figure 5 Absorbancy values versus time for diazoketone (peak X: 3091 cm^{-1}), carbonyl (peak Z: 1645 cm^{-1}), and azide (peak Y: 2102 cm^{-1}) functional groups in compound **A** after heating at 150°C.

similar path. The residual absorption at 3080 cm^{-1} in compound **B** after 60 min is attributed to the C—H stretching for the alkene group, which has not completely decomposed by the end of this time interval.

Figure 5 shows the absorbancy values versus time for peaks X, Y, and Z in compound **A.** Each of these peak heights was normalized to correct for differing amounts of sample on the IR disk by dividing each absorbancy value by the methylene absorbancy at 2928 cm^{-1} (labeled R). The values were then converted to the same scale for illustration purposes. Complete decomposition of a group is thus seen by a reduction in the peak height to zero. It should be noted that the diazoketone group (peak X at 3091 cm^{-1}) is completely decomposed within 20 min at 150°C. The carbonyl peak reaches a plateau at the same time as a result of some overlapping absorbancies from other carbonyl species that form during the decomposition. Peak Y in **A** consisting of an overlap of N=N absorbancies from both the diazoketone and azide groups is only partially depleted at 60 min.

NMR Results

Figures 6 and 7 show the NMR spectra for the decomposition of **A** and **B** at 150°C. For compound **A** (Fig. 6) the resonances at 3.25 and 5.20 ppm correspond to the sets of hydrogens that are α to the azide group and the C—H hydrogen of the diazoketone, respectively. Loss of amplitude in these peaks is thus related to the decomposition of the azide and diazoketone groups. For compound **B** (Fig. 7) the key resonances are 5.20 ppm for the hydrogens α to the diazoketone group, and 4.95 and 5.80 ppm for the alkene hydrogens. Normalization in both cases was undertaken by comparison to the hydrogens positioned β to the carbonyl group ($\delta = 1.60$), which are unaffected by chemical changes that take place in the diazoketone group during decomposition. Figure 8 indicates a plot of normalized peak areas versus time for the diazoketone, azide, and alkene groups taken from Figures 6 and 7. The decomposition of the diazoketone group is complete within 20 min, whereas approximately one-half of the resonance associated with the azide group is present at 60 min. The alkene group is also substantially present at 60 min.

Effect of UV–Vis Radiation

Samples of both **A** and **B** were exposed to UV light over a period of 8 h. The decomposition of these compounds under UV light is similar, although much slower, than a heat treatment at 150°C. As with heat, the peaks at 3091, 2102, and 1645 cm^{-1} for compound **A** are reduced after exposure to UV, and new peaks form in the carbonyl region at values greater than 1645 cm^{-1}. The decomposition curves for **A** are shown in Figure 9, indicating the relative loss in absorbance versus time for each peak. It can be seen that peaks corresponding to the diazoketone group (3091 and 1645 cm^{-1}) are reduced to zero over a 6-h interval. As in Figure 5, where decomposition was initiated by a heat treatment, some residual absorbancy in the carbonyl region is attributed to overlapping carbonyl species that appear during the decomposition. The azide group (2102 cm^{-1}) in **A** decreases at a much slower rate.

