

The effect of crosslinking and thermal ageing on the morphology of ethylene-vinyltrimethoxysilane copolymer

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Abstract: This paper investigates the behavior and property evolution of silane crosslinked polyethylene upon thermal ageing in oven at two different temperatures. It was investigated the influence of crosslinking catalyst, thermal stabilizer and temperature on the chemical structure, morphology by differential scanning calorimetry and fourier transform infrared spectroscopy. It was found that two parallel processes influence the final properties: crosslinking reactions and improvement of crystalline order. These two processes play different role depending either an ageing proceed below melting temperature or above melting temperature.

Key-Words: Ethylene-vinyl silane copolymer, Moisture crosslinking, Thermal ageing, Fourier transform infrared spectroscopy, Differential scanning calorimetry

1 Introduction

Polyethylene (PE) is one of the most produced polymers in the world and it is used for a wide range of applications. Thermoplastic character with rather low melting temperature limits its use in many applications. In this respect, molecular crosslinking enables to reach better properties such as heat deformation resistance, resistance to crack propagation, abrasion, weather resistance or shape memory [1].

The first crosslinked PE was prepared in the late 1930s via electron irradiation. Later, the crosslinking process was perfected by using peroxide as a crosslinking agent. The other discovered methods include a grafting of silane compounds onto polymer chains because these silane compounds are capable of crosslinking by reaction with water. These two patented methods – Sioplas and Monosil – still require small amount of peroxide for grafting and thus chemical reactions of radicals must take place before crosslinking reactions. Crosslinking then proceed through two reaction steps: hydrolysis and condensation (Fig. 1) [2]. However, a formation of radicals often causes many issues during processing of polymer and thus deterioration of final products due to rapid reaction kinetics of radicals and macroradicals. For this reason, Mitsubishi P.C. in 1978 developed ethylene-vinyl silane (EVS) copolymer crosslinkable by moisture but it does

not require peroxide for grafting of silane compounds and thus radical reactions does not take place, which is significant in term of stability and processing [3-5].

It is necessary to note that despite of crosslinking mechanism, creation of crosslinks has a significant impact on morphology of semicrystalline polymers. First at all, it is important to recognize whether crosslinking proceeds in molten state or in the solid state. Above melting point, a distribution of crosslinks is homogenous because a polymer melt is completely amorphous. By contrast, heterogeneous distribution of crosslink is not unusual for semicrystalline polymers in solid state [6, 7].

A study of crosslinking and thermal ageing is important not only due to oxidation of material but also due to significant morphological evolution observable mainly for semicrystalline polymers. This evolution during long-term thermal ageing has not been investigated yet properly for relatively new ethylene-vinyl silane (EVS) copolymer. It can be expected that phenomena, such as further crosslinking, oxidation and recrystallization, may occur and thus it was chosen several methods for investigation. Thus, present paper focuses on joint changes in molecular and supermolecular structure of EVS copolymers upon crosslinking in water bath and subsequent thermal

ageing at the temperatures below and above the melting temperature of polymer.

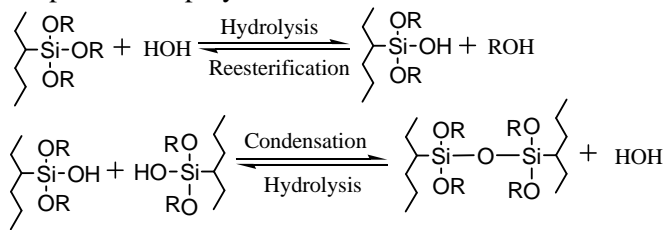


Fig. 1: Crosslinking reactions of EVS copolymer

2 Experimental

A commercial ethylene-vinyl trimethoxysilane (EVS) copolymer supplied by Borealis AB, Stenungsund, Sweden was used. One part of EVS copolymer was blended with catalyst masterbatch (EVS-C) also supplied by Borealis AB and second part was without of this catalyst masterbatch (EVS-0).

