Shrinkage in Extruded Moisture Crosslinked Silane-Grafted Polyethylene Wire Insulation

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ABSTRACT: Shrinkage studies were conducted on silane-grafted moisture crosslinkable linear low-density polyethylene (LLDPE) insulation stripped from extrusion-coated copper conductors. The insulation, which possesses orientation imparted during melt processing, showed remarkable levels of shrinkage when heated above the melting point of the polymer, though the shrinkage can be greatly reduced by moisture crosslinking the insulation below the melting point of the LLDPE. Shrinkage along the direction of orientation was accompanied by swelling in the other dimensions. Differential scanning calorimetry (DSC) revealed several trends, including a decrease in both melting point and degree of crystallinity with increasing crosslinking. In the first heat after annealing, crosslinked samples exhibited a shoulder in the DSC endotherm several degrees below the normal melting point of the LLDPE. In agreement with prior studies in silane-grafted HDPE, relaxation of orientation by annealing appeared to result in an increase in the enthalpy of melting. The degree of shrinkage was also found to be dependent on the insulation thickness, which is attributed to faster cooling in thinner insulation immediately following extrusion coating. The results highlight the extensive built in stresses that can be frozen into polymer layers in fabricated articles due to melt orientation. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1796–1802, 2010

Key words: orientation; crosslinking; polyolefins; moisture cure; shrinkage; shrinkback

INTRODUCTION

Extrusion, injection molding, and other processes that impart orientation to semicrystalline polymers in the melt state can lead to built in anisotropic stresses once the polymer is cooled below its melting point. Relief of these stresses by heating the polymer above its melting point can result in significant shrinkage in the direction of orientation. In a process such as extrusion coating of a copper wire with a thermoplastic semicrystalline polyolefin polymer, the presence of the copper/polymer interface on the inside and external insulation surface on the outside serves to increase the potential to lock in anisotropic stresses. Factors affecting the propensity to lock in such stresses include polymer branching, molecular weight, molecular weight distribution, cooling rate, polymer melt temperature, and draw down ratio.[1,2]

Shrinkage in oriented polyethylenes has been extensively studied. Liu and Harrison studied shrinkage of low density polyethylene film.[3] Studies of polyethylene crosslinked while in the oriented state[4,5] or oriented after crosslinking[5,6] have also been reported. Effect of orientation in crosslinked polyolefins has been reviewed.[7]

Narkis et al. studied orientation effects in injection molded silane-grafted polyethylene that was moisture crosslinked below the polymer melting temperature after orientation.[8] Molecular orientation was found to become mostly irrecoverable even at 150°C after crosslinking.

Yagi and Mantoku reported studies on ultra-high-molecular weight polyethylene (UHMWPE) that was silane crosslinked after or during drawing.[9] The resulting material was able to retain its shape and not fuse even after 10 min at 180°C. This approach was noted for achieving creep resistance while maintaining the beneficial high elastic modulus and high tensile strength inherent to a draw-molded article of UHMWPE.

Shrinkage resulting from relaxation of stresses imparted by orientation in the melt during extrusion is known to be a practical consideration in the wire and cable industry,[2] where the specific extrusion conditions, tooling, and the presence of a conductor set up conditions for locking in orientation-related stresses.

This paper reports interesting shrinkage results observed in uncrosslinked and moisture crosslinked wire insulation based on linear low density polyethylene (LLDPE) grafted with vinyltrialkoxysilanes. In such materials, orientation imparted during melt

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processing is frozen in during wire coating. Specimens of insulation that are stripped from the conductor show remarkable levels of shrinkage when heated above the melting point of the polymer, though the shrinkage can be reduced by crosslinking the insulation below the melting point. Differential scanning calorimetry (DSC) and shrinkage studies are reported as a function of degree of crosslinking and annealing.

