2 Samples, Previous Work and DSC Measurements

This chapter describes the samples used for this work and the way they were obtained. The non-NMR methods like Differential Scanning Calorimetry and Dynamic Mechanical Analysis, used usually for polymer characterization are briefly introduced. The previous work of this study consists in sample preparation and DMA results. The results of DSC measurements for representative sample are discussed.
2.1 Samples and non-NMR Methods

2.1.1 Ethylene-Propylene-Diene-Monomer (EPDM)

At room temperature, polyethylene is a partial crystalline plastomer, but on heating, it passes through an "elastomeric" phase. By incorporating in the polymer chain elements which inhibit crystallization, the melting temperature and therefore the elastomeric phase can be reduced considerably to below room temperature. Such amorphous and curable materials can be considered as rubbers, and they can be obtained by co-polymerizing ethylene and propylene with certain catalysts of the Ziegler-Natta type. The resulting, so-called EPMs are amorphous and rubbery, but they do not contain un-saturation, therefore, they can only be cross-linked with peroxides. If, during co-polymerization of ethylene and propylene, a third monomer, a diene, is added, the resulting substance, EPDMs, will have un-saturation, and it can then be vulcanized with sulfur².

In the production of EPM and EPDM rubber the following parameters are considered⁷:
- concentration ratio of ethylene and propylene (amorphous or segmented grades);
- co- or terpolymerization (EPM or EPDM);
- type and amount of termonomer (vulcanization properties, mechanical properties);
- solution and suspension polymerization (highest obtainable molecular weight);
- molecular weight (differences in Mooney viscosity and processibility);
- processibility, price.

Copolymers, which contain between 45 and 60% ethylene, are completely amorphous.

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_2=\text{CH}_2 + \text{CH}_2 =\text{CH} + \text{CH}_2 =\text{CH}_2 & \rightarrow \uparrow \\
& \text{CH}_3 \\
-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} - \text{CH}_2 - \text{CH}_2 -
\end{align*}
\]

**Figure 2.1.** The principle of ethylene and propylene copolymerization
At higher ethylene contents of the order ranging between 70 to 80%, the polymers contain long ethylene sequences, which are partially crystalline. These polymers are referred to as “sequential” grades, and their processing behavior differs considerably from that of the normal amorphous grades. The partially crystalline domains form thermally reversible physical cross-links, which, as with the thermoplastic elastomers, give the elastomers an already high mechanical strength without chemical cross-links. At higher temperatures though, this strength deteriorates\(^7\).

The choice of a suitable termonomer poses several problems. Firstly, the two sets of double bonds of the diene should have different reactivities, so that one will co-polymerize with the second remaining un-reacted in the polymer chain, enabling it to be used in subsequent vulcanization reactions. The other requirement is that of a high reactivity of the second double bond in sulfur vulcanization reactions. In the production of commercial rubbers the most used diene are the following: dicyclopentadiene (DCP), ethylidene norbornene (ENB) and trans-1,4 hexadiene (HX).

Sulfur vulcanization is technologically the most important chemistry employed in the production of diene elastomer vulcanizates. It is agreed that the accelerator and activators react to generate an active accelerator complex. This complex reacts with the unsaturated elastomer by substituting a labile allylic hydrogen atom, which results in the attachment of accelerator residues to the elastomer chain, namely, pendent sulfur or cross-link precursor. This intermediate is converted into a sulfur cross-link either via disproportionation with a second pendent sulfur structure or by allylic substitution of the un-saturation of a second elastomer chain. During accelerated sulfur vulcanization dialkenylsulfides are predominantly formed, indicating that the un-saturation is not consumed during reaction but that it activates the \(\alpha\)-position, whereas during un-accelerated sulfur vulcanization mixtures of dialkenylsulfides, dialkylsulfides and alkenylalkylsulfides are formed. If a prolonged vulcanization is performed network maturation reactions may occur. The sulfidic cross-link may exude sulfur, resulting in cross-link shortening, and it may be converted into cyclic sulfides\(^{23}\).
Recently, high-resolution carbon solid-state NMR measurements with ENB unsaturation of EPDM fully isotopically enriched with $^{13}$C were performed\textsuperscript{24}. It was found that sulfur cross-linking take place at the allylic positions of the ENB and the substitution at the 9-position of ENB is always preferred over the two 3-positions. In turn, the substitution at the 3-exo position is always preferred over the 3-endo position, which is different from earlier studies.

