Influence of Hydrogen Donors on Peroxide-Initiated Melt Grafting of Vinylsilane to Poly(ethylene-*co*-vinyl acetate)

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ABSTRACT: A technique has been examined for reducing the extent of crosslinking resulting from 1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane (L-231) initiating melt grafting of vinyltriethoxysilane (VTEOS) onto poly(ethylene-*co*-vinyl acetate) (EVA). Using measurements of crosslink density and VTEOS conversion, a standard of selectivity for the EVA/VTEOS/L-231 system at 145 °C was defined and used to assess the influence of a range of additives (0.25 mol per mole VTEOS). The data indicated that compounds such as 4-nonene, *N,N*-dimethylaniline, and cumene improve reaction selectivity, whereas dodecane and cyclohexyl acetate have no effect. A strong correlation between the minimum C—H bond dissociation energy and the influence of a given compound is evident, suggesting that a labile C—H bond is the key element of an effective additive. A mechanism of additive function on the basis of hydrogen atom donation is proposed. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2397–2402, 2002

Key words: vinylsilane; poly(ethylene-*co*-vinyl acetate); melt grafting

INTRODUCTION

The chemical modification of commodity polymers is an important method of generating value-added materials with improved mechanical, thermal, or chemical properties. A particularly important class of modification reactions is the peroxide-initiated grafting of functionalized monomers onto polyethylene and ethylene copolymers.[1] A significant commercial example is the melt grafting of vinyltrialkoxysilanes to poly(ethylene-*co*-vinyl acetate) (EVA) to create a moisture-curable resin that bonds with siliceous fillers.[2]

Conventional melt-grafting technology provides few means of exercising simultaneous control over silane graft content, silane conversion, and peroxide-induced crosslinking. For example, strategies to improve monomer conversion are often complicated by increases in the extent of crosslinking arising from macroradical combination.[3] Techniques that decrease the crosslink density of modified resins but enhance or maintain graft yield are therefore expected to have practical value in the marketplace.

Two approaches to controlling peroxide-induced crosslinking have been disclosed in the literature. Recent work indicates that a secondary monomer may increase the grafting yield of a primary monomer, suppressing undesirable processes such as β scission in polypropylene[4,5] and crosslinking of polyethylene.[6,7] In most cases, styrene has been used as a "synergistic comonomer" to assist in maleic anhydride grafting to polyolefins. Another approach developed by Gaylord and Mehta[8] utilizes polar organic compounds to re-

duce the gel content of maleic anhydride grafted polyethylene. Additives such as dimethylformamide and *N*-methylpyrrolidone were shown to reduce the gel content of the modified polymer at the expense of graft yield.

We have recently demonstrated the ability of select vinyl comonomers to reduce the crosslink density of EVA during peroxide-initiated vinylsilane graft modification.[3] In the presence of 0.50 molar equivalents of 1-dodecene relative to vinyltriethoxysilane (VTEOS), the crosslink density of the modified polymer was reduced by 66% while suffering a loss in silane conversion of just 25%. In this article, we present our recent advances in this field along with insight into the mechanism of additive function.

EXPERIMENTAL

Materials

The ethylene-vinyl acetate copolymer (AT-EVA 1821, AT Plastics, Brampton, ON) contained 18 wt % (6.7 mol %) vinyl acetate and approximately 100 ppm of a phenolic antioxidant. The melt-flow index of the resin was 3.0 g/10 min (ASTM D1238, 190 °C, 2.16 kg load),[9] and its melting temperature was 87 °C (DSC). The pelletized material was dried for 12 h at 25 °C under high vacuum prior to use.

Lupersol L-231 [1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane, Atochem, Buffalo, NY, 92%] was stored under refrigeration and used as received. VTEOS (Sigma–Aldrich, Oakville, ON, 97%) was distilled at 1 atm (bp 160–161 °C) and analyzed by ^{1}H NMR prior to use. *N*-VP [1-vinyl-2-pyrrolidone, Sigma–Aldrich (Fluka), Oakville, ON, 97%] was eluted through a column of alumina to remove sodium hydroxide stabilizer. Cyclohexyl acetate (99%), cumene (99.7%), di-*t*-butylcresol (99%), *N,N*-dimethylaniline (98%), dodecane (99%, anhydrous), 1-dodecene (95%), *N*-methylpyrrolidone (98%), and 4-nonene (98%) were used as received from Sigma–Aldrich, Oakville, ON.