EXPERIMENTAL

Materials

A LLDPE, made by The Dow Chemical Company, and available in pelletized form, was used as the base polymer for silane grafting for all the experimental runs. The density and melt index of the.polymer are reported as 0.92 g/cm^3 and 0.7 g/10 min, respectively. Both vinyltrimethoxysilane (Z-6300) and vinyltriethoxysilane (Z-6518) were procured from Dow Corning. Luperox 101 (2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, Arkema), was used as the peroxide initiator for grafting.

Wire fabrication

The formulations for the wire line runs were made by first drying the polyethylene pellets overnight at 60°C in a laboratory oven, and then mixing them with specific amounts of silane and peroxide. The soaked formulations were then mixed with a predried catalyst master batch (LLDPE pellets containing 2.6 wt % dibutyltin dilaurate) in a 95 to 5 wt % ratio.

Wire fabrication was carried out by charging the resin mixture through a gravity-feed hopper to a single-screw extruder (0.75″ bore and L : D ratio 25 : 1). Typical extrusion melt temperature at the die was between 195 and 210°C. Post extrusion cooling was achieved by passing the wire through a water trough with incoming water at 23°C. For most of the runs, the wires were constructed on a 14 AWG (diameter ∼ 1.63 mm) copper conductor. The insulation thickness was maintained at ∼ 0.76 mm for most of the runs, resulting in a finished wire diameter of around 3.15 mm. For selected runs, thinner conductors were coated with thinner insulations, as noted later.

Moisture curing

The conductors were stripped from the finished wires by slightly drawing the copper to make the insulation easy to remove. Wire samples were cured for different times in a water bath, maintained at 90°C. By keeping both ends of the stripped insulation outside the water-bath, it was ensured that only the outer surface was directly in contact with water.

TABLE I
Silane Graft Levels for Various Wire Insulation Samples for Different Silane and Peroxide Levels, Silane Type, and Extrusion Temperature

Insulation samples	VTES-1	VTES-2	VTES-3	VTMS-1
VTES added (wt %)	1.8	1.8	1.8	0
VTMS added (wt %)	0	0	0	1.0
Luperox-101 added (ppm)	800	720	360	800
Extrusion melt temperature (°C)	195	195	195	210
Silane graft level (wt % VTMS or VTES)	0.96	0.84	0.63	0.90

Annealing

The samples that were stripped and cured were annealed at a temperature of 152°C over 10 min in an air-circulating oven. A 76 mm long piece of each sample was hung with a clamp by one end from the oven ceiling. After the sample was withdrawn and cooled, the shrinkage or percentage decrease in length was calculated by measuring the final length of a marked center portion that had an original length of 25.4 mm.

Gel measurement

The gel content was determined as the insoluble fraction remaining after extraction in refluxing decalin. Amount of gel was determined according to ASTM 2765. Weighed samples were wrapped in 120-mesh stainless steel screen and extracted in refluxing decalin for 6 h. Extracted samples were dried to constant weights in vacuum oven and the amount insoluble was determined for each of them.

DSC analysis

Thermal properties were recorded by DSC using a TA Instruments DSCQ1000. Approximately 5–8 mg of insulation material was cut and weighed into a hermetic pan with lid and crimp sealed. The first heat-cool cycle (30–230°C and back to 0°C) was followed by a second heat cycle (0–230°C) at a rate of 10°C/minute.

FTIR analysis

Immediately after extrusion, each insulation was pressed to make 10 mil film from which the level of grafted silane was determined. Before conducting the FTIR analysis, the cable samples were placed in a vacuum oven for 24 h to remove all of the free silane. Silane contents were calculated based on the ratio of the absorbance of silane at 1196 to 2021 cm^{-1}, where 2021 cm^{-1} is the internal polyethylene standard to account for small variations in sample
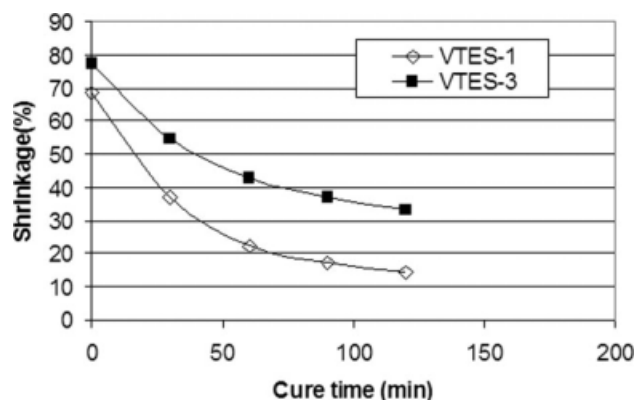
Figure 1 Shrinkage of insulation during annealing as a function of different cure times in a 90°C water bath.