Percentage Recovery from Fiberglass After Treatment

When coated samples of fiberglass were treated with heat or UV–vis radiation, the amount of unreacted **A** or **B** was reduced with increased
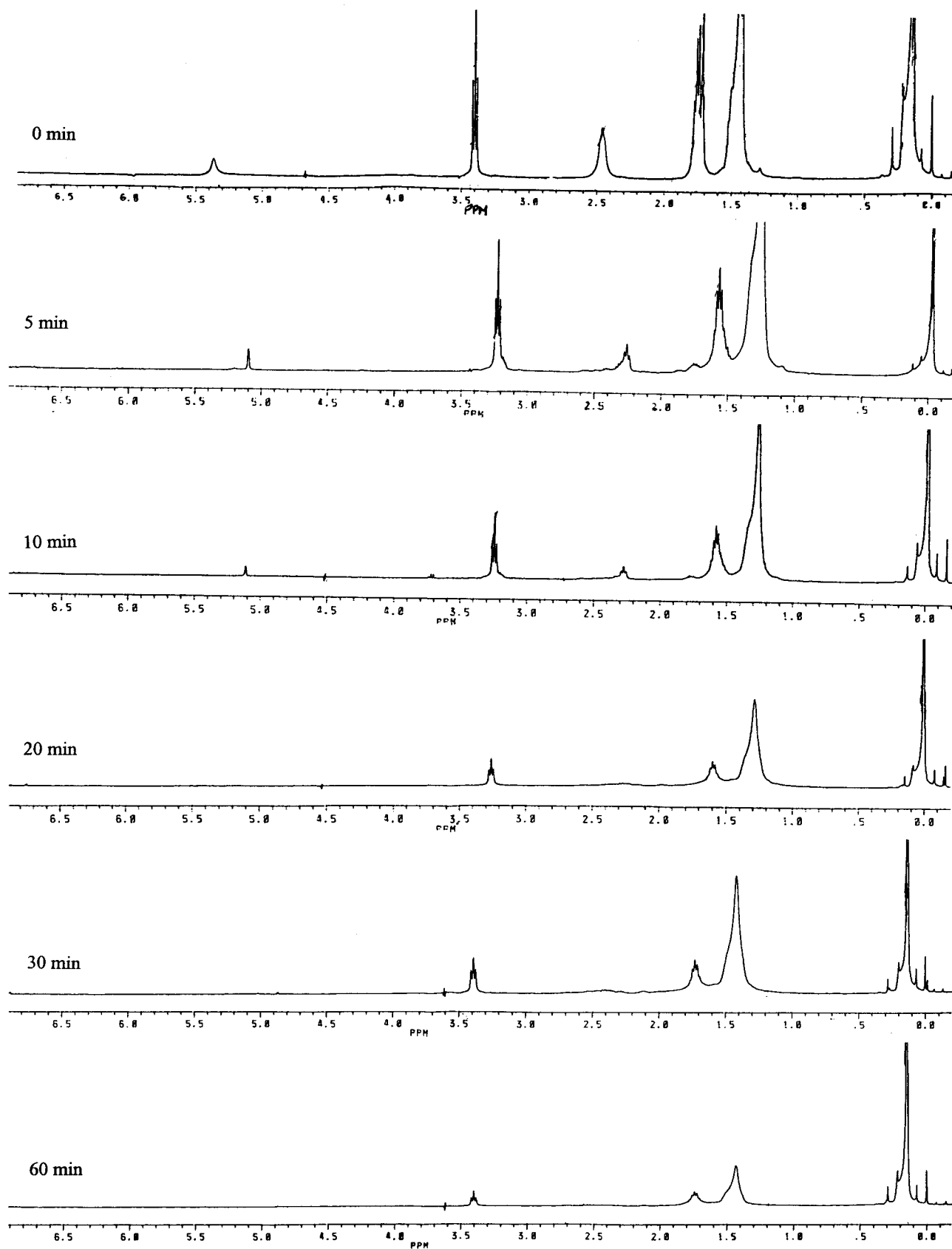
Figure 6   NMR spectra of compound **A** heated at 150°C after 0, 5, 10, 20, 30, and 60 min.
