Film Blowing of Silane-Modified Polyethylene

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ABSTRACT: The grafting of vinyltriethoxysilane (VTES) onto polyethylene (PE) with the help of small amounts of peroxides was investigated to film-blow these modified materials. The degree of crosslinking was kept very low to achieve good melt processability and improved mechanical properties. The possibility of obtaining modified PE films with improved properties and regularly distributed crosslinking with a single processing step demonstrates the uniqueness of this study. The additive concentration was established through preliminary studies; with a batch mixer, it was possible to process the modified PE in the film-blowing operation. Water treatment of the modified films after film blowing allowed for improved properties without the processability being affected. The modification of PE was followed with mechanical, rheological, and extraction tests and with calorimetric analyses. The variations of the main mechanical properties of the films were very important from an application point of view. The elastic modulus and tear strength of the films for both extrusion directions (machine and transverse) increased with the VTES concentration increasing and even more with the addition of a small quantity of a peroxide. Some reductions of the tensile strength and elongation at break were observed, but these reductions were not considerable. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 503–508, 2009

Key words: films; mechanical properties; polyethylene (PE)

INTRODUCTION

Crosslinked polyethylene (PE) can be achieved via a free-radical reaction process with a peroxide through silane modification or irradiation. The initial thermoplastic material, consisting of linear polymer chains, is transformed into a polymer network with rubberlike, elastic properties. The resulting polymer network can, therefore, be described as a statistical alkyl-chain homogeneous network. Network analysis generally shows a high gel content (ca. 80–90% w/w) increasing with increasing crosslinker concentration. Crosslinked PE shows considerably changed material properties (in particular, the thermal stability and mechanical properties). The high gel content and consequently modified material properties can be profitable only for some practical applications, such as insulation for electrical cables and liquid-transport pipes.[1–16]

Shieh and Liu[4] investigated silane grafting and crosslinking reactions of low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE). The extent of the silane grafting reactions of PE was in the order of LLDPE > LDPE > HDPE. Also, Shieh and co-workers[5,6] investigated factors such as the time, temperature, morphology, sample thickness, extent of silane grafting, and diffusion of water that affect the rate and degree of crosslinking reactions of silane-grafted PE. They concluded that at a low temperature, the rate-determining step of crosslinking is the diffusion of water, whereas at a high temperature and with a high percentage of silane grafting, chemical reactions dominate the crosslinking.

Scott Parent et al.[7] studied the influence of the type of silane modifier on a crosslinking reaction using poly(ethylene-*co*-vinyl acetate) for masterbatch preparation.

Fabris et al.[10] studied the radical melt functionalization of LDPE with vinyltriethoxysilane (VTES) employed as a coupling agent in polymer composites. Instead, Alagar and Kumar[9] prepared silanized EPDM/thermoplastic blends for cable insulation at low and medium high voltages. The silane-modified polymer blends revealed better properties than the unmodified blends.

Some interesting research[11] concerns the relationship between the technological performance and cost of both chemically crosslinked (through silane grafting) PE and electron-beam-irradiated crosslinked PE. The irradiation method produces a product with superior characteristics.

The incorporation of carbon black into silane-grafted crosslinked PE reduces the degree of

crystallization and decreases the extent of silane grafting and the gel fraction.[15,16]

In our previous works,[17,18] we studied the possibility of reprocessing via a film-blowing operation postconsumer PE films from agricultural applications, keeping the degree of crosslinking at a low level. The regradation of photooxidized postconsumer PE films (coming from agricultural applications), which contain naturally formed carboxyl groups, usually occurs through branching and crosslinking reactions. It has been demonstrated that the use of suitable additives, such as a hydroxyl amine derivative and an ethylene–glycidyl methacrylate copolymer, can enlarge the molecular distribution and/or partially rebuild the molecular structure of photooxidized PE. Different reaction paths have been invoked to explain the formation of branching and/or crosslinking: the hydroxyl amine derivative is a typical radical generator that acts through hydrogen extraction, whereas ethylene-*co*-glycidyl methacrylate, which contains epoxy groups, reacts with the carboxyl groups in the photooxidized PE. Excessive crosslinking was obtained with high concentrations of additives, and long processing times led to a significant worsening of the mechanical properties. The final material properties of the somehow regraded films were estimated with the aim of reprocessing these postconsumer materials for the same applications.