Figure 3 Gel content and shrinkage vs. cure time for VTES-2 showing the inverse relationship between gel content and shrinkage.

thickness. Results reported are based on calibration standards of vinyltrimethoxysilane (VTMS) and vinyltriethoxysilane (VTES), and are believed to be accurate within ±6%.

RESULTS AND DISCUSSION

Initially, wires were made by grafting different levels of VTES by varying the peroxide content of the mixture while keeping the starting VTES level at a constant value. An additional wire sample was also prepared using VTMS instead of VTES. Table I shows the silane graft level measured by FTIR for all these samples.
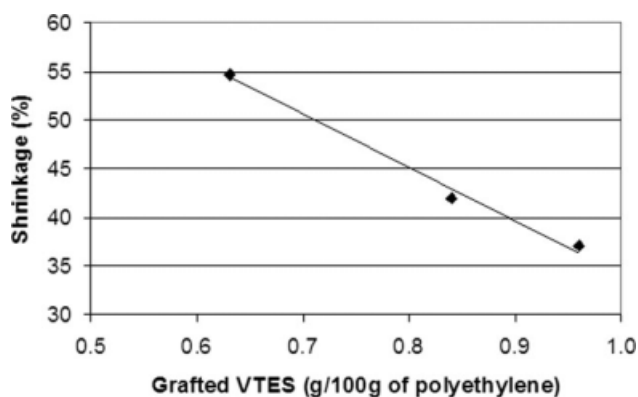
The insulated wires were then cured for different times in a water bath at 90°C, and gel contents were measured as a function of cure time for each sample. Cured and uncured samples were also annealed in a 152°C oven for 10 min, and then measured for shrinkage after cooling. The shrinkage was calculated as

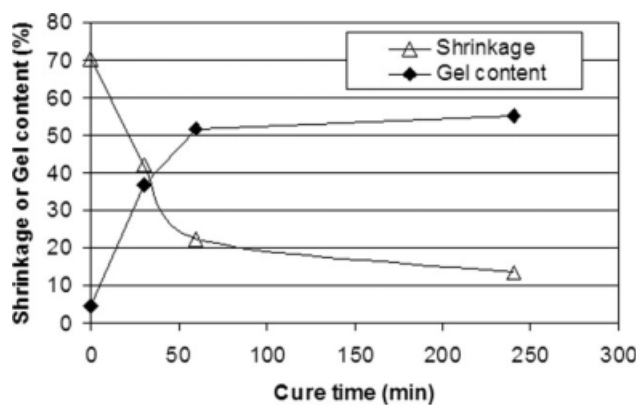$$Shrinkage\% = \frac{L_O - L_f}{L_O} \times 100$$

where L_o is the original postextrusion length of the insulation, and L_f is the final length after cooling postannealing.

Figure 1 shows the percent shrinkage as a function of cure time for VTES-1 and VTES-3, including uncured specimens that were not subjected to the water bath curing step (i.e. cure time = 0 minutes).