Grafting Reactions—Oscillating Disk Rheometer

EVA\L-231\VTEOS\comonomer masterbatches were prepared at 95 °C using a Haake Rheomix 600 internal batch mixer (50 cm³) controlled by a Haake Rheocord System 40 microprocessor. Thirty grams of AT-EVA 1821 were charged to the mixer at 60 rpm. After 5 min L-231, VTEOS, and additive (0.25 mol equiv relative to VTEOS, where required) were added sequentially, and the masterbatch was mixed for 10 min. Integration of ^{1}H NMR spectra of select masterbatches verified the correct VTEOS content. Purified masterbatches showed no evidence of silane grafting during the mixing procedure, and no crosslinking was detected by rheometry over a 20-min period at the mixing temperature of 90 °C. We are therefore confident that no grafting or crosslinking took place during masterbatch preparation.

Melt-grafting reactions were conducted at 145 ± 1 °C within the cavity of a TechPro Oscillating Disk Rheometer for a total of 20 min (approximately 9 $t_{1/2}$ of L-231 at 145 °C) after which the sample was cooled to 25 °C in a dessicator. The cavity was completely filled and melt-sealed, thereby eliminating monomer vaporization problems. The torque required to oscillate a biconical disk embedded within the sample through a 5° arc at 1.3 Hz was recorded with a resolution of ±0.1 dNm. This measurement represents the low-frequency elastic modulus of the material. Therefore, the extent of crosslinking at any time was inferred from the difference of the instantaneous torque (τ) and minimum torque (τ_{min}). The ultimate crosslink density was derived from the change in torque, $\Delta\tau = \tau_{max} - \tau_{min}$, where τ_{max} represents the maximum torque recorded over the course of the experiment. This difference is largely unaffected by inert plasticizers that decrease both the maximum and minimum torque to comparable degrees at low crosslink density.

Modified EVA Structural Characterization

Modified EVA resin (1 g) was dissolved in boiling toluene (20 mL) and precipitated with acetone (100 mL). The purified sample was filtered and dried under vacuum at 25 °C for 24 h. Films of 2.5 mm thickness were pressed at 95 °C and analyzed for silane graft content by a Fourier transform infrared (FTIR) method on the basis of the 744–825 cm^{-1} resonance of the silane relative to the 1978–2098 cm^{-1} internal standard region originating from the resin. A Nicolet Avatar 360 FTIR ESP was used for this purpose.

RESULTS AND DISCUSSION

Additive performance is quantified by changes in crosslink density ($\Delta\tau$) and VTEOS conversion (percentage) relative to a baseline experiment.
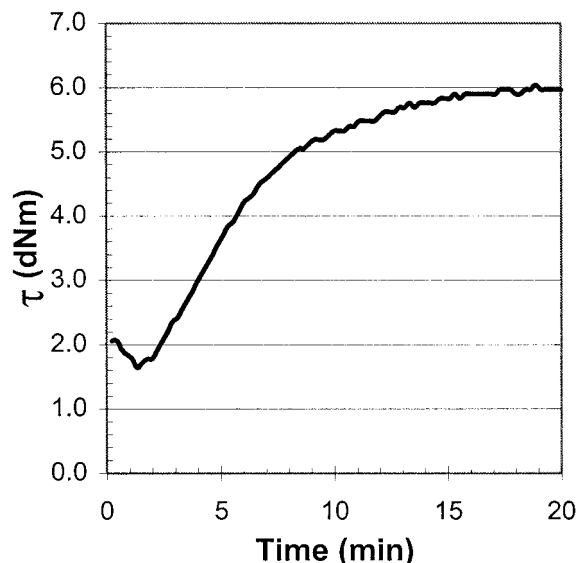
Figure 1 Oscillating Disk Rheometer crosslinking profile for the baseline condition (5 wt % VTEOS/0.05 wt % L-231/145 °C).

This experiment, derived from an EVA masterbatch containing 5 wt % VTEOS, 0.05 wt % L-231, and no additive, is illustrated in Figure 1. Consistent with our previous work, τ approached a plateau of 4.5 dNm within 20 min, corresponding to complete decomposition of the initiator at 145 °C. The graft-modified resin was stable with respect to thermal and silane moisture crosslinking; no change in torque was recorded for 20 min beyond the plotted time interval. Four replicates of this experiment yielded 95% confidence intervals for a crosslink density of $\Delta\tau = 4.5 \pm 0.3$ dNm and VTEOS conversion to silane grafts of 52 $\pm$ 4%.

