Silane-Modified Poly(ethylene-*co*-vinyl acetate): Influence of Comonomers on Peroxide-Initiated Vinylsilane Grafting

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ABSTRACT: Functionalization of poly(ethylene-*co*-vinyl acetate) (EVA) with vinyltriethoxysilane (VTEOS) has been carried out by a free-radical melt-grafting procedure in the presence of added comonomers. The influence of comonomers on silane graft yield and crosslink density has been assessed. Experiments were performed on masterbatches of EVA, VTEOS (5 wt %), peroxide initiator (L-231, 0.05 wt %), and comonomer (0–1 comonomer : VTEOS mole ratio) prepared at 90°C. Melt-grafting experiments were carried out at 145°C in an oscillating disk rheometer (ODR), which measured crosslink density during the grafting process. Silane graft yields were determined by proton NMR spectroscopy. Comonomers evaluated were maleic anhydride (MAn), 1-vinyl-2-pyrrolidone (VP), and 1-dodecene (DD). At the comonomer ratios examined, MAn suppressed both silane grafting and peroxide-initiated crosslinking. Both VP and DD, however, exhibited greater selectivity in suppressing crosslinking than silane grafting; optimum performance was found at a comonomer : vinylsilane mole ratio of 0.2. None of the comonomers studied enhanced the level of silane grafting. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1308–1314, 2000

Key words: vinylsilane; poly(ethylene-*co*-vinyl acetate); graft modification; peroxide; comonomer

INTRODUCTION

Crosslinking of semicrystalline polymers such as poly(ethylene-*co*-vinyl acetate) (EVA) enhances such high-temperature properties as heat deformation and improves stress cracking resistance. Therefore, crosslinking is widely used as an inexpensive means of extending the useful range of commodity polymers to meet the demands of specialty applications. Although EVA is readily crosslinked by treatment with organic peroxides or radiation, moisture curing of silane-modified resin provides unique advantages in terms of processing and product quality.[1] Because the melt index of a silane-modified EVA is not altered during extrusion or injection molding, it may be processed at relatively high rates and cured off-line by exposure to a humid environment at temperatures below the melting point of the resin. With respect to product quality, the dimensional accuracy of moisture curing is superior to peroxide-based processes and the density of the crosslinked product is generally higher.

Silane-modified EVA is prepared by melt-grafting of vinyltrimethoxysilane (VTMOS) or vinyltriethoxysilane (VTEOS) onto the resin through a peroxide-initiated process. Although this radical-initiated modification is relatively simple, inexpensive, and solvent-free, low levels of undesirable crosslinking results from the termination of macroradicals by combination. At the low concentrations of peroxide required for efficient vinylsilane grafting, the modified resin usually remains
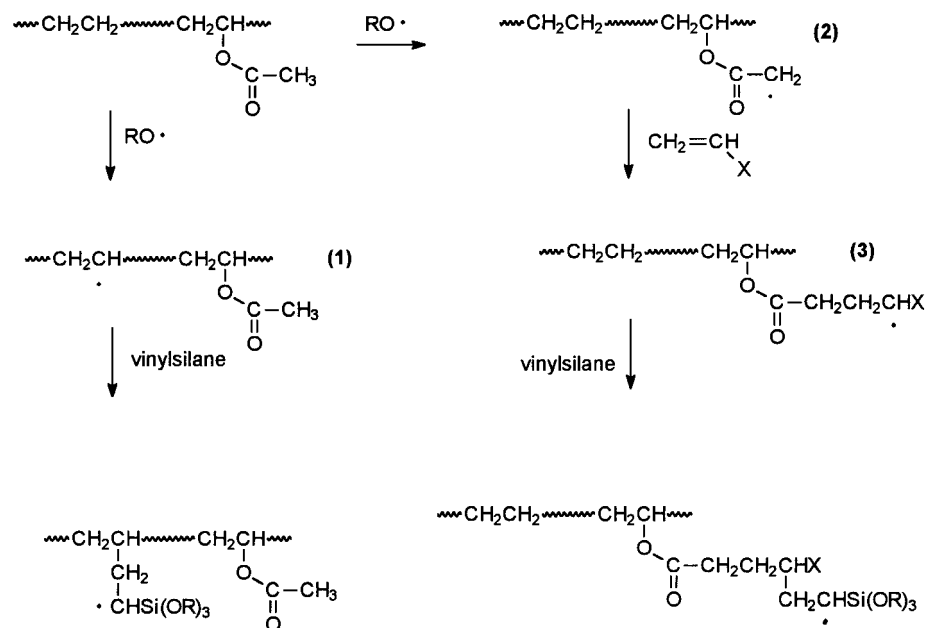
Scheme 1.   Sites for macroradical generation on EVA during vinylsilane grafting.