The observed shrinkage of up to 80% in these LLDPE insulation compounds is indicative of high levels of orientation. The polymeric melt as it passes through the die undergoes stress-induced deformation, and the increase in stored energy caused by this deformation is partially frozen as the insulation is cooled by water at the outer surface and by contact with cold conductor at the inner surface. The stored energy is relieved
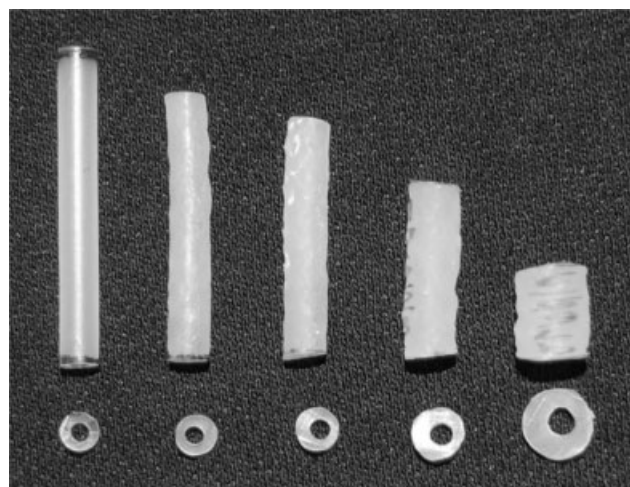

Figure 2 Shrinkage of insulation during annealing vs. VTES grafting level; all samples cured in 90°C water bath for 30 minutes.
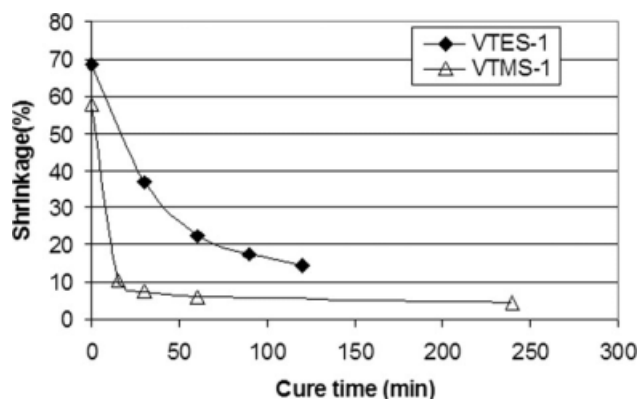
Figure 4 Shrinkage vs. cure time for VTES and VTMS-grafted LLDPE; level of grafted vinyltrialkoxysilane is around 5×10^{-3} mole/100g in both specimens.

Figure 5 Pictures of VTES-2 at various stages of curing and annealing, from left: (a) extruded and stripped of conductor, (b) cured for 240 min and annealed, (c) cured for 60 min and annealed, (d) cured for 30 min and annealed, (e) uncured and annealed.

(relaxation) when temperature of the polymer is subsequently increased above its melting point during annealing, resulting in shrinkage of the polymer in a direction parallel to orientation. In this study, clearly the moisture crosslinking was carried out after the orientation was frozen in the fabricated cable, and that too at a temperature of 90°C, which is below the melting point of the polymer. Thus, the decrease in shrinkage as a function of increasing cure time is attributed to the fact that crosslinking at lower temperature fastens the polymer chains with one another and results in partial fixation of the frozen stress, thus reducing subsequent shrinkage during annealing. The extent of this fixation of built up stress by crosslinking is evident in Figure 1, with the extent of shrinkage decreasing with higher cure times and with higher silane graft level. The slightly lower percent shrinkage for VTES-1 compared to VTES-3 at time zero in Figure 1 is believed to be due to small amounts of cure from ambient moisture in the specimens during handling and storage, which is expected to occur to

a greater extent in the specimen with higher amount of grafted silane (VTES-1).

As the samples differ in VTES grafting level, the crosslinking density is also expected to vary between samples for a given cure time. As shown in Figure 2, percent shrinkage decreases with increasing VTES graft level for VTES-1, VTES-2, and VTES-3 cured in the 90°C water bath for 30 min, further illustrating the effect of higher degree of crosslinking on the ability to prevent shrinkage upon heating beyond the polymer melting point. Figure 3 shows the relationship between shrinkage, gel content, and cure time for VTES-2. As gel content is a direct measurement of cross-linked network density in a polymer, the data in Figure 3 again demonstrates the role of cross-linked network in counteracting the relaxation behavior of oriented chains.