Over the limited range of conditions studied, ultimate crosslink density and VTEOS conversion are approximately linear functions of the initial peroxide concentration.[3] Therefore, a plot of $\Delta\tau$ against silane conversion for samples prepared with different peroxide levels is also linear, as demonstrated in Figure 2. Decreasing the L-231 dosage from the baseline concentration of 0.05 wt % reduced $\Delta\tau$ and silane conversion; an extrapolation to zero peroxide concentration passes nearly through the origin. This relationship between $\Delta\tau$ and graft content serves as a measure of process selectivity. Effective additives would reduce crosslink density relative to the base condition (0.05 wt % L-231, 5 wt % VTEOS) while either maintaining or enhancing graft conversion. This appears as a shift to the left of the peroxide concentration line in Figure 2.
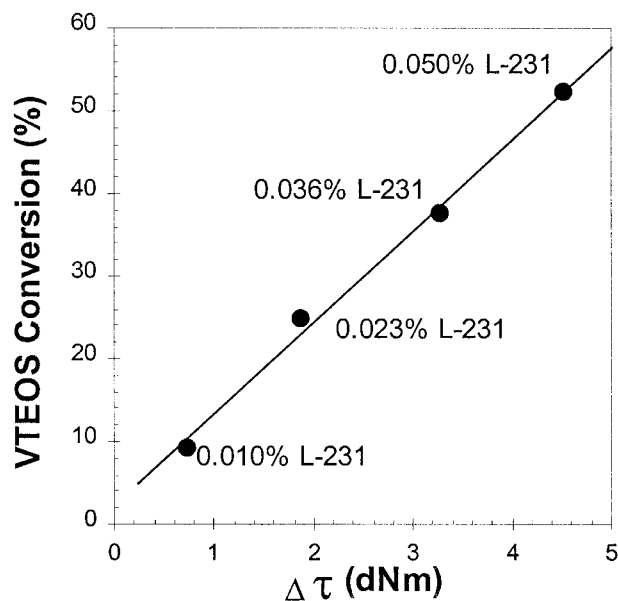
Figure 2 Selectivity baseline plot (5 wt % VTEOS/ 145 °C).

Selectivity induced by several additives is illustrated in Figure 3. These include 1-dodecene and N-vinylpyrrolidone that we previously applied to the VTEOS/EVA system[3] as well as the saturated additives N-methylpyrrolidone and N,N-dimethylaniline that Gaylord and Mehta[8] applied to the MAn/polyethylene system. The effect of a given
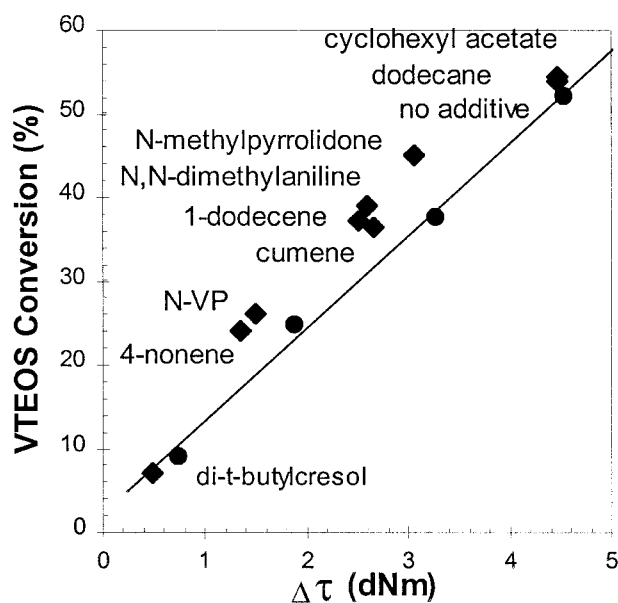
Figure 3 Influence of 0.25 mol additive per mole VTEOS on selectivity (5 wt % VTEOS/0.05 wt % L-231/ 145 °C).

additive on the process is gauged through comparison to the 0.05 wt % L-231 data point labeled "no additive" in Figure 3. The influence of an additive relative to the effect produced by reduced peroxide concentrations is determined through comparison with the peroxide concentration line. These compounds reduce both crosslink density and silane conversion. However, when the data are compared with the peroxide control experiments, it is clear that crosslinking is depressed to a greater extent than VTEOS conversion.