In this study, we attempted to investigate the modification of virgin LDPE through silane grafting while keeping a low crosslinking level (in particular, less than ca. 5% w/w). The low degree of crosslinking (obtained during the single processing step) and, in particular, the regular distribution of the crosslinking allowed us to obtain a properly modified PE for film-blowing processing applications with improved mechanical properties. The mechanical resistance of the films improved in the presence of a low gel content, and no worsening in the processability of the PE film was observed. The modification of LDPE was followed with mechanical and rheological tests, with extraction tests using *p*-xylene as the solvent, and with calorimetric analyses.

EXPERIMENTAL

Materials

The PE used in this work was a film-grade LDPE [Riblene FC30, Polimeri Europa, San Donato Milanese, Milan, Italy; weight-average molecular weight = 175,000 g/mol, weight-average molecular weight/number-average molecular weight = 5.76, melt flow index (190°C and 2.16 kg) = 0.28 g 10/min, density (23°C) = 0.922 g/cm]. The PE sample used in this work did not contain any kind of antioxidant.

This commercial PE was blended with additives, such as VTES and dicumyl peroxide (DCP), both from Sigma–Aldrich, (Milan, Italy), at various concentrations.

Processing and characterization

LDPE was compounded with the additives at different concentrations in a Brabender (Duisburg, Germany) mixer at two temperatures (180 and 240°C), at a mixing speed of 60 rpm, and for a mixing time of about 10 min; this was enough to get a practically constant value of the torque. Pure PE was subjected to the same treatments.

The films were prepared with a single-screw extruder equipped with a film-blowing head and a Brabender film-blowing unit. The thermal profile was 120–140–160–180°C, and the screw speed was 60 rpm.

The concentrations adopted for both mixing and film blowing were 0.15 and 0.30% w/w for VTES and 0.05 and 0.15% w/w for DCP.

Tensile properties were determined at room temperature with an Instron model 4443 (Buckinghamshire, UK) machine according to ASTM test method D 882. The specimens were cut from films and were tested at two strain rates. For modulus measurements, the speed was 1 mm/min until a deformation of 10%, and it was then increased to 500 mm/min until breaking; for Young's modulus, the tensile strength (TS) and the elongation at break (EB) were recorded. The reported data are average values obtained by an analysis of the results of eight tests per sample, the reproducibility being ±3% for pure LDPE and ±7% for all the samples.

Rheological tests in shear flow were performed with a Rheometrics RDA II (Piscataway, NJ) in a plate–plate mode at a test temperature of 180°C in the range of 0.1–500 rad/s.

The rheological behavior in nonisothermal elongational flow was tested with a capillary viscometer (Rheologic 1000, Ceast, Turin, Italy) equipped with a drawing system. The capillary diameter was 1 mm, the length-to-diameter ratio was 40, and the test temperature was 180°C. The extruded filament passed through a pulley system and was then drawn by two counter-rotating rolls. The run was carried out by the pulling of the filament, extruded at a given flow rate, at a rotational speed that increased with a linear acceleration of 1 rpm/s. The test ended with the breaking of the filament. The force in the molten filament at breaking was read directly and is known as the melt strength (MS). The breaking stretching ratio (BSR) was calculated as the ratio of the drawing speed at breaking to the extrusion velocity at the die.

The calorimetric data were evaluated by differential scanning calorimetry with a PerkinElmer DSC7 (Norwalk, UK) at a scanning rate of 10°C/min.

Extraction tests were performed by Soxhlet extraction with *p*-xylene as the solvent. Approximately 0.3 g of any sample was exposed to refluxing in *p*-xylene close to its boiling point. The extraction time was about 48 h.

The samples for the rheological tests were prepared by compression molding at 180°C.