Figure 4 shows shrinkage data for VTES-1 and VTMS-1, which have comparable effective graft levels of $\sim 5 \times 10^{-3}$ mole of vinyl trialkoxysilane per 100 g of material. Consistent with an expected slower cure rate for VTES-grafted LLDPE compared to VTMS-grafted LLDPE due to increased steric hindrance of the triethoxy versus the trimethoxy silane group, shrinkage is higher for VTES-1 than VTMS-1 at any given cure time. The sharp drop in shrinkage within 30 min of cure and then flattening of the curve suggests that most of the maximum achievable curing is completed in a very short time for VTMS-grafted polyethylene.

Figure 5 shows the appearance of various VTES-2 specimens as they progress through the shrinkage process. Qualitatively, it is evident in the picture that as the length shrinks the other dimensions increase. Generally speaking, both inner and outer diameters of samples increase upon shrinkage, with the latter increasing to a greater extent as insulation thickened with a reduction in length. The length, outer diameter and thickness of these shrunk specimens were measured and the average values are shown in Table II. Volumes calculated from these data reveal that overall volume changes due to annealing lie in the range of −6.2 to 0.2% with no particular trend seen with increasing cure.

TABLE II
Average Values for Length, Outer Diameter, and Thickness for Annealed Insulation Samples Cured for Different Times in a 90°C Water Bath; Volume Changes Are Relative to Unannealed and Uncured Samples

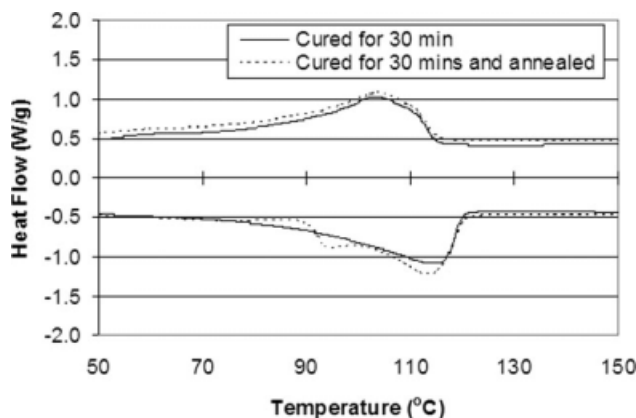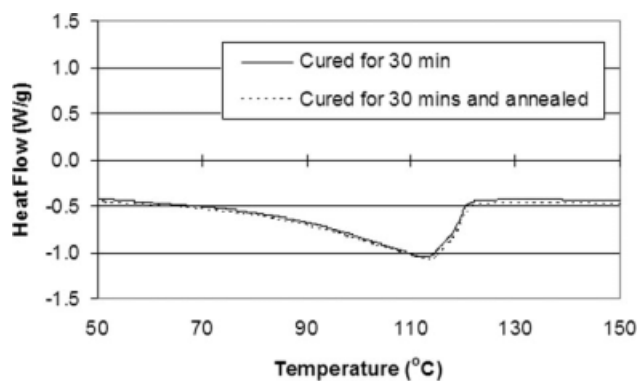|	Uncured and unannealed	Cured for 240 min and annealed	Cured for 60 min and annealed	Cured for 30 min and annealed	Cured for 0 min and annealed
Length (mm)	25.4	22.0	19.8	14.8	7.50
OD (mm)	3.24	3.33	3.56	4.14	5.57
Thickness (mm)	0.90	0.97	1.03	1.24	1.81
Volume change (%)	0.0	−6.2	−4.1	0.2	−4.8
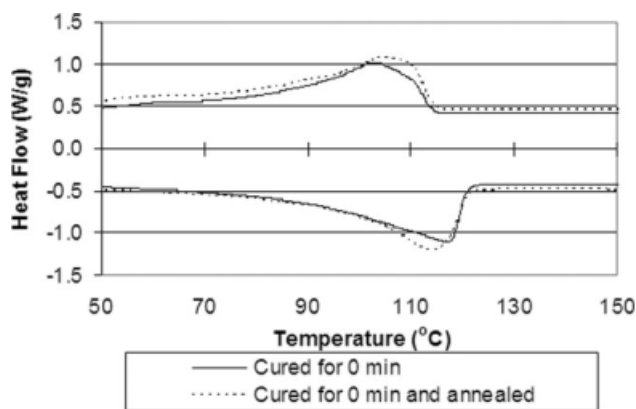
Figure 6 DSC heat-flow curves during 1st heat and cool for uncured wire insulation samples of VTES-2, before and after annealing.

