

# Crosslinking and Ageing of Ethylene-Vinyl Silane Copolymer in Water Bath

Petra Trňáčková<sup>a</sup>, Miroslav Pastorek<sup>a, b</sup>, Roman Čermák<sup>a, b</sup>, Martina Polášková<sup>a, b</sup>

<sup>a</sup>*Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlín,  
nám. T. G. Masaryka 275, 762 72 Zlín, Czech Republic*

<sup>b</sup>*Centre of Polymer Systems, University Institute, Tomas Bata University in Zlín,  
nám. T. G. Masaryka 5555, 760 01 Zlín, Czech Republic*

**Abstract.** The paper focuses on chemical and morphological changes of ethylene-vinyl silane copolymer upon exposure to hot water. Within processing, the exposure to hot water is the final step causing crosslinking and stabilization of material against high temperatures, which can occur in application to wire insulation. For these purposes, commercially available copolymer and catalytic system have been used. A strong effect of catalytic system on kinetics of crosslinking and subsequently ageing was observed. Chemical evolution was followed by infrared spectroscopy and differential scanning calorimetry was involved for evaluation of morphological changes.

**Keywords:** ethylene-vinyl silane copolymer, ageing, hot water, infrared spectroscopy, differential scanning calorimetry  
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## INTRODUCTION

Polyethylene (PE) is beside polyvinylchloride (PVC) one of the most frequently applied polymer in wire insulations. In 1950, it has been introduced for electrical and transmission cables, followed by underground applications. In comparison with PVC, PE is less thermally stable and flame resistant. Fortunately, these properties can be improved by crosslinking [1].

Crosslinking causes intermolecular chemical bonding of polyethylene chains. As a consequence, the material exhibits common behavior of thermoplastics below its melting temperature ( $T_m$ ), and rubber viscoelasticity above  $T_m$ . PE possesses no functional groups which would provide the possibility of crosslinking, therefore, a specific approach has to be employed to achieve network structure [2, 3]. The saturated structure of PE can be crosslinked by peroxides, high-energy irradiation and silane group incorporation.

For silane-assisted crosslinking of PE, presence of water is an important prerequisite. In the first step, the silane groups are hydrolyzed. Then, the silanol groups can condense creating siloxane linkages between the polymer chains. These reactions proceed in both, the melt and solid state. The significant improvement of crosslinking homogeneity in silane-modified polyethylene can be achieved by the addition of catalytic systems [4, 5].

In the industry scale, the crosslinking of silane-modified PE is rather performed in 90 °C hot water bath. At such conditions the material is in close vicinity to its  $T_m$  and not only chemical but also morphological changes can be expected [6].

The present work focuses on the effect of catalytic system and exposure to hot water on crosslinking and ageing of ethylene-vinyl silane copolymer. For these purposes, neat and catalyzed materials have been exposed to 90 °C hot water for 0-720 hours. Changes in molecular structure and morphology were determined by a combination of experimental methods.

## MATERIAL AND METHODS

Ethylene-vinyl silane copolymer LE 4423 (EVS) was used in this work. The material is produced within high-pressure VISICO method and was catalyzed by 5 wt. % of AMBICAT LE 4476 catalytic master batch (CS) supplied by Borealis AB.

Neat EVS and catalyzed (EVS+CS) were extruded in strip form using a Brabender extruder. The extruded strip was cut to pieces. The strips were placed in a bath with distilled water for 0-30 days at 90 °C and taken at certain time intervals to be analyzed.

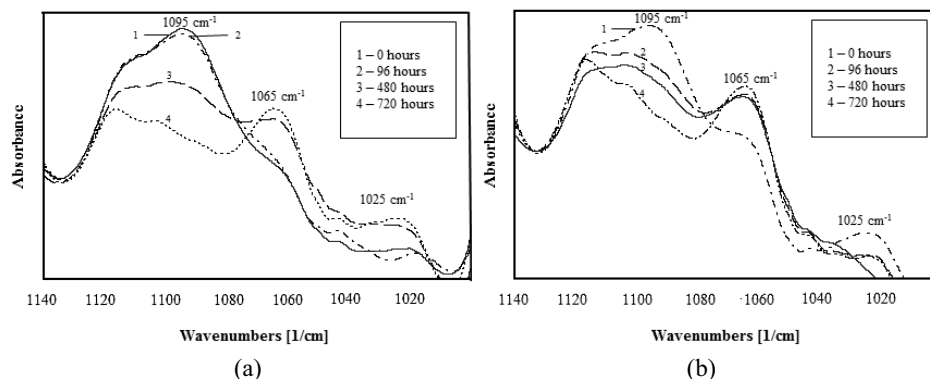
To measure infrared transmission spectra of the 100  $\mu\text{m}$  thick samples, the equipment FTIR AVATAR 320 NICOLET with a resolution 2  $\text{cm}^{-1}$  was used. The measured range was from 4000  $\text{cm}^{-1}$  to 550  $\text{cm}^{-1}$  and number of scans was 32.

All the samples were analyzed by differential scanning calorimeter (Perkin Elmer Pyris – 1 instrument). The measurements were carried out in a nitrogen atmosphere. The specimens were cut out from the extruded tapes and loaded into standard aluminum pans.

The following temperature mode was used: 1<sup>st</sup> heating 40 °C – 120 °C, cooling 120 °C – 40 °C, 2<sup>nd</sup> heating 40 °C – 120 °C. In all the cases heating/cooling rate was 10 °C/min.