![Figure 2.2. Ethylidene norbornene (ENB)](image)

Among the samples chosen for study in this work is EPDM Buna EP G 5567 (Bayer AG, ML (1+4) 125 °C = 46, ENB 5%, Ethylene 66%, Propylene 29%, $M_w$=620 000g/mol) vulcanized according with tree different recipes, see Table 2.1. EPDM is cross-linked by accelerated sulfur vulcanization. With respect to ultimate and dynamic properties sulfur-vulcanized EPDM is superior to peroxide-cured EPDM as a result of the dynamic

<table>
<thead>
<tr>
<th>composition</th>
<th>EPDM\textsubscript{A} (phr)\textsuperscript{a}</th>
<th>EPDM\textsubscript{B} (phr)</th>
<th>EPDM\textsubscript{C} (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TMTD</td>
<td>0,5</td>
<td>0,5</td>
<td>0,5</td>
</tr>
<tr>
<td>ZDEC</td>
<td>0,3</td>
<td>0,5</td>
<td>0,5</td>
</tr>
<tr>
<td>MBTS</td>
<td>0,3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>
rearrangement of sulfidic cross-links during sulfur vulcanization, yielding a rubber network which is relatively free of internal stresses.

Using ethylidene norbornene (ENB) as termonomer it is possible to introduce 4 to 15 double bounds for each 1000 carbon atom chain length, with the polymer remaining free of gel\textsuperscript{2}. This is a low amount of un-saturation and sulfur vulcanization of EPDM is rather slow and a relatively large amount of accelerators is needed. The tetramethylthiurium disulfide (TMTD) and dibenzothiazyl disulfide (MBTS) were used as accelerators. For development of the full activity of accelerators, addition of ZnO and stearic acid is necessary.

The isotherms of vulcanization represented in the graphic below shows that EPDM C sample presents the highest cross-linked density\textsuperscript{25}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.3.png}
\caption{The isotherms of vulcanization for EPDM A, -B and -C (Göttfert elastograph, temperature 160\textdegree{} C)}
\end{figure}

From EPDM’s properties we mention that it has a very high resistance against heat, light, oxygen and ozone as a result of his fully saturated polymer backbone. The high
performance/price ratio explains the fact that EPDM rubber is by volume the largest non-tire elastomer (approx. 1000 kton/yr)\textsuperscript{26}. Its main applications are to be found in automotive sealing systems, in building and construction and in a variety of technical products (tubes, seals etc.).

2.1.2 The Blends of Polypropylene/Ethylene-Propylene Diene Monomer

Because it is possible to blend EPDM and polypropylene (PP), for example, in any ratio, there is theoretically a continuous spectrum from elastified PP to EPDM reinforced with thermoplastics. Where the PP component predominates, which is by far the chief field of application, PP constitutes the continuous phase with uniformly and finely dispersed rubber segments. With a very high EPDM component, by contrast, the structure reverses and the material is a PP-reinforced EPDM. The properties of the blends containing a high quantity of PP depend on the quantity of EPDM and the uniformity and size of the micro-heterogeneous rubber phase. They have a relatively low level of elasticity, display a low elongation at break and high values for compression set. They have only a low-level elastomeric character in the service temperature range, making them difficult to classify them as TPEs in the true sense of the term\textsuperscript{2}.

Through dynamic cross-linking in situ of EPDM with PP during mixing, elastomeric alloys (TPOs) can be made with rubber-elastic behavior over a wide range of temperatures (- 40 °C to + 125 °C). The rubber elastic behavior of such elastomeric alloys is quite different from that of non-crosslinked EPDM/PP blends. The morphology of in situ cross-linked polymer blends differs from those of non-cross-linked ones. The distribution of rubber particles is much finer and, therefore, the heterogeneous phase distribution is much better for the TPOs. The properties of the fully crosslinked elastomer particles do not change even at processing temperatures up to 180 °C - 225 °C\textsuperscript{27}. In general the properties of each individual TPO type depend, apart from the EPDM and the polyolefine types, also on the blend ratios, the degree of cross-linking and kind of compounding of EPDM phases, and, of course, of the micro-heterogeneous phase distribution of EPDM in polyolefines. These products can replace covalently cross-linked elastomers in a lot of applications and they fill the gap between elastomers and thermoplastics.
Fully or partially cured thermoplastic polyolefinic systems are called thermoplastic vulcanizates or TPVs.