Measuring the density of the samples also showed insignificant differences, which were within the experimental variation of the test employed. Therefore, no firm conclusion on the effect of shrinkage on insulation density can be made from these results other than to say that no large changes in overall density occurred upon shrinkage. Thermal characterization of these specimens by DSC, discussed below, provides additional information pertaining to density changes (deduced from differences in crystallinity).

DSC was obtained on uncured samples as is (no annealing) and after annealing, as shown in Figure 6 for VTES-2. Enthalpy changes for melting from the first heat on these uncured/unannealed and uncured/annealed samples are 73 and 95 J/g, respectively. The higher crystallinity in the annealed (less oriented) sample is consistent with observations by Narkis et al. in uncrosslinked silane-grafted HDPE,[8] but is contrary to the general trend in oriented PE that increased chain alignment results in
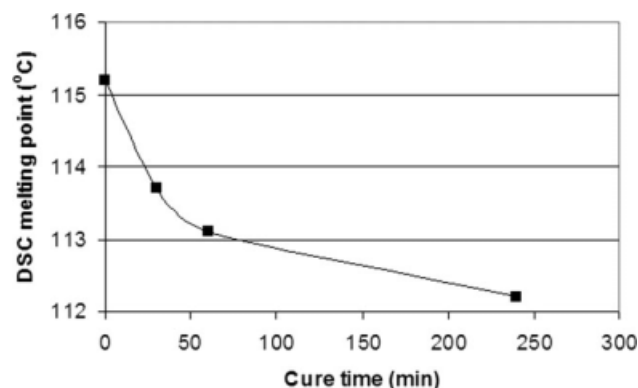
an increase in crystallinity due to a decrease in energy barrier to crystallization.[10] In addition to generally having a positive effect on crystallinity, increased orientation generally increases average crystallite thickness and melting temperature.[10]

For cured samples (30 minutes at 90°C), the results are more interesting. The cured/annealed sample shows a second peak around 95°C in the first heat after annealing (Fig. 7). In fact, all of the cured/annealed samples (cured for 30, 60, and 240 minutes) show this second peak in the DSC on the first heat after annealing. The smaller peak probably points to small or imperfect crystals formed by partial crystallization of the crosslinked domains or smaller crystallites resulting from the presence of crosslinks throughout the specimen when crystallization happens after annealing.[11] In the first heat of the unannealed crosslinked samples, such domains may not yet exist since crystallization occurred before crosslinking. Interestingly, evidence for this distinct second peak around 95°C was not present in the second heat after annealing, perhaps becoming obscured by peak broadening resulting in inability to discern a distinct peak or shoulder in the second

Figure 8 DSC 2nd heat curves for 30min-cured VTES-2 sample before and after annealing.

Figure 7 DSC curves showing a low-temperature shoulder for the 1st heat for cured/annealed sample of VTES-2 samples.