RESULTS AND DISCUSSION

In Figure 1, the torque of the modified PE, measured after 10 min of processing in the batch mixer at two different temperatures, is summarized. The torque was calculated as the final torque value after 10 min of processing of modified samples divided by the final torque value after processing of unmodified PE. With the addition of the silane modifier, the torque values slightly increased, and this enhancement was more pronounced in the presence of the peroxide at both temperatures. A significant rise in the torque values was observed in the presence of only the peroxide, particularly at the highest processing temperature. This behavior can be attributed only to an increase in the viscosity due to the rise in the molecular weight caused by reactions with the additives. The grafting of VTES onto PE was more effective with the temperature increasing and with the help of a small amount of the peroxide as a radical initiator; this agrees with reports found in the literature.[2,5,6] In this preliminary step of the work, an attempt was also made to extend the modification of PE in the presence of two additives by immersion of the sample, after mixing, in hot water.

In Figures 2 and 3, the viscosity of modified PE samples processed in a batch mixer at 180 and 240°C, respectively, is reported. The dimensionless values of the viscosity were calculated as the values of the viscosity of modified samples at each fre-
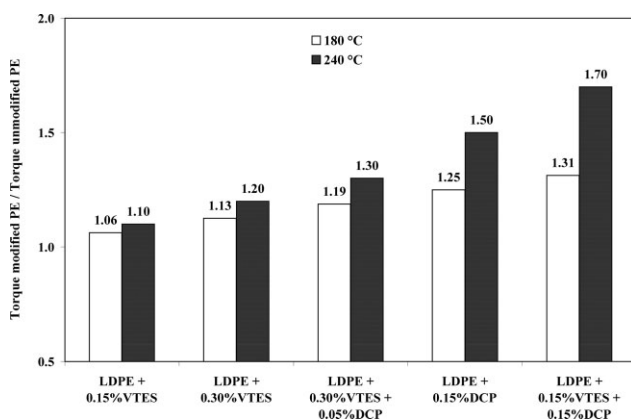

Figure 2 Dimensionless viscosity of the modified PE samples with VTES, DCP, or both additives processed at 180°C in the batch mixer.

quency divided by the values of the viscosity of unmodified PE at the same frequency. The viscosity increased as a function of the VTES content at 180°C (Fig. 2). A further rise in the viscosity was observed for the sample modified with two additives. The viscosity in the presence of only the peroxide was higher than that of the silane-modified samples, especially at low shear rates, but the water-treated sample showed the highest viscosity. The increases in the dimensionless viscosity in the presence of only VTES at 240°C (Fig. 3) were similar to those obtained at a lower mixer temperature. At this temperature also, the enhancements of the viscosity in the presence of only the peroxide and in the non-water-treated VTES/DCP-modified samples were comparable. These latter two showed significant decreases in the dimensionless viscosity at high frequencies. The water treatment of the VTES/DCP-modified sample led to a sharp increase in the dimensionless viscosity, especially in the low frequency range.

Figure 1 Final torque values after 10 min of processing in a batch mixer of the modified PE sample with different additives divided by the final torque values of the unmodified PE at two different temperatures.
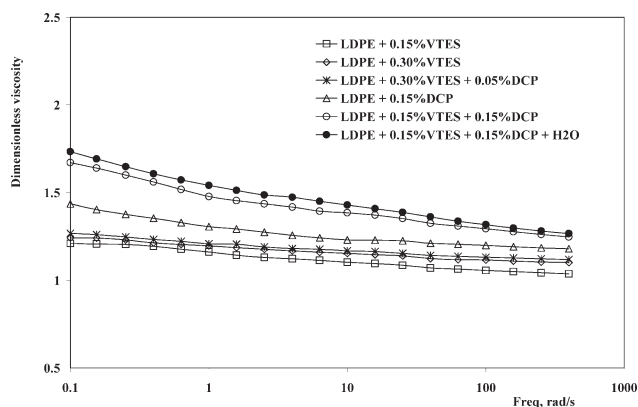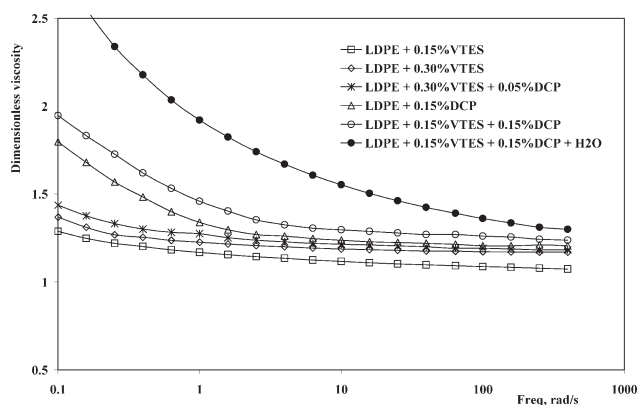