thermoplastic. Nevertheless, the decrease in melt index brought about by this peroxide-initiated crosslinking seriously reduces the processing characteristics of silane-modified EVA.

Recent literature[2–8] indicates that a synergistic comonomer has the potential to affect peroxide-initiated grafting by increasing the graft yield of a primary monomer while suppressing undesirable processes such as β-scission and crosslinking. Most studies have employed styrene to assist either maleic anhydride or glycidyl methacrylate grafting.[8] In the present work, the effect of select comonomers on the graft-modification of EVA with VTEOS has been examined with respect to graft yield and crosslink density.

Our rationale in using this comonomer approach for grafting onto EVA is based on the assumption that there are two general sites for macroradical generation, as shown in Scheme 1. A radical site **(1)** anywhere on the main chain of the polymer has four expected modes of reactivity: vinylsilane grafting, disproportionation (to introduce unsaturation), combination (to introduce crosslinking), and β-scission. A radical site **(2)** on the acetyl group has its expected reactivity modes reduced to only vinylsilane grafting or combination. If this radical site has poor kinetic reactivity toward vinylsilane, then macroradical combination may become its predominate reaction pathway. The presence of a comonomer with good re-

activity toward radical site **(2)** would generate a new radical site **(3)** with all four modes of reactivity restored; crosslinking through dimerization might then be suppressed.

Candidate comonomers for these experiments have been selected on the basis of several criteria. First, the comonomer must add to a macroradical to generate a new radical site that will be reactive toward vinylsilane. In addition to simple olefins, there are indications[9] that vinyl esters, maleic anhydride, maleates/fumarates, and vinylpyrrolidone have some propensity for copolymerization with vinylsilanes, whereas styrene does not. Second, the electron-deficient nature of radical site **(2)** should make it reactive toward electron-rich olefins, such as vinylpyrrolidone, thereby altering the reactivity of the macroradical **(3)**. Third, comonomers must be sufficiently involatile to allow masterbatch preparation without significant comonomer loss. On this basis, 1-vinyl-2-pyrrolidone (VP), maleic anhydride (MAn), and 1-dodecene (DD) were selected for the present study. Additionally, dodecane (DDane) was included in the study to assess the effect of a low molecular compound lacking unsaturation. The primary monomer, VTEOS, was chosen in preference to VTMOS because of its higher boiling point which was expected to reduce monomer loss during masterbatch preparation.

EXPERIMENTAL

Materials

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

Vinyltriethoxysilane (97%, Sigma Aldrich, Canada, Oakville, Ontario) was distilled at atmospheric pressure (bp 160–161°C) and analyzed by ^{1}H-NMR prior to use. Lupersol L-231 (92%, Atochem, Buffalo, NY) [1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane] was stored under refrigeration and used as received. DD (95%, Sigma Aldrich) and DDane (99%, Sigma Aldrich, anhydrous) were used as received. MAn (99%, Sigma Aldrich) was recrystallized from chloroform prior to use. VP (Fluka, Sigma Aldrich, Canada, Oakville, Ontario) was eluted through a column of alumina to remove sodium hydroxide stabilizer prior to use.