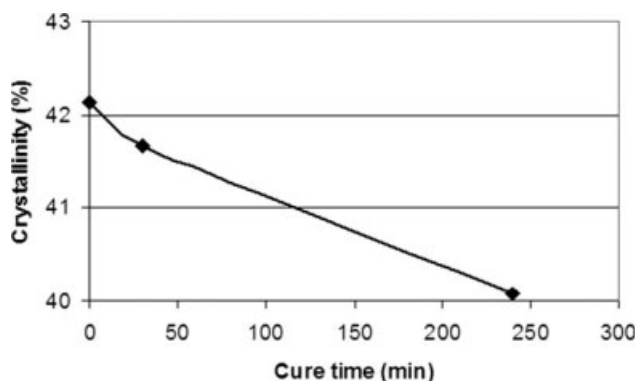**Figure 9** Peak melting temperature obtained during DSC 2nd heat vs. cure time for VTES-2 annealed samples.

Figure 10 Crystallinity calculated from DSC 2nd heat curves vs. cure time for VTES-2 annealed samples.

heat (Fig. 8). The heat of melting (first heat after annealing) for the 30 minute cured/annealed sample is calculated as 91 J/g, which is less than 95 J/g for the uncured/annealed sample, as shown in Figure 7, consistent with a reduction in the number of crystallites that can form upon cooling after annealing due to the presence of crosslinks. The 30 minute cured/unannealed sample shows a heat of melting (first heat) of 73 J/g, the same as seen in the uncured sample and consistent with the previously-mentioned reduction of crystallinity due to orientation seen in the uncured sample.

Heat of melting data are subject to some errors originating from subjective consideration of a less-than-perfect baseline. This was more of an issue for the second heat in the current study. However, the second heat data are significant in the sense that they reveal the true differences between samples after previous heat history is erased by the first heat. From the second heat after annealing data we can see a slight drop in the peak melting temperature and total crystallinity with increase in cure (Figs. 9 and 10). This is again consistent with the previous observation that crosslinking causes slight disruptions in the ability of the polymer to form crystals, which decreases the average crystallite size.

Theoretical interpretation of all of the aforementioned DSC data is not straightforward due to the large number of factors, including the fact that some peroxide and/or silane crosslinking occurs in the melt during grafting and before orientation (in addition to the intended silane crosslinking after orientation and cooling). It is expected based on theoretical considerations that crosslinking oriented chains results in increase in melting temperature whereas crosslinking of unoriented chains should decrease the melting point.[4,12] In many types of specimens, it is expected that both of these effects can come into play, since rarely will a specimen undergoing crosslinking contain only oriented chains. Irradiation crosslinking in oriented HDPE was found experimentally to increase the percent crystallinity.[6] A different study in peroxide crosslinked HDPE reported that the crosslinking resulted (before stretching) in a shift in both melting and crystallization temperatures to lower values, accompanied by decreased enthalpy of transition; stretching the crosslinked HDPE at 90°C and 140°C increased the percent crystallinity.[5] Silane crosslinking of melt oriented (injection molded) specimens below the melting point resulted in a decrease of melting point and enthalpy of crystallization (second heat) compared to uncrosslinked specimens.[8] In another study, irradiation crosslinking was found to decrease crystallinity in oriented LLDPE after heat shrinking.[11] Additional work is needed to further understand the DSC results in the present systems.

Previous results show that for the same wire construction size and same level of alkoxysilane grafted (Fig. 4), the speed of curing is faster for VTMS-grafted resin than its VTES-grafted counterpart, as evidenced by the rapid and drastic drop in shrinkage% vs. cure time for the former. Since the level of grafting is equivalent for the two cases, it is expected that at long cure time, the shrinkage for the VTES grafted material will also reach a value of less than 10%. On the other hand, it can also be shown that for a given VTMS graft level, the final value of shrinkage at longer cure times will vary depending on the amount of stress frozen during the cooling of the cable. To demonstrate this effect, wires of three construction sizes were made with a formulation containing VTMS and Luperox-101 (1 wt % VTMS added, 800 ppm L-101 added, 0.8% VTMS grafted). The residence times in the extruder were kept constant by maintaining the extruder RPM at a fixed