Figure 3 Dimensionless viscosity of the modified PE samples with VTES, DCP, or both additives processed at 240°C in the batch mixer.

TABLE I
Heat of Fusion (ΔH) Related to the Second Heating and Gel Content of Modified PE and Unmodified PE Processed in the Batch Mixer at Two Different Temperatures

Sample	180°C		240°C	
	ΔH (J/g)	Gel content (%)	ΔH (J/g)	Gel content (%)
LDPE	117	0	106	1.5
LDPE + 0.15% VTES	116	1.0	107	5.2
LDPE + 0.30% VTES	119	2.1	110	8.8
LDPE + 0.30% VTES + 0.05% DCP	119	2.5	111	9.5
LDPE + 0.15% DCP	120	6.4	128	28.5
LDPE + 0.15% VTES + 0.15% DCP	118	4.5	119	23.0
LDPE + 0.15% VTES + 0.15% DCP + H_2O	105	26.5	98	42.3

Adding a single additive (VTES or DCP) or the two additives together caused an increase in the melt viscosity that was even greater when the VTES/DCP-modified sample was water-treated at both processing temperatures. This rheological behavior was attributed to structural modifications of PE due to the presence of VTES and/or the peroxide. The grafting of VTES onto PE was less efficient without the peroxide, but some modification was obtained. Instead, the presence of the peroxide led to more rapid radical formation and subsequently high crosslinking degrees. The peroxide radicals helped the grafting of VTES onto PE. Silane-grafted groups through hydrolysis formed silanol groups on PE. However, the formation of silane-crosslinked PE occurred with silanol condensation and could be accelerated by the presence of a specific catalyst.[2] The water treatment, in our case, likely helped to export the secondary product of the hydrolysis and the silane crosslinking reactions.

To evaluate the structural modification, calorimetric analyses and Soxhlet extraction tests were carried out on the modified PE and unmodified PE processed in the batch mixer at two different temperatures. The related results are reported in Table I.

The values of the heat of fusion of unmodified PE decreased with the processing temperature increasing; however, an insoluble residual fraction appeared. Under these processing conditions, simultaneously with the chain breaking, crosslinking formation occurred. With the addition of only VTES, no variation of the heat of fusion was observed, regardless of the processing temperature. Furthermore, the gel contents increased with the VTES contents, especially for the samples processed at high mixing temperatures. The presence of a small quantity of only the peroxide led to a significant rise in the gel content and to some variation of the values of the heat of fusion, particularly for the sample processed at 240°C. The modified samples with VTES and DCP showed a gel content lower than that of the samples modified only with DCP at both temperatures. It is interesting to highlight the substantial increases in the insoluble fraction of the water-treated VTES/DCP-modified samples at both temperatures. However, the values of the heat of fusion for the water-treated samples were lower than those for the unmodified PE. The extraction results and the calorimetric analyses were in agreement with the rheological response of the modified samples.

In Table II, the main mechanical properties [in particular, the elastic modulus (E), TS, and EB] of the unmodified PE and their relative variations for modified PE with respect to the pristine polymer processed in the batch mixer are reported. In the presence of DCP, with and without VTES, some increases in E and TS and simultaneous reductions of EB were observed. The latter significantly

TABLE II
Mechanical Properties (E, TS, and EB) of the Unmodified PE and Their Relative Variation for Modified PE with Respect to the Pristine Polymer Processed in the Batch Mixer