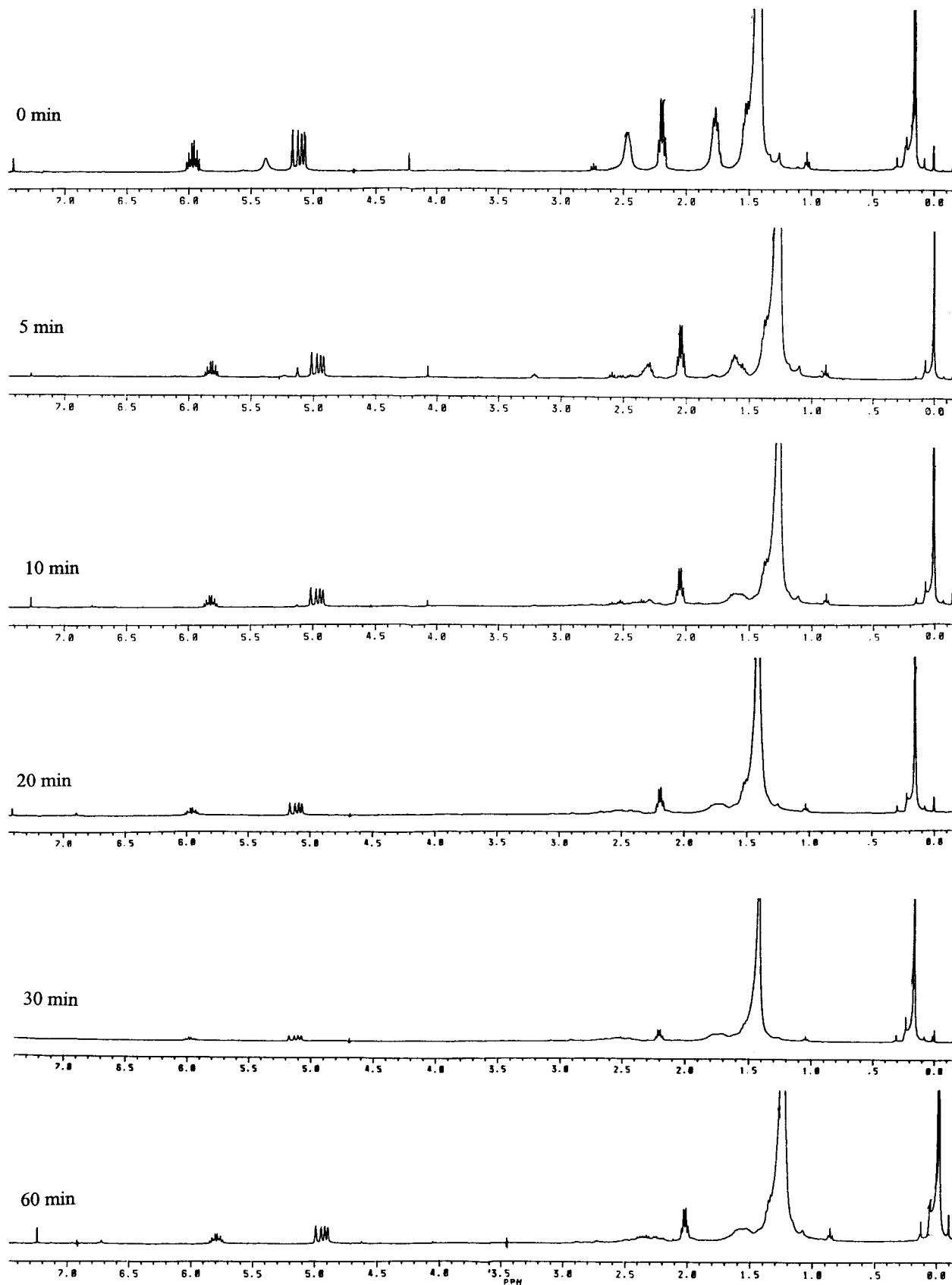
Figure 7   NMR spectra of compound **B** heated at 150°C after 0, 5, 10, 20, 30, and 60 min.
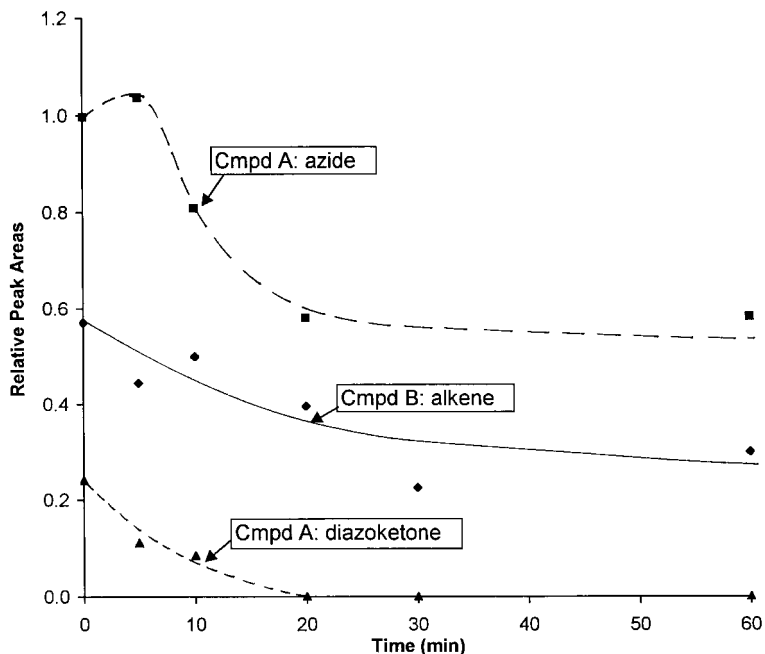
Figure 8   Relative peak areas versus time indicating the relative decomposition rates for diazoketone, alkene, and azide functional groups taken from NMR studies in Figures 6 and 7.