Grafting Reactions–Oscillating Disk Rheometer

EVA\L-231\VTEOS\comonomer masterbatches were prepared at 90°C using a Haake Rheomix 600 internal batch mixer (50 cm^3) controlled by a Haake Rheocord System 40 microprocessor. AT-EVA 1821 (30 g) was charged to the mixer at 60 rpm. After 5 min, VTEOS, comonomer, and L-231 were added sequentially at the appropriate weight percentage relative to the quantity of EVA resin and the masterbatch was mixed for 15 min to ensure homogeneity. Integration of ^{1}H-NMR spectra (*vide infra*) of select masterbatches confirmed the correct VTEOS content. After purification, these samples showed no spectroscopic evidence of silane grafting during the mixing procedure. Furthermore, no crosslinking was detected by rheometry during a 20-min period at 90°C. These control studies demonstrated that crosslinking and monomer grafting were absent in all masterbatches prepared by this method.

Melt-grafting reactions of the prepared masterbatches were conducted at 145 ± 1°C within the cavity of a TechPro oscillating disk rheometer (ODR). Because this cavity is completely filled and melt-sealed, problems derived from monomer vaporization were substantially reduced. The torque required to oscillate the biconical disk embedded in the sample through a 5° arc at 1.67 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 can be inferred from the difference of the instantaneous torque (M) and minimum torque (M_1). The ultimate state of crosslinking is derived from the change in torque, $\Delta\tau = M_h - M_1$, where M_h represents the maximum torque recorded over the course of the experiment.

All melt-grafting reactions were allowed to proceed for 20 min (corresponding to ~ 9 × $t_{1/2}$ of L-231 at 145°C), after which the sample was removed from the instrument and cooled to room temperature within a dessicator.

Structural Characterization

Graft-modified polymer was dissolved in boiling toluene and then precipitated by dropwise addition to acetone at room temperature. The purified sample was filtered from the solution and dried under vacuum at 25°C for 24 h to remove residual solvent. ^{1}H-NMR spectra were recorded at 60°C using a Bruker AM-400 spectrometer (400 MHz). The NMR solvent CDCl$_3$ (Cambridge Isotope Laboratories) was dried over molecular sieves to prevent hydrolysis of the alkoxysilane during analysis. Silane content was determined from a comparison of peak areas for signals at 4.8 ppm (1H, —CH—OAc, 18 wt %, 6.7 mol %) and at 3.88 ppm [6H, —SiO(CH$_2$—)$_3$] relative to chloroform (7.24 ppm).

RESULTS AND DISCUSSION

VTEOS Grafting onto EVA

The first series of experiments was conducted to test the stability of the base resin and to monitor the extent of crosslinking over the lifetime of the initiator. Figure 1 illustrates the results of three experiments that differ in either VTEOS or L-231 concentration. The ODR trace of an EVA/VTEOS masterbatch in the absence of peroxide reaches a stable plateau in a short period of time, indicating that thermally induced crosslinking of EVA was not appreciable under these conditions. As further evidence of the stability of the resin during processing, no change in torque was recorded for
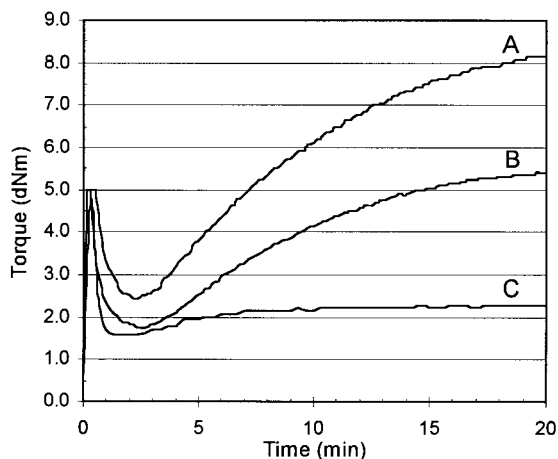
Figure 1 Peroxide crosslinking of EVA at 145°C. A: No VTEOS, 0.05 wt % L-231; B: 5% VTEOS, 0.05 wt % L-231; C: 5 wt % VTEOS, No L-231.