Sample	180°C			240°C		
	E (MPa)	TS (MPa)	EB (%)	E (MPa)	TS (MPa)	EB (%)
LDPE	101	10.0	396	115	9.0	331
LDPE + 0.15% VTES	+1.0	+1.0	−9.0	−4.3	−5.5	−39.3
LDPE + 0.30% VTES	+1.9	+5.0	−3.5	−3.5	−5.5	−37.5
LDPE + 0.30% VTES + 0.05% DCP	+2.0	+5.2	−3.2	−2.0	−4.1	−36.5
LDPE + 0.15% DCP	+4.9	+3.0	−7.8	+5.2	+8.8	−47.1
LDPE + 0.15% VTES + 0.15% DCP	+1.9	+10.0	−4.8	+10.4	+1.0	−53.2
LDPE + 0.15% VTES + 0.15% DCP + H_2O	+6.9	+7.0	−8.6	+11.3	+5.5	−45.0

TABLE III
MS and BSR at a 60 1/s Apparent Shear Rate of Modified PE and Unmodified PE Processed in the Batch Mixer at 180°C

Sample	MS (cN)	BSR
LDPE	9.5	4.5
LDPE + 0.15% VTES + 0.15% DCP	12	3.7
LDPE + 0.30% VTES + 0.05% DCP	10.5	3.9

decreased for all modified samples at the higher processing temperature because the kinetics of cross-linking formation was faster.

However, the reported tests did not give information about the filmability of these modified materials. During processing by film blowing, nonisothermal elongational flow was involved. The measurements of MS and BSR permitted the evaluation of the filmability of the samples. The values of MS and BSR of the unmodified and VTES/DCP-modified samples in Table III are reported at one fixed apparent shear rate (ca. 60 s^{-1}) and at 180°C. The modified samples showed higher values of MS in comparison with the pure PE. The last one depended on the increase in the viscosity due to the presence of branching and crosslinking. MS is a technological parameter that is very sensitive to the structural variation of a material. Furthermore, a small decrease in the values of BSR of the modified samples was observed in comparison with the unmodified sample. The increase in MS and the subsequent decrease in BSR are usually correlated with reduced stretchability of the materials.[21]

However, processing in a film-blowing operation (with an extrusion thermal profile of 120–140–160–180°C and 60 rpm) of the VTES/DCP-modified sample in the presence of 0.15% VTES and 0.15% DCP was not possible, although the variation of the values of MS and BSR was not significant. The processing difficulties were not easily predictable because the increase in the dimensionless viscosity of the non-water-treated VTES/DCP sample with 0.15% VTES and 0.15% DCP at 180°C in the range of 100–300 rad/s (a typical shear rate range for extrusion operation) was close to the improvements obtained for the samples modified with only VTES at both concentrations and for the VTES/DCP-modified sample with 0.30% VTES and 0.05% DCP. In fact, only VTES at both concentrations and VTES/DCP with 0.30% VTES and 0.05% DCP did not create any difficulties during the film blowing.

In Figure 4, the dimensionless viscosities of all extruded samples are reported. The presence of a small amount of the peroxide (0.05%) and VTES led to some increases in the viscosity. The water-treated VTES/DCP sample, after film blowing, showed a higher dimensionless viscosity. All the modified
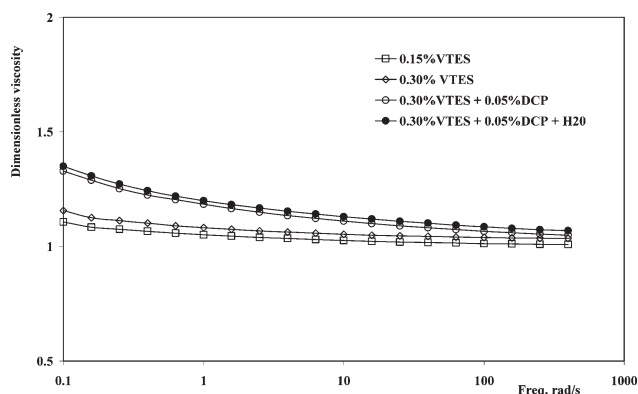

Figure 4 Dimensionless viscosity of all of the modified film samples.

samples, with and without water treatment, showed values of the dimensionless viscosity that were close to one another in the range of 100–300 rad/s. In fact, the insoluble fraction of the non-water-treated modified films, reported in Table IV, remained at a low level (<1%). A significant increase in the gel content was obtained for the water-treated VTES/DCP-modified film. In Table IV, the values of the heat fusion of all the extruded samples are reported as well. Some variation was observed only for the water-treated sample, and this was in agreement with the extraction test results and rheological behavior. The short residence time during the extrusion, about 80–120 s (with respect to the residence time during the mixing, i.e., 10 min), was enough to graft VTES; this was helped by a small quantity of DCP. The increase in the molecular weight during the extrusion operation due to the grafting of VTES in the presence of DCP onto PE did not compromise the processing in film blowing.