time of exposure. With heat the percentage recovery parallels the rate of decomposition of the diazoketone group that was observed by IR and NMR spectroscopy. Figure 10 shows that the decomposition reaction of the diazoketone group and subsequent reaction with the glass surface is 90%

Figure 9   Absorbancy values versus time for diazoketone (3091 cm^{-1}), carbonyl (1645 cm^{-1}), and azide (2102 cm^{-1}) functional groups in compound **A** after exposure to UV radiation.

Figure 10   Percentage recovery of compounds **A** and **B** from coated samples of fiberglass after heating at 150°C.
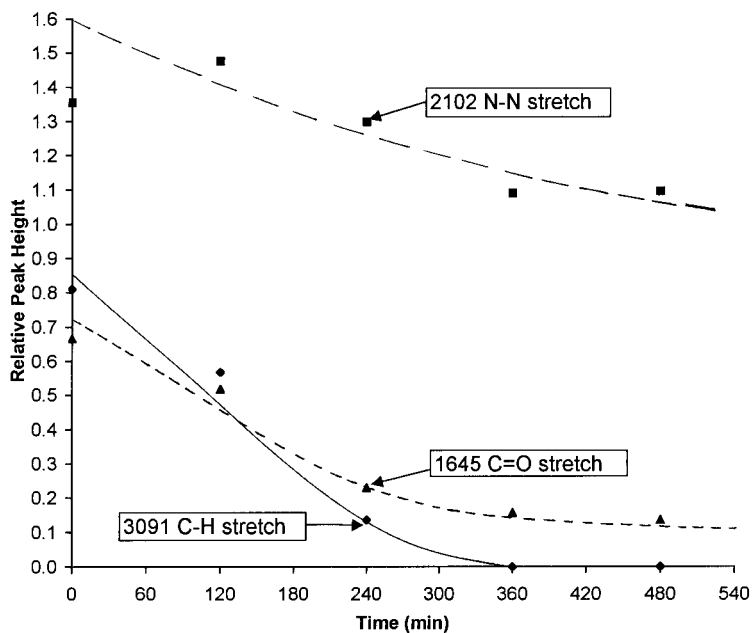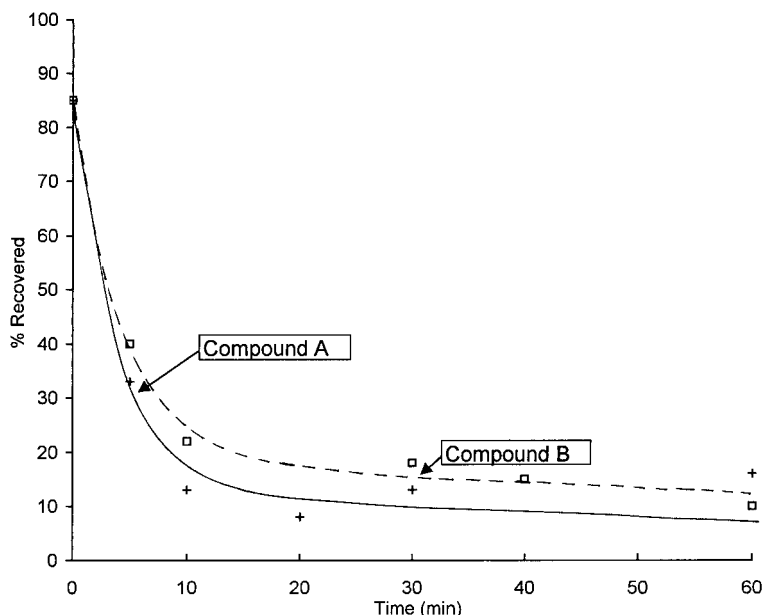
complete after 10 min of heating at 150°C for both compounds **A** and **B.** Figure 11 shows that a much faster reaction with the diazoketone group in **A** occurs with heating than exposure to UV light. Similar results are obtained with compound **B.** Extracted samples of **A** and **B** showed comparable
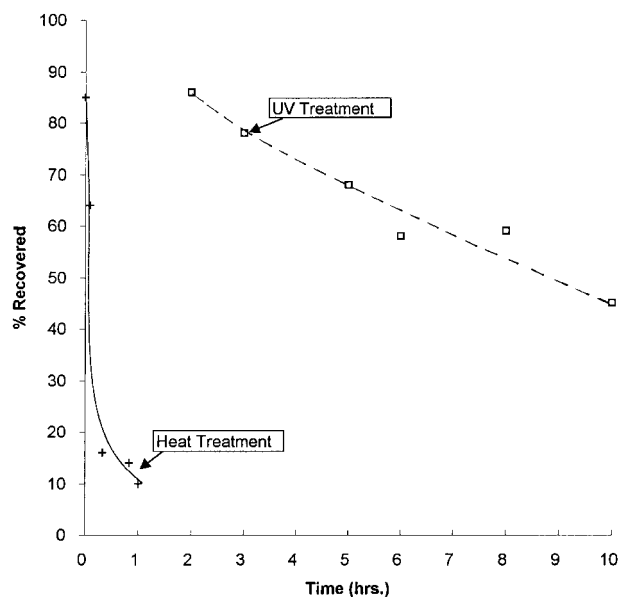

Figure 11   Comparison of percentage recovery of compound **A** after heating at 150°C versus exposure to UV radiation.

IR and UV spectra to the starting compounds, indicating that these agents had not decomposed significantly before reaction with the surface of fiberglass.

The slow rate of reaction under UV light may result from the difficulty of passing UV light into a bulk sample contained in a rotating quartz flask, where sticking of the fiberglass to the surface of the flask often occurs. This problem was always greater in larger samples prepared for extrusion studies. In general, a successful treatment under UV light did not occur unless the coated fiberglass was spread thinly onto a flat surface and irradiated with UV light from above. Because of the difficulties in using UV, all of the treated fiberglass samples used in the extrusion studies were prepared by heat.

In general the percentage recovery of compound **A** decreases at a slightly greater rate in air than in N_2; however, at long exposure times the percentage recovery becomes similar.