20 min beyond the time interval plotted in Figure 1. In contrast, a torque increase to a maximum of 8.14 dNm from the minimum of 2.43 dNm resulted from the addition of 0.05 wt % L-231 to the masterbatch. This difference in torque ($\Delta\tau = M_h - M_1$) reflects the change in the stiffness of the material and is the primary indicator of crosslink density used throughout the study. According to the ODR trace, 0.05 wt % of L-231 generates $\Delta\tau$ = 5.71 dNm within pure EVA.

The ODR trace recorded for an EVA/L-231/VTEOS masterbatch (Fig. 1) illustrates two important principles. In the first place, τ reaches a plateau after 18 min, which corresponds to complete decomposition of the initiator. Given that moisture curing is not a radical-initiated process, siloxane crosslinking of grafted ethoxysilane groups is not, therefore, operative in these experiments. Second, it is clear that the presence of VTEOS reduces the extent of peroxide-induced crosslinking, as the observed $\Delta\tau$ for the 5 wt % VTEOS masterbatch is 2.09 dNm less than that recorded for EVA with L-231 alone. However, τ is not reduced to the level of the base resin. Therefore, although the combination of macroradicals leading to crosslinking is less favorable in the presence of VTEOS, it persists to a significant degree.

The crosslink density of graft-modified EVA as a function of initiator and VTEOS concentrations is presented in Figure 2. Replicated experiments at various initiator and VTEOS levels provided a pooled estimate of the variance of $\Delta\tau$ measurements. The 95% confidence interval derived from this variance and plotted with the data is ±0.52 dNm. The results clearly demonstrate that higher VTEOS concentrations reduce crosslink density. In absolute units of τ, the effect is greatest in the high L-231 masterbatches. Although the mode of radical termination in melt-grafting processes is poorly understood, it is clear that VTEOS moderates the amount of macroradical combination. Whether an alternate termination pathway is established by the vinyl monomer, or macroradical combination is hindered, the observed result is a reduction of crosslink density.

As expected, the extent of crosslinking increases with increasing concentration of L-231. Although not immediately apparent from Figure 2, $\Delta\tau$ is a linear function of the peroxide level at each concentration of VTEOS. That is, the ultimate crosslink density is directly proportional to the L-231 dosage in the 0.022 to 0.05 wt % range. If extrapolated to $\Delta\tau$ = 0, the L-231 dosage is consistently positive, likely due to L-231 purity (92%) and the 100 ppm of phenolic antioxidant within the resin.

All VTEOS-grafted polymers generated in this work dissolved in boiling toluene within minutes and could therefore be purified by precipitation from toluene with acetone and analyzed for silane-graft content by ^{1}H-NMR. Figure 3 illustrates the silane content of the grafted material as a percentage of the VTEOS charged to the masterbatch. Once again, replicated experiments provide the information required to determine the
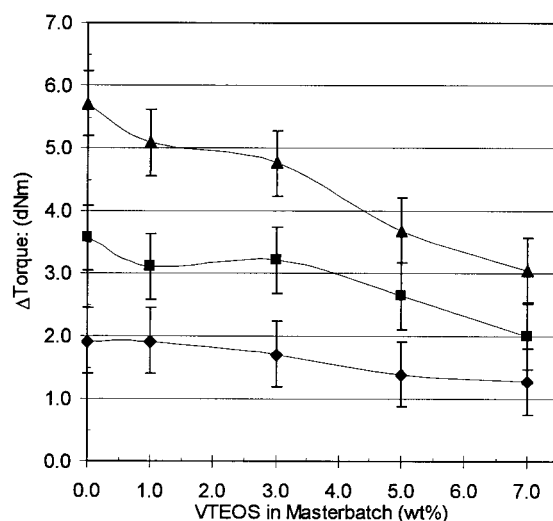

