6. Experimental Part

6.1 Materials and Preparation

Polyethylene blends were prepared using a commercially available low-density polyethylene (LDPE) with a melt flow index of 0.28 g/10 min (ASTM D1238) and a density of 0.920 g/cm$^3$ (ASTM D792) and an EVA random copolymer, having vinyl acetate content of 28 wt.-%. In the following, the LDPE used in the experiments presented here is referred to as PE. The EVA contained 2.5 wt.-% carbon black. PE was blended in an extruder with different contents of EVA (1.8, 3.6, 5.4, 7.1, and 8.9 wt.-% EVA). Blends were compression molded between two rigid metal plates (having an area of 200 mm x 230 mm) at a temperature of 165-170°C and with a maximum force of 200 kN. The details of the molding process are described in the international standard IEC 811-4-1.\[47\] Molded plates were conditioned in an oven at 145°C for 1 h, then cooled down to 30°C. Test specimens with a specific geometry were cut from the plates. The geometry of the test specimen is shown in Figure 6.1. Each specimen was notched to a depth of 0.50-0.65 mm lengthwise using a razor blade fixed in a notching device.

![Figure 6.1 Geometry of the test specimen for the Bell-telephone ESCR test.](image)

Dimensions in millimeters

Depth 0.50-0.65
(the depth must be uniform along its depth)
6.2 Environmental Stress Cracking Resistance Test

The Bell telephone test was performed in order to study the ESCR of LDPE/EVA blends. This is a constant-strain bent-strip test method with Igepal CO-630 as stress cracking agent.\cite{1} The chemical structure of Igepal is shown in Scheme 6.1. Water solution of Igepal was prepared by paddle-stirring the mixture at 60°C to 70°C for at least 1 h.

\[
\begin{align*}
C_9H_{19} & \quad \bigcirc \quad O \quad (CH_2CH_2O)_8 \quad CH_2CH_2OH
\end{align*}
\]

Scheme 6.1 Chemical structure of Igepal CO-630.

Test specimens were bent with the notch pointing upwards in a metal U-shaped specimen holder (Figure 6.2). The holder was placed in a glass tube containing a 10 vol.-% Igepal solution. The tubes were sealed and put in a water bath at 50°C. Failure is defined as the appearance of any crack visible to the naked eye. Five specimens were used for each test.

Figure 6.2 Bent strips in the U-shaped specimen holder.

6.3 Thermal Analysis

Thermal behavior of the blends was estimated from differential scanning calorimetry (DSC) traces. DSC measurements were carried out with a Perkin-Elmer DSC-2C. Samples (approximately 15 mg) were heated at a constant rate of 20°C/min and cooled at a rate of 10 °C/min.
6.4 X-Ray Analysis

Wide angle X-ray scattering (WAXS) was performed using a URD 63 diffractometer (Seifert-FPM). CuK$_\alpha$ radiation with a wavelength $\lambda = 0.154$ nm was used. Investigations were carried out at room temperature in reflection mode.

Small angle X-ray scattering (SAXS) investigations were performed in an evacuated Kratky compact camera (Anton Paar KG, Graz, Austria) with CuK$_\alpha$ radiation ($\lambda = 0.154$ nm, Ni-filter). The scattered intensity was recorded by a scintillation counter in a step-scanning mode at room temperature or at 140°C. The scattering profiles were corrected for background scattering and desmeared. Thin samples (thickness about 1-2 mm) were cut from the surface of the samples and then investigated by SAXS.

6.5 Microscopic Techniques

Different microscopic techniques (atomic force microscopy AFM, transmission electron microscopy TEM, scanning electron microscopy SEM, high voltage electron microscopy HVEM) were used to investigate morphology and deformation behavior of the samples. Morphology of the samples was studied by transmission electron microscopy (JEM 2010). For the TEM studies, ultra-thin sections (~ 80 nm thickness) were cut from the bulk sample at room temperature and were stained with RuO$_4$ vapor in order to make the EVA phase detectable by the microscope.

Scanning electron microscopy was used to study the fracture surfaces of the failed samples after the Bell-telephone ESCR test in Igepal at 50°C. The fracture surfaces were covered with thin gold film prior to the SEM investigations.

To investigate the deformation behavior of a few selected samples, semi-thin sections (ca. 0.5 – 0.8 $\mu$m thickness) were cut and studied using high voltage electron microscope (1000 kV Joel HVEM). The semi-thin sections were strained in a special tensile device fixed to the HVEM.

For comparable study of morphology of some samples, atomic force microscopy (Nanoscope IIIa, Digital Instruments) was used. The microscope was operated in tapping mode at room temperature. The samples were scanned using a silicon cantilever.
6.6 Tensile Testing and Mechanical Properties

Mechanical behavior of the samples was characterized by uniaxial tensile testing. Tensile tests were performed using Instron 4507 testing machine at speed of 50 mm/min and at temperatures of 23, 50 and 70°C in the temperature chamber of the Instron machine. At least 10 samples were measured in order to prevent preparation artifacts and to obtain a good statistics of data. Blends were compression-molded between two rigid metal plates. Dumbbell shaped specimens were cut from the plates (ca. 4 mm thickness). The main objective of this test is to have a comparative insight into the mechanical behavior of the investigated samples. Stress-strain curves were recorded using following equations for the calculation of stress ($\sigma$) and strain ($\varepsilon$):

$$\sigma = \frac{F}{A_0}$$  \hspace{1cm} (6.1)

where $F$ is the applied force in N and $A_0$ is the cross-sectional area of the sample in mm$^2$.

$$\varepsilon = \frac{(L - L_0)}{L_0} \times 100 = \frac{\Delta L}{L_0} \times 100 \%$$  \hspace{1cm} (6.2)

where $\Delta L$ is the change in the gauge length of the specimen relative to the initial sample length $L_0$.

The modulus of elasticity (Young’s modulus) was determined by the slope of the initial part of the stress-strain curves.

Tensile strength at yield $\sigma_y$ is the stress at which the sample yields, divided by its cross-sectional area:

$$\sigma_y = \frac{F_y}{A_0}$$  \hspace{1cm} (6.3)

where $F_y$ is the applied force at yield in N and $A_0$ is the initial cross sectional area of the sample in mm$^2$.

6.7 Image Processing System analySIS 3.1

This software was used for determination of the average particle size of the EVA particles and the average particle-particle distance (surface-to-surface) distance. A circle was drawn around each EVA particle visible in the TEM images of PE/EVA-5.4 and PE/EVA-8.9 samples by using the computer mouse and following the edge of the particle. The surface area of the
particles was automatically calculated by the computer program. The diameter of the particle
was calculated by using following well known equation:

\[ d = \sqrt[4]{\frac{4S}{\pi}} \text{, nm} \]  

(6.4)

where S is the surface area of the EVA particle in nm\(^2\).

The average diameter of the EVA particles is equal to \( \frac{\sum_{i=1}^{m} d_i}{n} \) where \( d_i \) is the diameter of i

EVA particle and \( n \) is the total number of the measured EVA particles.