TABLE III
Outer and Inner Surface Area to Volume Ratio for Different Construction Sizes

Insulation thickness (mm)	Conductor type	Conductor dia(mm)	Outer surface area/volume (cm^{-1})	Inner surface area/volume (cm^{-1})
0.23	18 AWG/19 strands Cu	1.2	50.9	36.6
0.48	18 AWG/19 strands Cu	1.2	26.8	14.7
0.76	14 AWG Cu	1.6	17.3	8.9
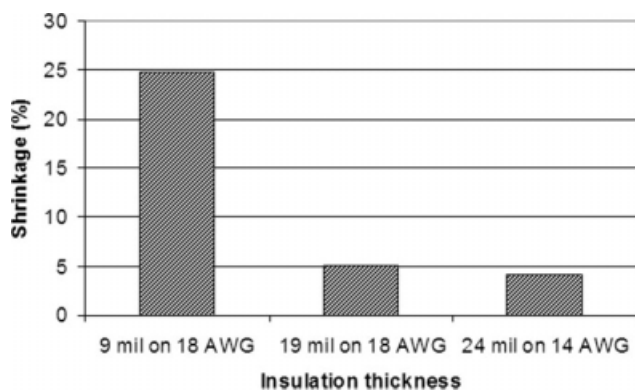
Figure 11 Level of shrinkage at full cure for wire construction varying in insulation thickness and conductor sizes.

setting which was to ensure similar level of grafting for all the three cases. Different insulation thicknesses were arrived at by varying the line speed of the polymer-coated conductor through the die. This was expected to lead to varying resulting stresses which would in turn produce different degree of molecular orientation in the coating. Also, it is expected that for the thinner insulations, a greater degree of orientation will be frozen as it will be cooled much faster than a relatively thicker insulation. In other words, cooling resulting from water at the outer surface and from cold copper conductor at the inner surface will be much more efficient for the thinner insulations due to its high surface area to volume ratio. Table III lists the critical external and internal surface area to volume ratio for the three constructions.

Unfortunately, due to high sensitivity of VTMS-grafted polyethylene to crosslinking from moisture in air, shrinkage values for noncrosslinked conditions could not be obtained for all the wire samples. Therefore, the shrinkage values were measured only at the full cure conditions. Figure 11 shows the shrinkage numbers after four hours of water-bath curing for the three insulation sizes, at which point all the VTMS-grafted samples are expected to be fullly cured for the given graft level. The data reveal that the thinnest insulation still exhibits a high level of shrinkage, indicating that the cross-linked network formed after curing can not prevent the high degree of orientation from relaxing during the shrinkage test. However, the difference between the other two construction sizes is not significant at this cure level, possibly suggesting that the stresses built up during orientation have been immobilized by the extent of crosslinking masking any differences among them.

Liu and Harrison[3] similarly studied contraction for LDPE films as a function of film thickness using films which were made by varying the speed of the take up rolls. They also observed an inverse relationship between contraction and film thickness.

CONCLUSION

Un-crosslinked wire insulation underwent shrinkage by up to about 80% when annealed above the melting point of the polymer. Moisture crosslinking below the melting point was able to reduce the shrinkage level to about 10%, with the degree of reduction being proportional to the amount of crosslinking. Shrinkage parallel to the direction of orientation was accompanied by swelling in the other dimensions.

DSC revealed several trends, including a decrease in melting point and degree of crystallinity with increasing crosslinking. In the first heat after annealing, crosslinked samples exhibited a shoulder in the DSC endotherm several degrees below the normal melting point of the LLDPE. Contrary to some general trends in the literature, but consistent with prior studies in silane-grafted HDPE, relaxation of orientation by annealing resulted in an increase in the enthalpy of melting.

The degree of shrinkage was also found to be dependent on the insulation thickness, which is attributed to faster cooling in thinner insulation.

The results highlight the extensive built in stresses that can be frozen into polymer layers in fabricated articles due to melt orientation and the need to account for the phenomenon during material and process design.

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