The UV and ozon resistance of TPOs and TPVs is excellent and they are resistant also in most inorganic chemicals as well as in a lot of polar organic solvents like break liquids, but not in aliphatic and aromatic solvents in which they exhibit a great volume swell. TPOs also have good abrasion resistance and excellent electrical insulation properties. The compression set resistance between low minus degrees up to approximately 70 °C is low and it will rapidly be enlarged above 100 °C, coming at 125 °C near to 100%.

For the present study two series of blends were prepared, each of them composed of isotactic polypropylene (PP – Huels AG Verstolen P7000, 46% crystallinity) in different ratios (-30%, 50% and 70%) and the three different ethylene propylene-diene terpolymers (EPDM_A, EPDM_B and EPDM_C). The former (PP%_A, PP%_B and PP%_C) contain EPDM vulcanized powder (diameter < 80 µm) mixed at high temperature with PP, while the latter (PP%N_A, PP%N_B and PP%N_C) were obtained by additional dynamic cross-linking \textit{in situ} of EPDM during mixing.

All the PP/EPDM blends were produced through a melting mixing process in a 60 cm³ Brabender Plasticorder, equipped with a pair of high shear roller-type rotors. The Brabender is connected to a computer to allow monitoring of mixing properties such as torque and temperature as well as control mixing parameters. The starting temperature of the electrically heated chamber was 190 °C, the filling grade 0,67, the total mixing time 10 minutes and the rotor speed was set at 100 rpm. The polypropylene was introduced into the mixer during the first two minutes and after another two minutes the rubber powder was added. In the case of additionally cross-linked blends a vulcanization system was added. The vulcanization system used is Struktol 120 (Schill & Seilacher) and is composed by 83% soluble sulfur, 16% organic dispersing agent and 1% inorganic dispersing agent.
2.1.3 Non-NMR Methods

2.1.3.A. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a technique which is part of a group of techniques called Thermal Analysis (TA). Thermal Analysis is based upon the detection of changes in the heat content (enthalpy) or the specific heat of a sample with temperature. As thermal energy is supplied to the sample its enthalpy increases and its temperature rises by an amount determined, for a given energy input, by the specific heat of the sample. The specific heat of a material changes slowly with temperature in a particular physical state, but alters discontinuously at a change of state. As well as increasing the sample temperature, the supply of thermal energy may induce physical or chemical processes in the sample, e.g. melting or decomposition, accompanied by a change in enthalpy, the latent heat of fusion, heat of reaction etc. Such enthalpy changes may be detected by thermal analysis and related to the processes occurring in the sample.

Among the thermal analysis techniques the DSC is the one with the most widespread applications. In DSC the energy difference (heat enthalpy) between the sample and the reference is measured. The sample is very small (3-20mg) and is placed in a small aluminium vessel (pan). An empty pan is always used as a reference. When the sample is heated up at a constant rate, any kind of change in its calorimetric properties will cause a temperature difference between the sample and the reference. In the DSC apparatus the measured temperature difference is controlling the electrical power to the sample and the reference in order to keep them at the same temperature. In this technique the difference in the power supply to the sample and reference is recorded. This means that a peak area from the output recording directly corresponds to the heat consumed or produced by the sample.

The typical application for DSC is determination of: important transition temperatures like $T_g$ and $T_m$, heat of fusion of a crystalline phase and the degree of crystallization, heat capacity, rate of cross-linking reactions, miscibility in polymer blends, structural relaxation like enthalpy relaxation during physical aging.
2.1.3.B Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) is a thermal analysis technique used to measure changes in the viscoelastic response of a material as a function of temperature, time, or deformation frequency. DMA is particularly useful for qualitatively characterizing the glass transition temperature and other sub-Tg transitions of polymer and composite materials.