Density of the blend is 923 kg/m^3 and MFI is 1.0 g/10 min ($190 \text{ }^\circ\text{C}$, 2.16 kg). A catalyst masterbatch contains other additives such as antioxidant, metal deactivator, drying agent and permanent scorch retardant.

The blend was extruded using a Brabender extruder with temperature setting of $120 \text{ }^\circ\text{C}$, $135 \text{ }^\circ\text{C}$, $165 \text{ }^\circ\text{C}$ and $165 \text{ }^\circ\text{C}$ and rotation speed 20 rpm . Approx. 2 mm thick tape was cut out to the pieces and subsequently crosslinked in the water bath at $90 \text{ }^\circ\text{C}$ for 4 hours.

After crosslinking, the samples were aged in an oven with airflow at two temperatures, $90 \text{ }^\circ\text{C}$ and $135 \text{ }^\circ\text{C}$. Then, the samples were collected successively from the oven after 0, 24, 240 or 480 hours of ageing.

The melting behavior of the samples was subsequently analyzed by PerkinElmer Pyris-1 differential scanning calorimeter (DSC). The used thermal regime consisted of one thermal scan from $0 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$. Scanning rate was $10 \text{ }^\circ\text{C/min}$.

Fourier transform Infrared spectroscopy (FTIR) was carried on a Perkin-Elmer FTIR-system 2000 with a resolution of 4 cm^{-1} . The range of scans was from 580 to 4000 cm^{-1} . Absorbance spectra were obtained at 32 scan summations from $50 \text{ }\mu\text{m}$ thin cross-sections cut out using microtome from the extruded tape.

3 Results and Discussion

3.1 Fourier transform infrared spectroscopy

Fourier transformation infrared analysis (FTIR) enables to follow the chemical evolution of material during

crosslinking and ageing, i.e. degree of crosslinking and thermo-oxidative reactions.

Characteristic bands for silane groups are in the area from approx. 1200 cm^{-1} to 750 cm^{-1} , namely: Si-OCH₃ at 1190 cm^{-1} , 1095 cm^{-1} , 795 cm^{-1} ; Si-O-Si at 1065 cm^{-1} and $1015\text{-}1020 \text{ cm}^{-1}$. According to the Fig. 1 it is clear that the absorbances of methoxy bands (Si-OCH₃) should decrease, whereas the absorbances of siloxane bands (Si-O-Si) should increase during the crosslinking and/or ageing in the presence of moisture. Characteristic band associated with thermo-oxidative reactions is around $1745\text{-}1715 \text{ cm}^{-1}$ of wavenumber (carbonyl region).

Fig. 2 shows FTIR spectra of EVS-0 material at different stages of ageing, focused on the regions of carbonyl and silane bands. A spectrum of non-crosslinked sample is very similar to a spectrum of crosslinked and non-aged sample. Because this material does not contain a catalyst masterbatch, the crosslinking reactions proceed very slowly in water bath at $90 \text{ }^\circ\text{C}$. There is visible only small peak at approx. 1050 cm^{-1} related with siloxane band. Spectra of other samples aged in oven at $90 \text{ }^\circ\text{C}$ up to 240 hours are basically identical with non-aged sample (they are not in figure). The peaks in carbonyl region remain also constant. Dramatic changes occur when the material is aged at $135 \text{ }^\circ\text{C}$. Decrease of peaks at 1190 , 1095 and 795 cm^{-1} and developing of peaks at approx. 1065 and 1015 cm^{-1} suggests that crosslinking proceed rapidly at this temperature of ageing.

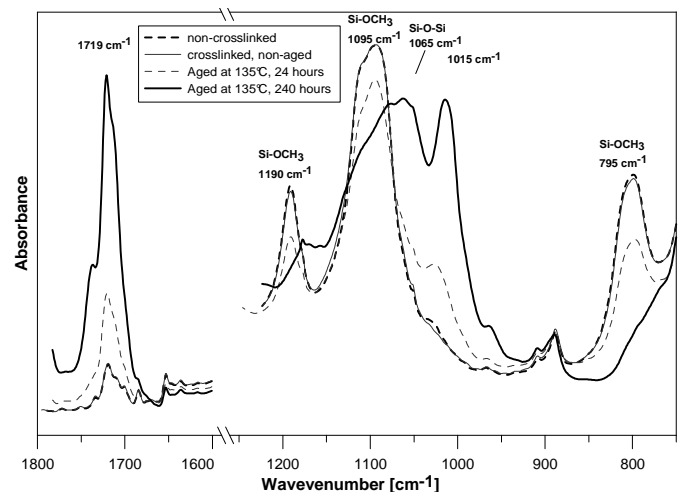


Fig. 2: FTIR spectra of EVS-0 non-crosslinked, crosslinked and/or aged samples.