The baseline experiment produced a crosslink density of $\Delta\tau = 4.5 \pm 0.3$ dNm and a graft yield of $52 \pm 4\%$. The addition of 0.25 equiv of 1-dodecene relative to VTEOS reduced the crosslink density to $\Delta\tau = 2.5 \pm 0.2$ dNm and graft yield to $38 \pm 5\%$. This represents a 45% reduction in the extent of crosslinking and just a 28% reduction of silane graft content. As detailed subsequently, effective additives reduce the macroradical concentration in the system by hydrogen atom donation. However, an equivalent product cannot be generated by simply reducing the peroxide concentration. Although an L-231 dosage of 0.036 wt % produced a similar VTEOS conversion ($39 \pm 3\%$) to that of the 1-dodecene assisted process, the crosslink density of the material was $\Delta\tau = 3.3 \pm 0.2$ dNm. The difference of 0.76 ± 0.48 dNm is statistically significant, indicating that effective additives such as 1-dodecene selectively reduce crosslinking over VTEOS conversion.

Additives such as dodecane, cyclohexyl acetate, and vinyl *t*-butylbenzoate had no effect on either silane conversion or $\Delta\tau$ and, hence, are inert with respect to radical-mediated processes. Each of these compounds lowers the melt viscosity of the resin but does not affect the difference between the maximum and minimum torque ($\Delta\tau$) that relates directly to crosslink density. Conversely, 2,6-di-*t*-butyl-*p*-cresol suppressed virtually all grafting and crosslinking activity. Gaylord and Mehta[8] reported a similar effect of this common antioxidant on the maleic anhydride-polyethylene system.

Structural analysis of all VTEOS-modified resins revealed no evidence of additive incorporation, including samples prepared with unsaturated additives such as *N*-VP. In the absence of VTEOS, *N*-VP is readily grafted to EVA. The FTIR spectrum in Figure 4 clearly shows the amide carbonyl resonance of an *N*-VP graft.[10] However, the spectrum of a graft-modified EVA resin in which both vinylsilane and *N*-VP were present contains no evidence of significant *N*-VP incorporation, but
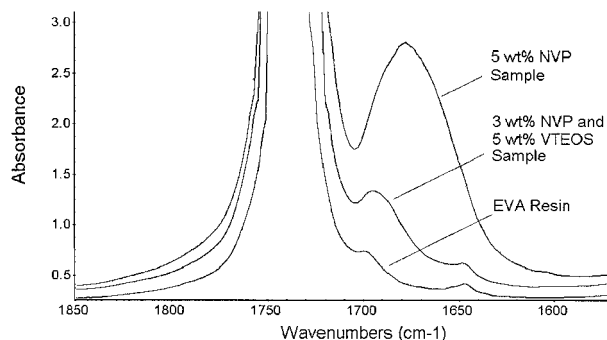
Figure 4 FTIR spectra illustrating selectivity for VTEOS over N-VP grafting (0.05 wt % L-231/145 °C).

a silane conversion of 36%. This apparent selectivity for VTEOS addition versus *N*-VP addition likely stems from the electron density of the olefin, with the nucleophilic alkyl radical of the polymer backbone favoring vinylsilane over the more electron rich *N*-vinylpyrrolidone.

A lack of significant additive incorporation, coupled with the observed efficacy of saturated additives such as *N*-methylpyrrolidone and *N,N*-dimethylaniline suggests that the "synergistic comonomer" mechanism[4–7] does not apply to this case. An alternate mechanism of additive function, developed by Gaylord and Mehta[8] for the MAn/polyethylene system, is also inapplicable. Citing the potential to excite MAn in the presence of a free radical, Gaylord and Mehta[8] propose that an effective additive functions by electron donation to an MAn-excimer complex. Although their results are consistent with this work, VTEOS cannot form such an excimer. Therefore, we must propose a different mechanism of additive function.