Polymeric materials have *viscoelasticity*, which is a combination of viscosity and elasticity in varying amounts. When this viscoelasticity is measured dynamically, there is a phase shift between the force applied (stress) and the deformation (strain) which occurs in response. The tensile stress $\sigma$ and the deformation (strain) $\varepsilon$ are related via the elasticity modulus $E$ as follows

$$\sigma = E \varepsilon \quad (2.1)$$

If the stress is applied in a sinusoidal fashion, the measurements are represented as a complex modulus $E^*$

$$E^* = E' + iE'' \quad (2.2)$$

DMA measures the amplitudes of the stress and strain as well as the phase angle ($\delta$) between them. This is used to resolve the modulus into an in-phase component - the storage modulus ($E'$) - and an out-of-phase component - the loss modulus ($E''$).

$$E' = E* \cos \delta \quad (2.3)$$
$$E'' = E* \sin \delta$$

A useful quantity is the damping factor or loss tangent (tan $\delta$) which is the ratio $E''/E'$ and is the amount of mechanical energy dissipated as heat during the loading/unloading cycle. The loss tangent is zero for a perfectly elastic material and infinite for a perfectly viscous one.
2.2. Results and discussions

2.2.1 Previous Results

For dynamically vulcanized blends the variation of tensile properties with the composition is illustrated in Figure 2.4. The elongation at break increases with the rubber content and with the increase of cross-link density in the EPDM.

![Stress-strain plots for blends containing different quantities and kinds of EPDM](image)

**Figure 2.4** Stress-strain plots for blends containing different quantities and kinds of EPDM (Zwick 1425, $L_E = L_0 = 50$ mm, $v_T = 200$ mm/min)

The dynamic mechanical properties were determined using Eplexor 150 N at a heating rate of 1 $^\circ$C/min. The temperature range chosen was from -120 $^\circ$C to 160 $^\circ$C. The plots were recorded for blends with different PP/EPDM content (30/70, 50/50, 70/30) before and after vulcanization in order to detect the effects of dynamic vulcanization process. The storage modulus versus temperature curves, as given in Figure 2.5, shows the characteristic biphasic structure of the blends. The modulus is decreasing, as expected, with increasing the rubber content.
Figure 2.5 The variation of storage modulus and loss tangent with temperature for the blends which contain different percentage of EPDM_C and the corresponding dynamically vulcanized blends (PP%N_C).  

2.2.2 Results from DSC Measurements

The DSC measurements were performed using a DSC 7 instrument (Perkin-Elmer) with DSC (TMDSC) software option. The sample mass was about 10-15 mg. The DSC was calibrated at zero heating rate according to the GEFTA recommendation. For all the measurements the heating and cooling rates were 10 K/min. Nitrogen gas with a flow rate of about 20 ml/min was purged to the cell.

Differential scanning calorimetry measures the heat flow into or from a sample as it is heated, cooled and/or held isothermally. In principle the technique provides valuable information on
softening temperatures \( (T_g) \), melting temperatures, heats of melting, percent crystallinities, and re-crystallization (temperatures and heats). In the present work we performed DSC measurements in order to answer to the following questions: a) does EPDM contain crystalline parts, and b) is DSC technique able to reveal differences between the non-crosslinked blends and the cross-linked ones?

![Figure 2.6](image)

**Figure 2.6** DSC results on sample EPDM_C during heating and cooling process^{25a}

As we can see in Figure 2.7, the softening and the melting processes are both present, but the corresponding peaks are partially overlapped. However, it is clear that EPDM sample contains crystalline parts.

The Figures 2.7 and 2.8 clearly shows that DSC cannot distinguish between the blends with different amount of cross-link density in the rubber phase. The samples PP73N_C (70% polypropylene) and PP37N_C (30% polypropylene) are the blends which were dynamically vulcanized.
Figure 2.7 DSC results on blended samples during heating segment\textsuperscript{25a}

Figure 2.8 DSC results on blended samples during cooling segment\textsuperscript{25a}