A peak at carbonyl region (1719 cm^{-1}) also dramatically rises during ageing at $135 \text{ }^\circ\text{C}$. It is due to absence of antioxidant, which is involved only in the catalyst masterbatch, and thus EVS-0 considerably degraded at this temperature. Furthermore, it can not be excluded that the carbonyl and/or other acid groups,

created due to the molecular degradation, can catalyze crosslinking reactions and thus the elevated temperature must not be the only factor influencing the crosslinking reactions.

Fig. 3 shows spectra of EVS-C material aged up to 480 hours. This material contains catalyst masterbatch and it can be assumed that crosslinking reactions proceed with appreciable rate in water bath as well as during ageing in the oven. This process can be clearly seen and the evolution of peaks associated to silane groups occurs at 90 °C and at 135 °C in oven. It should be noted that the crosslinking at 135 °C could proceed still to a higher extent as can be derived from higher decline of methoxy peaks especially at 1095 cm⁻¹ and 795 cm⁻¹ and, reversely, higher increase of siloxane peak at 1065 cm⁻¹.

The peak in carbonyl region is considerably higher even for non-crosslinked samples being related to the catalyst composition. On the other hand, this peak remains constant during the crosslinking and ageing. It can be thus assumed that the possibility of degradation of material followed by the evolution of the carbonyl groups can be completely excluded.

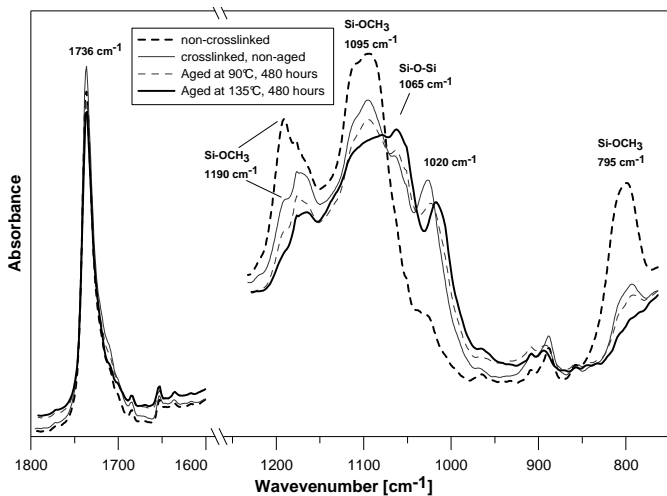


Fig. 3: FTIR spectra of EVS-C non-crosslinked, crosslinked and/or aged samples.

3.2 Differential scanning calorimetry

Differential scanning calorimetry has been applied to observe the overall thermal behavior, as the chemical reactions such as molecular degradation and crosslinking at elevated temperature influence crystallization of polymers and morphology then closely relates with mechanical properties.

Fig. 4 shows thermograms of the EVS-0 aged at 90 °C and at 135 °C. First heating scans, in this case, relate with a melting of initial morphology which reflects the final mechanical properties.

The samples aged at 90 °C exhibit completely different thermal behavior as compared to those aged at 135 °C. A melting temperature of non-aged samples (0 hours) subtracted from the highest peak is approx. 111 °C. A secondary peak at approx. 99 °C relates to recrystallization (lamellar thickening) due to annealing at 90 °C in water bath, when thermodynamic conditions allow an extensive morphology improvement. If the samples are subsequently aged at 90 °C (the same temperature) in the air, both temperatures of the main and also secondary peaks slightly increase due to further lamellar thickening.