Figure 2 Graft-modified EVA crosslink density at 145°C. ◆, 0.022 wt % L-231; ■, 0.035 wt % L-231; ▲, 0.050 wt % L-231.
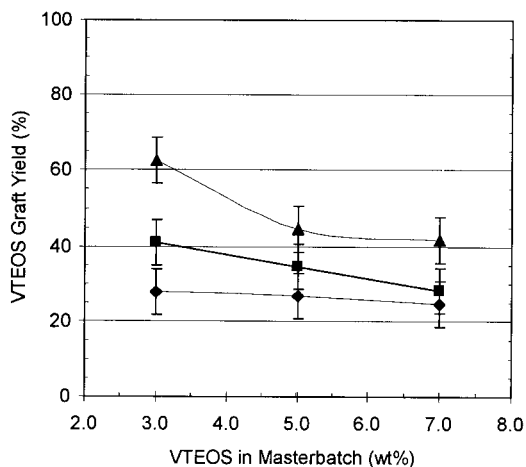
Figure 3 VTEOS graft conversion at 145°C. ◆, 0.022 wt % L-231; ■, 0.035 wt % L-231; ▲, 0.050 wt % L-231.

variance of the graft yield measurement. In this case, the 95% confidence interval is ±6.0%. The results demonstrate that VTEOS conversion to polymer grafts is promoted by higher concentrations of L-231. A maximum graft yield of 62% is observed for masterbatches containing 0.05 wt % L-231 and 3 wt % of vinylsilane. Although the absolute amount of VTEOS grafted increases as additional silane is charged to the masterbatch, the percentage converted to grafts decreases. The result is a decrease in grafting efficiency.

Based on the data presented in Figures 2 and 3, strategies to reduce the extent of crosslinking by varying monomer and initiator levels are offset by a decline in graft yield. Therefore, the objectives of reducing crosslink density and enhancing silane-graft conversion appear to be incompatible. Recent reports[2–8] have indicated that the use of a synergistic comonomer can enhance the graft yield of the primary monomer while suppressing undesirable processes, such as crosslinking, thereby resolving this apparent conflict. The merits of the synergistic comonomer idea for the EVA/L-231/VTEOS system have therefore been investigated.

Influence of Unsaturated Comonomers on Silane Modification of EVA

Three unsaturated compounds, VP, DD, and MAn, were chosen for their propensity to copolymerize to some degree with vinyl silanes,[9] and their low volatility which simplified masterbatch preparation. MAn, an electron-deficient alkene, is expected to differ from VP and DD in terms of its reactivity toward the electron-deficient radical

site generated at the acetate methyl group of EVA (structure 2, Scheme 1). Experiments using DDane were conducted to study the effect of the saturated analogue of DD which, presumably, simply lowers the viscosity of the polymer melt.

The influence of the various comonomers on the peroxide-initiated crosslinking is illustrated in Figure 4. In each experiment, an EVA masterbatch containing 5 wt % VTEOS, 0.05 wt % L-231, and the desired comonomer in a ratio of 2 mol VTEOS per mole of comonomer was reacted at 145°C. When compared with the ODR trace for the pure EVA/VTEOS/L-231 masterbatch, both the minimum and maximum torque recorded for the dodecane sample is reduced, reflecting the plasticizing effect of the hydrocarbon. However, the $\Delta\tau$ recorded in these two experiments are nearly equal, indicating that DDane does not influence the crosslinking process. In contrast, substantial decreases in crosslink density are observed for masterbatches containing unsaturated comonomers. Although differences in $\Delta\tau$ between VP, MAn, and DD masterbatches are not statistically significant, the extent of crosslinking in these samples clearly differs from the pure EVA/VTEOS masterbatch and that containing DDane. Therefore, it may be stated that unsaturated comonomers influence $\Delta\tau$ not by acting as plasticizers, but by intervening in the radical crosslinking process.