RESULTS OF EXTRUSION STUDIES

As fiberglass is added to polyethylene, the mechanical properties of the composite will be affected by the addition of this hard and chemically dissimilar material. Normally, one would expect the tensile modulus to rise, the elongation at yield

Table I   Expected Effects on the Mechanical Properties of Adding Untreated and Treated Fiberglass to Polyethylene

Addition of Untreated Fiberglass to Polyethylene	Subsequent Addition of a Coupling Agent to the Fiberglass/Polyethylene Interface
1. Yield strength decreased	1. Yield strength increased
2. Tensile modulus increased	2. Tensile modulus increased
3. Elongation at yield decreased	3. Elongation at yield decreased
4. Notched impact strength decreased	4. Notched impact strength decreased

to drop, and the flexibility of the composite, measured by impact strength, to be reduced. Furthermore, the yield strength should drop, because a lack of adhesion between the two materials promotes very little transfer of properties from the fiberglass component to the polyethylene component. In contrast, when a coupling agent is present between the two phases, the yield strength and tensile modulus should be higher than when coupling agent is absent, and the elongation at yield and impact strength should be lower, because the hard fiberglass component is now able to transfer more of its characteristics to the overall properties of the composite.

Previous work by Grellmann and Seidler[21] on the optimization of coupling conditions in polypropylene/glass fiber composites has indicated that improved coupling increases the resistance to crack initiation. Malik et al. have shown that tensile strength and modulus of mica and rutile–HDPE composites are enhanced by surface treatment of the fillers with silane-coupling agents.[7] Covalent bonding between HDPE and glass spheres with a silane-coupling agent has been shown to have a significant influence on the stress/strain behavior and creep properties of these composites at room temperature.[22] As glass is added, the modulus drops, but increases again as coupling agent is added. Creep behavior drops dramatically when a silane-coupling agent is present. Harding and Berg[23] suggest that yield strength is the property most reflective of interfacial strength. They have determined that it is the penetration of the silane organofunctional group into the polymer matrix, not the thickness of the silane coupling agent on the glass surface, that provides enhancement in adhesion and increased yield strength in aminosilane/polyvinylbutyrate composites. Jo and Blum[12] show that flexural strength is enhanced in acryloxy substituted silane/PMMA composites. Pukanszky and Fekete[11] have recently reviewed the effect of filler/matrix interactions on composite properties.

The expected effects of bifunctional coupling on polyethylene/fiberglass composites are summarized in Table I, and will be used to assess the effectiveness of the coupling agents used in this study.

Table II shows a comparison of polyethylene/fiberglass composites with treated and untreated fiberglass, each experiment representing the average of two or more runs. As expected, the addition of untreated fiberglass to HDPE reduces the yield strength, elongation at yield, and impact strength, while increasing the tensile modulus of the composite. Experiment 3 demonstrates that coupling takes place between the two phases when treated fiberglass (0.1% w/w compound **A** and heating for 60 min) is used. Both yield and tensile modulus increase in value, whereas impact strength and percentage elongation at yield both decrease. Experiment 4 shows that a relatively short heating time can be used to bind **A** to the fiberglass surface prior to mixing with polyethylene. Even after only a 6-min heat treatment the tensile and impact property changes are almost fully realized. When lower quantities of **A** are applied to the fiberglass (experiment 5), the evidence of strong coupling between the two phases is reduced. Experiment 6 shows that compound **B** can also act as a coupling agent, although it is not as effective as compound **A.** All of the above results were obtained using treated fiberglass samples that had been prepared under an N_2 blanket. When the fiberglass samples were prepared in air, the improvement in properties was only slightly less than that under N_2. Comparison of the above results is made to a standard commercially available organosilane compound (Dow Z-6032) in experiment 7, where coupling seems to take place with the silane agent, although with substantially less effect than for **A** or **B.**

Because LLDPE has a high degree of branching and a relatively larger proportion of tertiary hydrogens on its chains, a number of test compos-

Table II   Comparison of Treated to Untreated Fiberglass in HDPE[a,b]

Experiment	Treatment	Yield Strength (MPa)[c]	Tensile Modulus (MPa)[d]	Impact Strength (J/m)[e]	Percentage Elongation at Yield[f]
1	HDPE only	21.5	193	No break	27.2
2	HDPE/glass	18.9	228	402	22.4
3	HDPE/glass/**A** (0.1%)—60 min treatment	22.4	252	282	18.6
4	HDPE/glass/**A** (0.1%)—6 min treatment	21.6	262	297	17.2
5	HDPE/glass/**A** (0.025%)—60 min treatment	20.0	244	332	19.4
6	HDPE/glass/**B** (0.1%)—60 min treatment	19.5	226	557	20.6
7	HDPE/glass/0.1% Dow Z-6032[g]	23.1	239	No break	24.7