## RESULTS AND DISCUSSION

Crosslinking of ethylene-vinyl silane copolymer can be monitored by infrared spectroscopy. Within this process, characteristic peaks of the methoxy groups ( $\text{Si-O-CH}_3$ ) decrease as a consequence of water hydrolysis. On the other hand, an increase of the characteristic peaks of siloxane groups ( $\text{Si-O-Si}$ ) can be seen due to condensation. In Figure 1, a gradual decrease of peak intensity at 1095  $\text{cm}^{-1}$  ( $\text{Si-O-CH}_3$ ) and an increase of peaks at 1065  $\text{cm}^{-1}$  and 1025  $\text{cm}^{-1}$  ( $\text{Si-O-Si}$ ) reflect the crosslinking. As shown in Figure 1a, the kinetics of crosslinking reaction in neat EVS is rather slow; the equilibrium stage is achieved after 480 hours exposure to hot water. A significant effect of catalytic system on crosslinking kinetics is demonstrated in Figure 1b; EVS+CS reached the saturated level after 96 hours and following hot water exposure did not cause any significant chemical changes.



**FIGURE 1.** Infrared spectra of (a) EVS and (b) EVS+CS upon exposure to hot water

Differential scanning calorimetry allows monitoring of changes in the morphology induced by the exposure to hot water. Figure 2 shows the endothermic curves of 1<sup>st</sup> heating of EVS and EVS+CS reflecting the melting of supermolecular structure originated from processing and subsequent hot water exposure. It is seen that both materials exhibit only one melting peak immediately after processing. Upon exposure to hot water, an evolution of melting peak at 97 °C can be detected. With further exposure,  $T_m$  peak moves towards higher temperatures. This demonstrates partial recrystallization and further improvement of supermolecular structure due to exposure to temperature (90 °C) close to the  $T_m$  of materials.

In Figure 3, the thermograms of 2<sup>nd</sup> heating of EVS and EVS+CS are shown. In fact, these curves show the crystallizability and subsequent thermodynamic stability of crystallites upon crosslinking in hot water. In both cases, only one melting peak is detected. Upon the hot water exposure, the  $T_m$  gradually changes from 108 to 104 °C. It is interesting to note that the lower  $T_m$  limit (104 °C) is reached in both materials at the exposure time which corresponds to saturation time of crosslinking evaluated from infrared spectroscopy (480 hours for EVS and 96 hours for EVS+CS).

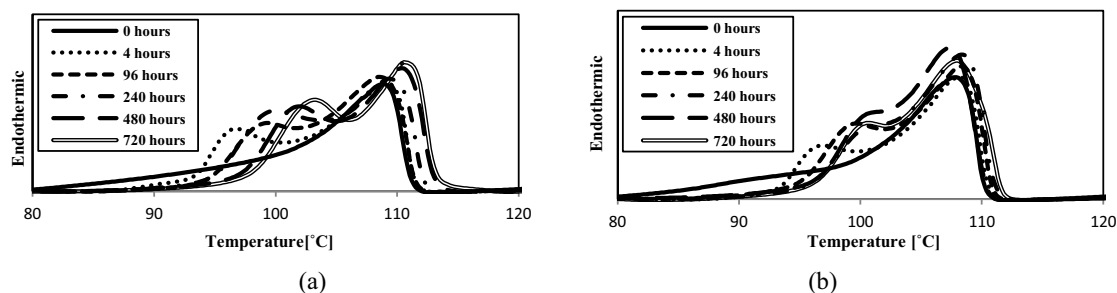


FIGURE 2. DSC thermograms of endothermic curves of 1<sup>st</sup> heating upon hot water exposure: (a) EVS, (b) EVS+CS

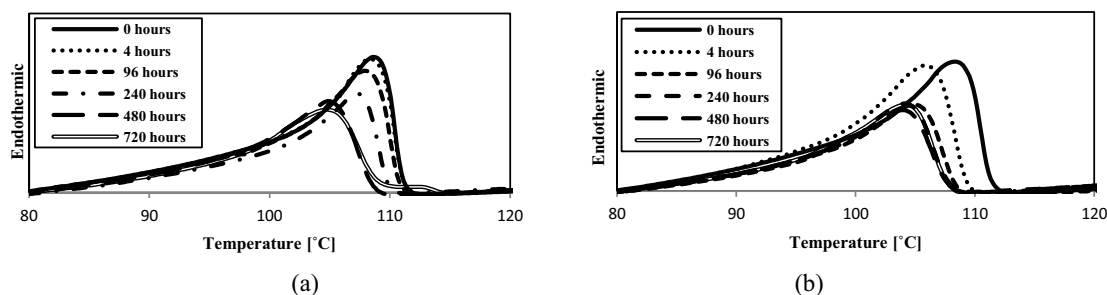


FIGURE 3. DSC thermograms of endothermic curves of 2<sup>nd</sup> heating upon hot water exposure: (a) EVS, (b) EVS+CS

## CONCLUSION

The aim of this work was to determine the effects of catalytic system and exposure to hot water on the evolution of chemical structure and morphology of ethylene-vinyl silane copolymer. It was demonstrated that incorporation of catalytic system dramatically accelerates the crosslinking kinetics of this material. Exposure to hot water causes not only crosslinking of EVS, but also partial recrystallization of amorphous phase reflecting in evolution of the second melting peak in the range of 97-103 °C. It was found that the presence of catalyst masterbatch influenced both crosslinking and ageing. Substantial changes occurred in neat EVS upon the whole exposure to hot water.

## ACKNOWLEDGMENTS

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