Comprehensive results on the degree of crosslinking and the silane graft yield as a function of comonomer concentration are presented in
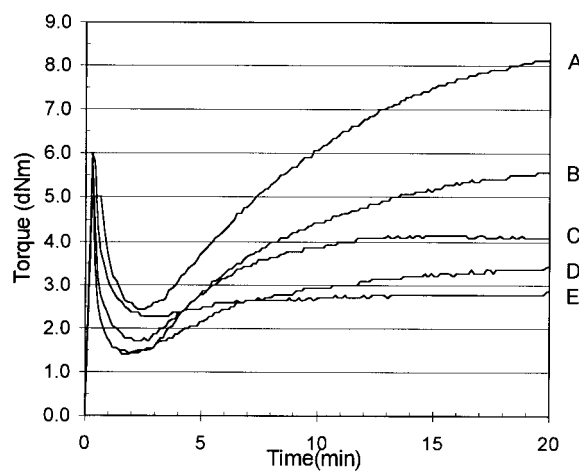

Figure 4 Influence of comonomers on EVA crosslinking (5 wt % VTEOS, 0.05 wt % L-231, 2 : 1 VTEOS : Comonomer, 145°C). A: No comonomer; B: DDane; C: VP; D: MAn; E: DD.
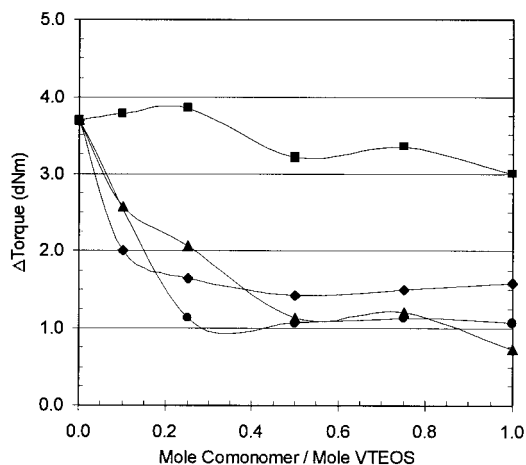
Figure 5 Influence of comonomers on graft-modified EVA crosslink density (5 wt % VTEOS, 0.05 wt % L-231, 145°C). ■, DDane; ▲, DD; ◆, VP; ●, MAn.

Figures 5 and 6, respectively. Throughout the entire concentration range studied, the influence of DDane on the extent of EVA crosslinking was marginal. The unsaturated analogue produces very different behavior, as the addition of DD to the EVA/VTEOS/L-231 masterbatch caused a notable decrease in crosslink density (Fig. 5). The benefit diminishes with increasing concentration, as DD had little influence on crosslinking above a mole ratio of 0.5 : 1 moles DD to mole VTEOS. It did, however, impact negatively on the degree of VTEOS grafting. The graft yield data show that although as much as 0.2 equiv could be tolerated without significant loss of grafting efficiency, a continuous decline results from further DD additions. Therefore, no more than 0.5 equiv of DD should be used under these conditions, as graft yield is compromised without an apparent improvement of crosslink density.

The results of VP addition to the standard EVA/VTEOS masterbatch are consistent with those of DD. Both crosslink density and graft yield decline with increasing VP concentration, albeit with different sensitivity. The optimum level of VP under the conditions studied is approximately 0.5 equiv, as observed for the DD case. Note that no such optimum exists for MAn, for even though crosslinking was reduced, VTEOS grafting was nearly completely suppressed. No more than 7% of the vinylsilane charged to the EVA masterbatch could be grafted in the presence of MAn, and no traces of grafting were detected in samples containing greater than a mole ratio of 0.7 : 1 MAn : VTEOS. A recent

report[11] on MAn grafting onto EVA copolymers suggests that, in our study, MAn is grafting at the expense of vinylsilane.

