

## 8. Summary and Conclusions

This work deals with ESCR of LDPE/EVA compounds in dependence on the test temperature and the EVA content in the blends, their thermal and mechanical properties, morphology, failure behavior and deformation mechanism of selected samples as a function of the EVA content. ESCR experiments were carried out with the final goal to find a solution for the acceleration of the test and to predict the ESC behavior of the blends much faster. The investigations carried out in this work can be employed for a better understanding of the fundamentals of the phenomenon of ESC in the special case of LDPE/EVA compounds. All these results can be taken to develop a criterion for the long-term ESC behavior of the materials used and finally it would be possible to develop a theoretical model for their ESC behavior.

It can be concluded that a strong interplay exists between composition, morphological features and the ESCR behavior of PE/EVA blends. Obtained results demonstrate that EVA containing 28 wt.-% VA is a very effective copolymer for the retardation of ESC in LDPE. Samples containing 8.9 wt.-% EVA always pass the ESCR test at all temperatures up to 1000 h. When the EVA content is 7.1 wt.-% and less, the affinity of polyethylene to ESC can be clearly seen. In most of the cases, cracking starts on both sides in a direction perpendicular to the notch as expected from the finite element calculations. TEM images of PE/EVA-5.4 and PE/EVA-8.9 samples, as received (before the ESCR test), reveal that the size of the EVA particles increases with increasing the EVA content in the blends. It seems that the size of the EVA particles and the interparticle distance govern the ESC process and therefore influence the ESCR behavior of the investigated LDPE/EVA compounds. Blends with 8.9 wt.-% EVA never failed during the ESCR tests in 10 vol.-% Igepal, which can be referred to the higher EVA content and the smaller particle-particle distance compared to the rest of the blends. It is obvious that the 8.9 wt.-% EVA content is enough for prevention of crack initiation and growth in the samples. The higher crack resistance attained through the addition of 8.9 wt.-% EVA is related probably to greater tendency of the blends to relax under stress.

TEM images of PE/EVA-5.4 and PE/EVA-8.9 samples as received show that a few thick crystalline lamellae penetrate into the EVA phase. The growth of lamellae in the EVA phase is probably fed by PE dissolved in the EVA phase due to the partial miscibility of the polymers or by long ethylene sequences in the EVA copolymer capable of crystallization.

For all samples, the time to failure was shorter during the ESCR test at 50°C than at 30, 60 and 70°C. The increase of the time to failure of the samples at 60 and 70°C as compared with that at 50°C might be as a result of melting of the semicrystalline material of

EVA. During the test at 60 and 70°C the system is in the range of the melting temperature of EVA copolymer, and thus the EVA particles are deformed more easily under the influence of stress. TEM images of PE/EVA-5.4 and PE/EVA-8.9 samples annealed at 70°C during the ESCR test show that the EVA particles are deformed and stretched in direction of bending of the samples which prevents crack initiation and growth.

Different reorganization processes can occur as a result of the long thermal treatment of the samples during the ESCR test. DSC measurements were carried out for investigation of the thermal properties of the samples before and after the ESCR test. DSC traces of the samples taken after the BTT show that a second endothermic peak is generated alongside the main one. The onset of this new peak was observed immediately above the annealing temperature  $T_a$  (the test temperature during the BTT). This second peak reflects the melting of the population of crystallites generated by annealing at  $T_a$  by a partial melting-re-crystallization mechanism.

WAXS investigations were performed for determination of the degree of crystallinity of the samples as received and after 48 h annealing at 50 and 70°C in 10 vol.-% Igepal solution. It was found that the degree of crystallinity does not change significantly after annealing of the PE/EVA samples at 50 and 70°C. We can expect increasing of the degree of crystallinity due to the annealing procedure. But it cannot be detected by WAXS measurements for both annealing temperatures.

SAXS measurements were carried out in order to determine any changes in the crystal structure and lamellae arrangement after the long thermal treatment of PE/EVA-5.4 and PE/EVA-8.9 samples during the BTT at 50 and 70°C. The peak for the long period of LDPE is at about  $0.5 \text{ nm}^{-1}$ . This peak broadens and shoulders appear in the case of annealing at 50°C. Even in the melt, in a  $q$ -range between  $0.1$  and  $0.7 \text{ nm}^{-1}$  some structures could be detected. The scattering at about  $0.33 \text{ nm}^{-1}$  is due to the carbon black particles, whereas the scattering at  $0.79 \text{ nm}^{-1}$  might be due to the EVA phase.

Broken PE lamellae and cavitation inside and around the EVA particles were observed in the case of PE/EVA-5.4 samples which failed the BTT in Igepal at 50°C within 24 h. BTT test was carried out in air at 50°C with PE/EVA-5.4 samples in order to check how the ESC agent influences the morphology. TEM images show that cavities around the EVA particles do not appear in the case of a sample thermally treated in air. Therefore, in the case of ESCR test in Igepal the semicrystalline PE matrix is very quickly attacked by the Igepal solution and this process is faster than the creep deformation of the EVA particles and crack initiation cannot be prevented.

Fracture surfaces of the samples which failed the BTT at 50°C, investigated by SEM, display a transition from flat and visually smooth to fibrous texture with addition of EVA in the blends. Deformed strands coming out from the surface were observed, indicating that the EVA phase makes the material tougher and the failure mechanism tends to be rather ductile than brittle with increasing the EVA content.

Phase structures and micromechanical deformation process were investigated by HVEM. It was established that PE/EVA/carbon black blends deform through shear yielding and a model was suggested representing the deformation mechanism in the blends. It can be concluded that the different annealing temperatures during the BTT do not influence the deformation mechanism in the samples and they deform through shear yielding.

Mechanical properties of PE/EVA samples were investigated at room temperature, 50 and 70°C by using Instron test machine. The results show that the increased temperature reduces the stiffness of the polymer as observed from the decreased Young's modulus. Both Young's modulus and yield stress fell monotonically with increasing temperature.