[a] Coupling agents **A** (12-azido-1-diazo-2-dodecanone) and **B** (1-diazo-17-octadecene-2-one) applied to Fiberglass Canada 739DD glass fibers. Standard application rate of 0.1% w/w based on fiberglass. Heat-treated at 150°C in open vessel under N_2 blanket.
[b] Treated glass dry-mixed with HDPE at 20% w/w level and extruded in a single-screw extruder with zones adjusted to 220, 270, 270, and 180°C, and residence time of 70 s.
[c] SE = ±0.2 MPa.
[d] SE = ±12 MPa.
[e] Impact strength for these samples measured with notch backward. SE = ±16 J/m.
[f] SE = ±0.7%.
[g] N-β-(N-vinylbenzylamino)ethyl-γ-aminopropyltrimethoxysilane.

ites were made from this polymer. The results of these experiments are indicated in Table III. Similar trends are exhibited for LLDPE as in HDPE, although the results are not as dramatic, despite an expectation that the results might be more pronounced in a polymer of this nature.

Table IV shows the effect of a variety of extrusion conditions on the mechanical properties of composites containing treated fiberglass. First of all, the standard temperature and residence time profile is compared to higher or lower temperature profiles but similar residence times. Second, a comparison is made for samples extruded with the standard temperature profile but a variety of residence times. The results indicate that the

properties of the composite are not greatly affected by a variety of extruder temperatures and residence times. Furthermore, the addition of a nitrogen blanket over the extruder also does not appear to change the properties.

An attempt to improve the adhesion between the coupling agent (compound **A**) and the polyethylene matrix was made by adding either BPO or AIBN to the extruder while the treated fiberglass was mixed with HDPE. The results of these experiments are given in Table V. When no coupling agent is present, the addition of BPO to a mixture of fiberglass and HDPE causes a toughening of the composite, as can be seen by higher impact strength (see experiment 19). The tensile charac-

Table III   Comparison of Treated to Untreated Fiberglass in LLDPE[a,b]

Experiment	Treatment	Yield Strength (MPa)[c]	Tensile Modulus (MPa)[d]	Impact Strength (J/m)[e]	Percentage Elongation at Yield[f]
7	LLDPE only	10.4	74	No break	34
8	LLDPE/glass	8.9	79	103	42
9	LLDPE/glass/**A** (0.1%)—60 min treatment	10.0	99	86	26

[a] Coupling agent **A** (12-azido-1-diazo-2-dodecanone) applied to Fiberglass Canada 739DD glass fibers. Standard application rate of 0.1% w/w based on fiberglass. Heat-treated at 150°C in open vessel under N_2 blanket.
[b] Treated glass dry-mixed with LLDPE at 20% w/w level and extruded in a single-screw extruder with zones adjusted to 220, 270, 270, and 180°C, and residence time of 70 s.
[c] SE = ±0.2 MPa.
[d] SE = ±3 MPa.
[e] Impact strength for these samples measured with notch forward. SE = ±5 J/m.
[f] SE = ±1.4%.

Table IV   Comparison of Extrusion Conditions[a,b]

Experiment	Extrusion Profile	Yield Strength (MPa)[c]	Tensile Modulus (MPa)[d]	Impact Strength (J/m)[e]	Percentage Elongation at Yield[f]
Effect of Temperature					
10	Standard profile[g]	22.4	253	281	18.1
11	Lower temperature profile[h]	20.8	226	283	19.6
12	Higher temperature profile[i]	22.4	201	333	20.8
Effect of Residence Time[j]					
13	30 s	21.1	193	356	22.2
14	55 s	21.2	188	300	22.2
15	85 s	21.1	221	337	21.1
16	170 s	22.1	213	307	19.8
Effect of Nitrogen Blanket					
17	Standard temperature and residence time profile	21.0	235	316	19.9

[a] Coupling agent **A** (12-azido-1-diazo-2-dodecanone) applied to Fiberglass Canada 739DD glass fibers. Standard application rate of 0.1% w/w based on fiberglass. Heat-treated for 60 min at 150°C in open vessel under N_2 blanket.
[b] Treated glass dry-mixed with HDPE at 20% w/w level and extruded in a single-screw extruder.
[c] SE = ±0.2 MPa.
[d] SE = ±20 MPa.
[e] Impact strength for these samples measured with notch backward. SE = ±15 J/m.
[f] SE = ±1.4%.
[g] Zones adjusted to 220, 270, 270, and 180°C, and residence time of 70 s.
[h] Zones adjusted to 190, 215, 215, and 215°C, and residence time of 70 s.
[i] Zones adjusted to 250, 300, 300, and 180°C, and residence time of 70 s.
[j] Standard temperature profile with zones adjusted to 220, 270, 270, and 180°C.

teristics do not change significantly. However, when compound **A** is applied to the surface of the fiberglass (experiment 20), the yield strength and modulus increase and the impact strength decreases, indicating a coupling of the fiberglass phase to the polyethylene phase. A similar situation is seen when AIBN is added to the extruder (experiments 21 and 22). When **A** is present as a coupling agent, the improvement in yield strength is moderate and the impact strength is