The variations of the main mechanical properties of the films are very important from an application point of view. The main mechanical properties (*E*, TS, and EB) were measured in machine and transverse directions and are reported in Table V. Also, the last column of Table V reports the values of the tear strength (Ts), a critical property for film applications.

TABLE IV
Melting Peak, Heat of Fusion (Δ*H*), and Gel Content of the Modified and Unmodified PE Films

Sample	Δ*H* (J/g)	Gel content (%)
LDPE	103.4	0
LDPE + 0.15% VTES	104.6	0.1
LDPE + 0.30% VTES	102.8	0.3
LDPE + 0.30% VTES + 0.05% DCP	105.9	1.5
LDPE + 0.30% VTES + 0.05% DCP + H$_2$O	98.4	4.4

TABLE V
Mechanical Properties (*E*, TS, EB, and Ts) of the Unmodified PE Film and Their Relative Variations (%) for Modified Blown Films with Respect to the Pure Film in the Two Drawn Directions

Sample	Machine direction			Transverse direction			
	E (MPa)	TS (MPa)	EB (%)	E (MPa)	TS (MPa)	EB (%)	Ts (N/mm)
LDPE	105	21.2	402	113	19.3	427	175
LDPE + 0.15% VTES	+6.9	−0.9	+2.0	+8.8	−4.7	−2.3	+6.8
LDPE + 0.30% VTES	+11.8	−2.8	+4.9	+8.8	−4.9	−6.1	+11.1
LDPE + 0.30% VTES + 0.05% DCP	+9.3	−5.3	−3.9	+8.2	−5.9	−1.8	+15.4
LDPE + 0.30% VTES + 0.05% DCP + H$_2$O	+14.2	−12.3	−10.3	+11.4	−11.1	−10.8	+1.8

For both directions, *E* increased with increasing VTES concentration and even more with the addition of a small quantity of the peroxide. Significant increases in Young's modulus were observed for the water-treated modified film: about 14 and 11% for the machine and transverse directions, respectively. The increase in *E* can be explained with the increase in the gel content and even more for the water-treated film by the formation of silane-crosslinked structures. Some reduction of TS and EB, except for the EB values of the samples with VTES in the machine direction, were observed, but these reductions were not considerable. A further reduction of the values of TS and EB for the water-treated VTES/DCP-modified film in comparison with the pure PE were observed in both drawn directions. The variation of the main mechanical properties after the water treatment were balanced for the machine and transverse directions, and this was indicative of a uniform distribution of the crosslinked structures.

Indeed, improved values of Ts were shown versus those of the pure PE film. Significant increases in Ts at a higher concentration of VTES were observed; in particular, the rise was more pronounced in the presence of a small amount of DCP. The water treatment of the VTES/DCP-modified film entailed minimal increases in Ts, probably because of the enhanced rigidity of the materials, in agreement with the increased values of Young's modulus and reduced values of TS and EB.

CONCLUSIONS

The modifications of virgin LDPE through silane grafting, with a low crosslinking level maintained (less than ca. 5% w/w), were investigated. The benefit of the grafting reaction was observed in the presence of small amounts of peroxides and even more

with the water treatment of the modified materials. It was possible to process the modified PE in a film-blowing operation with 0.30% VTES and 0.05% DCP.

The rheological behavior, extraction, and calorimetric analyses suggested that some crosslinking occurred during processing. The variations of the main mechanical properties, particularly for the water-treated modified film, were balanced for both extrusion directions (machine and transverse direction), highlighting the uniform distribution of crosslinked PE.

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