Although the potential for VP or DD grafting during the silane modification of EVA is of interest, we have found little evidence of comonomer grafting due to a lack of a strong spectroscopic signature that is either distinctive from the EVA resin or present in sufficient quantity to be detected with standard instruments. ^{1}H-NMR spectra of graft-modified samples reveal VTEOS grafting levels due to the abundance and unique chemical shift of —O—CH_2— groups within the silane. VP and DD are less amenable to NMR analysis, and many of the characteristic infrared absorbances are obscured by intense resonances of EVA. IR analysis of EVA/L-231/VP masterbatches (no VTEOS) that were heated to 145°C for 20 min revealed, after purification, a substantial amount of grafted VP through the presence of a strong C=O stretching absorbance at 1670 cm^{-1}. However, this characteristic absorbance[12] of grafted VP is completely absent in modified resins prepared in the presence of VTEOS.

Synergistic comonomers are reportedly[2–8] capable of improving graft yields while decreasing the degree of crosslinking. On the basis of our results, the addition of VP, DD, or MAn to EVA masterbatches cannot produce these effects. That is, none of these compounds improves both the efficiency of VTEOS grafting onto EVA while reducing the crosslink density. As a result, use of the term synergistic comonomer is not appropriate for the EVA/L-231/VTEOS system. Figure 7
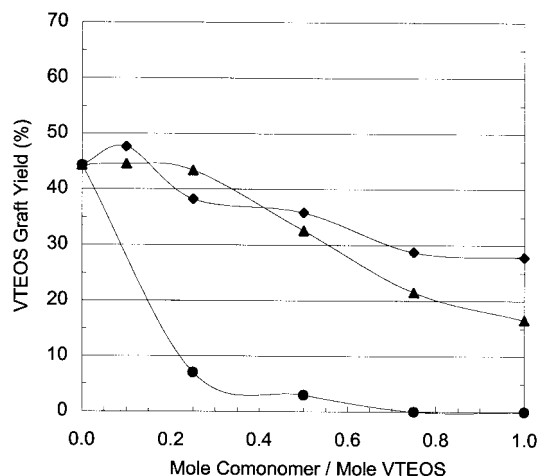

Figure 6 Influence of comonomers on VTEOS graft yield (5 wt % VTEOS, 0.05 wt % L-231, 145°C). ▲, DD; ◆, VP; ●, MAn.
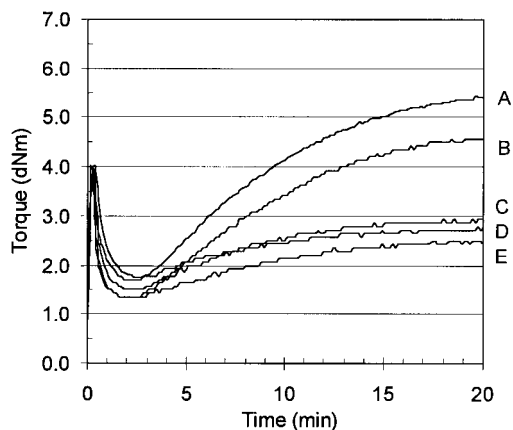
Figure 7 Influence of comonomers on EVA crosslinking in the absence of VTEOS (0.05 wt % L-231, 145°C, 0.132 mmol comonomer/g EVA). A: No comonomer; B: DDane; C: VP; D: DD; E: MAn.

illustrates the influence of each comonomer on the crosslinking process in the absence of VTEOS. In each case, the ODR traces are consistent with experiments conducted with VTEOS in the masterbatch (Fig. 4). Therefore, the mechanism through which VP, DD, and MAn influence crosslinking may be independent of VTEOS grafting.

CONCLUSION

It has been demonstrated through ODR experiments that peroxide-initiated vinylsilane grafting to EVA is subject to peroxide-induced crosslinking. Furthermore, the inclusion of low-molecular-weight additives, such as vinyl comonomers, can influence both the silane grafting and the crosslinking in apparently differentiable ways. Of the additives studied, MAn suppressed both silane grafting and crosslinking, whereas VP and DD suppressed crosslinking more extensively than VTEOS grafting. For

VP and DD, there was an optimum range for the mole ratio of vinylsilane to comonomer to maintain grafting levels while achieving significant reduction in crosslinking. The absence of structural information makes it difficult at this point to interpret the role of these additives in the peroxide-initiated grafting and crosslinking processes.

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