Table V   Comparison of Mechanical Properties When BPO or AIBN Is Added to the Extruder[a,b]

Experiment	Treatment	Initiator Added to the Extruder (0.1%)	Yield Strength (MPa)[c]	Tensile Modulus (MPa)[d]	Impact Strength (J/m)[e]	Percentage Elongation at Yield[f]
18	HDPE/glass/no **A**	None	18.9	228	402	22.4
19	HDPE/glass/no **A**	BPO	18.4	214	774	21.6
20	HDPE/glass/with **A**	BPO	21.3	235	362	19.1
21	HDPE/glass/no **A**	AIBN	18.7	227	352	20.4
22	HDPE/glass/with **A**	AIBN	19.8	240	311	18.7

[a] Coupling agent **A** (12-azido-1-diazo-2-dodecanone) applied to Fiberglass Canada 739DD glass fibers. Standard application rate of 1% w/w based on fiberglass. Heat-treated for 60 min at 150°C in open vessel under N_2 blanket.
[b] Treated glass dry-mixed with HDPE at 20% w/w level and extruded in a single-screw extruder with zones adjusted to 220, 270, 270, and 180°C, and residence time of 70 s.
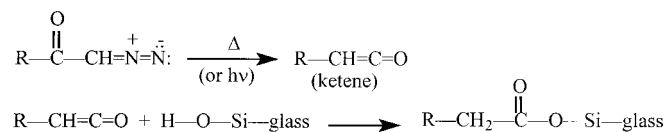[c] SE = ±0.3 MPa.
[d] SE = ±14 MPa.
[e] Impact strength for these samples measured with notch backward. SE = ±16 J/m.
[f] SE = ±0.9%.

A. Reaction of Diazoketone group with glass surface

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH=\overset{+}{N}=\overset{..}{N}: \quad \xrightarrow[\text{(or } h\nu)]{\Delta} \quad R-CH=C=O \atop \text{(ketene)}$$

$$R-CH=C=O \; + \; H-O-Si-glass \quad \longrightarrow \quad R-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O- Si-glass$$

B. Reaction of azide group with polymer

$$R-CH_2-\overset{..}{N}=\overset{+}{N}=\overset{..}{N}: \quad \xrightarrow[\text{(or } h\nu)]{\Delta} \quad R-CH_2-\overset{..}{N} \atop \text{(nitrene)}$$

$$R-CH_2-\overset{..}{\underset{..}{N}} \; + \; H-\overset{|}{\underset{|}{C}}- \quad \longrightarrow \quad R-CH_2-\overset{H}{\underset{..}{\underset{|}{N}}}-\overset{|}{\underset{|}{C}}-$$
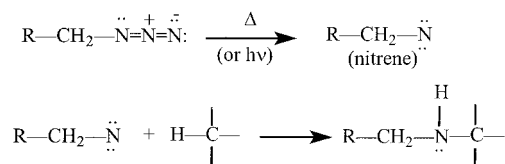
Figure 12   Mechanism for coupling compounds **A** and **B** to glass and polyethylene surfaces.

reduced, indicating that coupling takes place between **A** and the polyethylene plastic. None of the results of this series of experiments is substantially better than those undertaken in the absence of BPO or AIBN (Table II), with the exception that yield strength is a little higher in the presence of BPO.

DISCUSSION

The results indicate that both compounds **A** and **B** are able to act as chemical bridges between fiberglass and polyethylene, and **A** is generally more effective than **B** in these systems. The diazoketone group in both of these compounds is an effective chemical entity to attach itself to a glass surface, as demonstrated by the matching rates of decomposition to percentage recovery values for **A** and **B** on coated fiberglass samples during heat or UV treatment. The preferred application of **A** and **B** to a fiberglass surface is a heat treatment at 150°C, because UV radiation is a much slower treatment due to the difficulty of getting sufficient light flux into a bulk sample.

The characteristic reaction of the diazoketone functional group under heat or UV light is a Wolff rearrangement,[24] to produce a reactive ketene group, which reacts with the O—H groups on the glass surface, as illustrated in Figure 12(a). Using extraction by a reactive solvent on silica gel fillers treated with **A** and **B**, McGarvey and Holden[18] demonstrated that these compounds undergo chemical grafting to the surface of the filler.