The scans of samples aged at 135 °C (Fig. 4, right) exhibit completely different evolution. The thermograms show only single peak due to melting of initial morphology before first heating on DSC since the ageing proceeds at higher temperature than melting temperature of material (approx. 110°C). However, the crosslinking and degradation, which significantly occur at 135 °C, have a significant influence on crystallisability and morphology. Chemical changes and chain scission of molecules during degradation as well as introduction of crosslinks (molecular heterogeneities) cause a significant decrease of crystallization temperature; also the melting peak after subsequent heating show significant peak-broadening and melting temperature decrease.

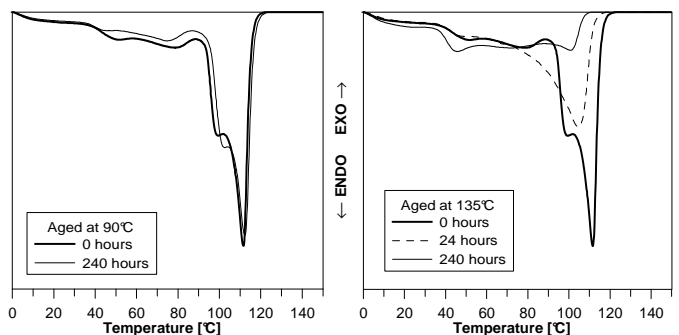


Fig. 4: DSC scans of crosslinked EVS-0 aged at 90 °C (left) and at 135 °C (right).

In Fig. 5, DSC scans can be seen for EVS-C material. Because this material contains a catalyst masterbatch with antioxidant, it can be expected that crosslinking plays a more significant role; it should be also considered that any degradation do not occur during ageing even at 135 °C. However, heating scans of samples aged at 90 °C are very similar to the scans of EVS-0 material. As can be seen, the lamellar thickening occurs also in this case and melting temperature and temperature of secondary peak rises.

Ageing of EVS-C at 135 °C caused remelting of material and, of course, higher extent of further crosslinking. Thus, DSC scans exhibit only single

melting peak. A melting temperature as well as a heat of fusion decrease in comparison to the non-aged samples.

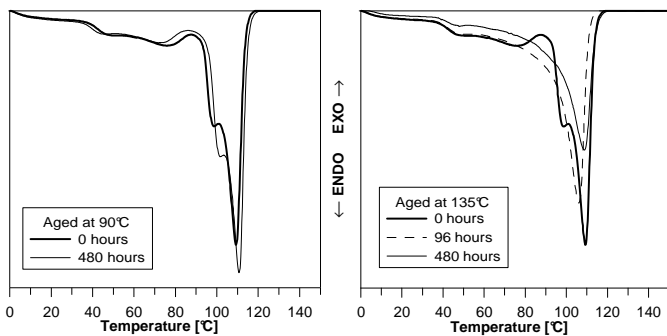


Fig. 5: DSC scans of crosslinked EVS-C aged at 90 °C (left) and at 135 °C (right).

4 Conclusion

The work demonstrates that several phenomena influence final morphology of the moisture crosslinked ethylene-vinyltrimethoxysilane copolymer.

A crosslinking catalyst significantly increases reaction rate and make it industrially useful; the crosslinks can consequently influence the crystalline order; this effect is further dependent on ageing conditions. Degradation process, followed by the carbonyl by-product evolution, has a considerable influence on crystallisability and subsequent morphology, especially if it occurs above the melting temperature. Furthermore, by-products of degradation can successively catalyze the crosslinking reactions. This was observed in EVS copolymer without crosslinking catalyst and stabilizers.

DSC measurement proved that ageing below melting temperature causes crystalline improvement, while ageing above melting temperature causes a remelting of initial morphology and a reduction of the crystalline order.

It was proved that the effect of thermal ageing and crosslinking on the final structural properties is not predictable easily in the case of semicrystalline EVS copolymer which is capable to crosslink even at room temperature. Since this copolymer crosslinks in the presence of moisture, the real impact of thermal ageing becomes more complicated.

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