The experimental data exhibit a strong correlation between C—H bond dissociation energy and an additive's influence on the process. This suggests that the key element of an effective additive is a labile C—H bond for which hydrogen atom abstraction is energetically favorable. Whereas the addition of dodecane has no effect on the resulting $\Delta\tau$ or silane conversion, the presence of 1-dodecene causes a reduction of $\Delta\tau$ by 2.0 dNm and decrease in graft yield of 15%. The minimum homolytic bond dissociation energy of dodecane is that of an alkyl C—H bond (412 kJ/mol for propane and 400 kJ/mol for cyclohexane), whereas the allylic C—H bond within 1-dodecene is substantially weaker (345 kJ/mol for 1-butene).[11] This difference reflects the propensity for hydrogen atom donation by an additive to an alkyl

Initiation

r_1:

Grafting (propagation)

r_2:

Macroradical Termination (combination)

r_3:

Scheme 1

r_7:

Scheme 3

macroradical and/or an oxygen-centered radical derived from L-231. 4-Nonene has a greater influence than 1-dodecene, presumably because of differences in the number of allylic hydrogens.

The remaining additives also demonstrate this correlation between additive effect and minimum C—H bond strength. Both $\Delta\tau$ and silane conversion increase in proportion to the expected smallest bond dissociation energy within di-t-butyl-cresol, N-VP, N,N-dimethylaniline, and cyclohexyl acetate.

Although we appreciate the number and variety of reactions occurring during radical-mediated grafting, we suggest that those illustrated in Schemes 1, 2, and 3 account for the behavior observed in this study. Processes responsible for VTEOS grafting and resin crosslinking are depicted in Scheme 1. Reactions r_1 and r_2 lead to macroradical generation and monomer grafting, respectively. Intra- or intermolecular hydrogen atom abstraction by the silane-derived radical **3** completes a propagation sequence. Termination by macroradical combination (r_3) is responsible for peroxide-induced crosslinking, whereas the

less favored disproportionation reaction has no direct influence on molecular weight.

We propose that additives (A-H) affect crosslink density and monomer conversion mainly through the reactions illustrated in Scheme 2. Additive-derived radical species (A ·) are generated by two principal reaction pathways. Hydrogen atom abstraction from the additive by an initiator fragment (r_4) yields A · , as does abstraction by a macroradical (r_5). Besides reducing the frequency of macroradical combination by lowering the concentration of **2**, additive-derived radical species (A ·) may terminate macroradicals through a benign combination reaction, r_6.

We present two plausible mechanisms by which additives may alter the selectivity of EVA modification. According to one mechanism, selectivity results from the saturation of a relatively unreactive species (Scheme 3). Hydrogen atom abstraction at the acetyl site (r_7) would yield a radical with a limited propensity to react with vinylsilane and an inability to undergo disproportionation. Similarly, abstraction at tertiary sites on polymer backbone would have a reduced capacity for vinylsilane grafting. Because chain transfer and combination are expected to be the principal modes of reactivity for these species, hydrogen donation by an additive to this site would have little, if any, effect on VTEOS conversion. However, saturation of such radical species would decrease the crosslink density of the resin, provided that reaction r_7 is significant.

The second potential mechanism for the observed selectivity considers the net effect of hydrogen atom donation by the additive. Reactions r_4 and r_5 decrease the yield of alkyl macroradicals that support both grafting and crosslinking. Therefore, both crosslink density and VTEOS conversion are expected to decline in the presence of an effective additive, as observed by experimentation. That crosslinking is decreased disproportionately with respect to monomer grafting in the presence of an additive may be due to the

Initiation

r_4:   A-H   →   A ·

Hydrogen Donation by A-H

r_5:

Benign Radical Combination

r_6:

Scheme 2

reactivity of A · . This species is not expected to attack VTEOS but can terminate alkyl macroradicals through reaction r_6. As a result, the generation of A · via hydrogen atom transfer promotes benign macroradical termination while having little further impact on VTEOS graft conversion. The net effect of reactions r_4 and r_5 is a slightly greater depression of crosslink density than silane conversion. Those additives for which hydrogen atom abstraction reactions (r_4, r_5) are particularly favorable are expected to suppress both grafting and crosslinking completely. This was observed for di-*t*-butylcresol.

CONCLUSIONS

Application of select additives can produce VTEOS-modified EVA with a crosslink density and silane conversion that cannot be obtained using conventional methods. Effective additives act as hydrogen atom donors, having no need to graft in significant quantity to produce the desired effect. A mechanism consistent with the experimental data attributes the induced selectivity to the creation of a benign macroradical termination process that disproportionately influences crosslinking over VTEOS grafting.

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