The reaction between the azide group and the polyethylene matrix is more difficult to follow. Chemical decomposition studies show that the azide group slowly decomposes at 150°C, and at the temperatures encountered during extrusion this rate of decomposition will increase. Decomposition of an azide group has been shown to produce a transient nitrene function, which has the ability to react with a carbon chain by an insertion reaction,[20,25,26] as illustrated in Figure 12(b). The reaction of the azide group with the polyethylene chains cannot be observed easily, however, and the coupling of this group with the polyethylene matrix must be inferred by reference to the properties of polyethylene/fiberglass composites, with and without the presence of the coupling agent. A similar situation is seen for the alkene functional group. Decomposition of this group at 150°C is slow; however, reaction with this group will be facilitated by the presence of free radicals produced by heat and shear within the polyethylene phase. Ultimately, as with azide, the coupling of polyethylene chains to this group can only be inferred by the effect this agent has on the mechanical properties of composites containing it.

The mechanical properties in fiberglass/polyethylene composites using compounds **A** and **B** generally show an increase in tensile strength and modulus, and a small decrease in elongation at yield with coupling. An increase in coupling also causes a marked reduction in the Izod impact strength. In the best composites produced to date the yield strength values increase by 20% and

impact strength values are reduced by approximately 35%. In general compound **A** appears to be a superior coupling agent to compound **B.** Because each of these has a diazoketone group, and treated fiberglass is easily made from either **A** or **B,** the main difference in these coupling agents is the functional group on the opposite end of the molecule. The azide group seems to be more effective than the alkene group in all cases.

Because all samples were injection molded under the same conditions, the orientation of the glass fibers will be similar in all test samples, and should not be a factor affecting comparison of the samples.

Experiments on LLDPE show similar trends to those in HDPE, indicating that compound **A** is also able to act as a coupling agent in this grade of polyethylene. It was expected that an abundance of tertiary hydrogens along the chains in this highly branched polymer would facilitate a higher degree of reaction, and thus greater coupling between C—H bonds in polyethylene molecules and the nitrene functional group formed during the decomposition of the azide group. The lack of increased response in this case may result from the fact that the extrusion conditions for LLDPE are not optimized. Thus the sensitivity of the system to the presence of a coupling agent may be reduced.

Larger quantities (0.1%) of coupling agent **A** yield superior results to lower quantities. Although sufficient quantities of **A** must be present to fully cover the surface of the filler, some losses may occur as the result of the heat treatment. This may explain why an effective application level is about four times the amount needed to provide a monolayer on the surface of the fiberglass.

The system is remarkably insensitive to the extrusion conditions used to mix the treated fiberglass with polyethylene. The best result, consisting of a balance between yield strength, tensile modulus, impact strength, and elongation at yield, is obtained with fairly high temperatures in the extruder (reaching 270°C) and a residence time of 70 s. Some modification of the properties can be obtained by addition of benzoyl peroxide to the extruder, but the properties are not substantially improved.

Both compounds tested are more effective as coupling agents than a commercially recommended organosilane agent, particularly when Izod impact strength test results are compared. Izod impact strength has consistently proved to be the most sensitive indicator of the effect of fiberglass on polyethylene. Values of this test parameter drop dramatically as fiberglass is added to polyethylene, and continue to drop as the polyethylene is coupled to the glass surface.

Although the mechanical tests show definite indications of coupling in composites containing **A** and **B,** the mechanical tests, with the exception of Izod impact, are not highly sensitive indicators of the presence or absence of coupling. Using longer fibers may provide composites that are more sensitive both to variations in the method with which compounds **A** and **B** are applied to the surface of the fiberglass and to the extrusion conditions used to bond the treated glass to the polyethylene matrix. Estimates by Bascom[27] of the minimum fiber length needed in composites containing discontinuous phases of glass or carbon, and a polymeric matrix of polypropylene, epoxy, polyester, or polycarbonate show that the important factors affecting the optimum length of fiber are the strength of the fiber itself and the sheer stress at the fiber–resin interface. Using values available for these systems, the appropriate minimum L/D for the fiber in these composites can be calculated, which for polypropylene in E-glass is calculated as 140. No calculated values are available for polyethylene, although the chemical similarity between polypropylene and polyethylene suggests that their L/D ratios should be reasonably similar. Thus it can be calculated that the desired length for fiberglass fibers in polyethylene is at least 2 mm. Fibers of this length may provide greater sensitivity in these studies.

CONCLUSIONS

12-Azido-1-diazo-2-dodecanone (**A**), containing the diazoketone and azide functional groups, has been shown to be an effective bifunctional coupling agent in fiberglass/polyethylene composites. This is indicated by an increase in tensile properties and a reduction in Izod impact strength. Its effectiveness is greater than that of a commercial silane-based coupling agent. 1-Diazo-17-octadecene-2-one (**B**), containing the diazoketone and alkene functional groups, has also been shown to have coupling properties, but to a lesser extent.

Polyethylene/fiberglass composites were chosen to demonstrate the use of a bifunctional coupling agent because the phenomenon is easily studied in polyethylene composites. Polyethylene is an easily formable material with reproducible

properties and uncomplicated chain-to-chain or fiber-to-chain/side group interactions. Work on these systems could be easily extended to a variety of polymer systems.

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