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# Applied Rheology for Polymer Modification

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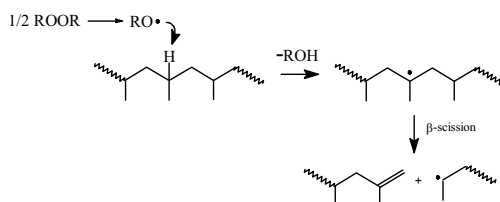
**Abstract.** EPDM and EPM were modified using different processing conditions and amounts of peroxide. Rheological measurements were performed in order to characterize and follow the reactions that took place during processing (branching/crosslinking and/or degradation). The experimental results evidenced that branching/crosslinking occurs for EPDM and degradation is the main reaction for EPM.

**Keywords:** Rheology, Polymer modification, Degradation, Crosslinking.

**PACS:** 47.50.Ef, 80, 83.85.Cg, 83.85.Vb, 83.60.Bc

## INTRODUCTION

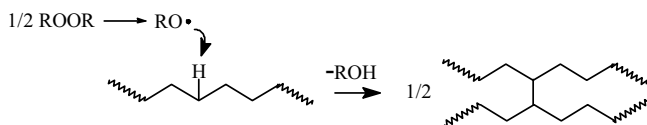
Polymer modification has been widely used to prepare polymers with specific properties. The use of controlled chain degradation became an important industrial application for the production of PP with controlled rheology [1]. As a result, a reduction of molecular weight is obtained, which corresponds to lower melt viscosity and improved processability. It is generally accepted that degradation of PP follows a series of free radical reactions, i.e., peroxide decomposition, hydrogen abstraction, chain scission and termination [1-7] (Figure 1). Some kinetic models for PP degradation have been developed and combined with a simplified model of the melting mechanism in the extruder, in order to predict the molecular weight average [3].



**FIGURE 1.** Mechanism of peroxide induced degradation of PP.

Long side chains can be formed when the macroradicals, formed by hydrogen abstraction experience bimolecular termination by combination (Figure 2). If this long chain branching continues, a three-dimensional network will form with high levels of insoluble gel (crosslinking). The formation of high molecular weight chains due to

branching increases the melt strength and the die swell and improves the strain hardening properties [8-12].



**FIGURE 2.** Mechanism of branching/crosslinking reaction of polyolefins.

Often, crosslinking is considered undesirable because of reduced processability. However, it may also bring some property enhancement to the polymer, such as increased service temperature, solvent resistance, flexural modulus and dimensional stability.

The occurrence of degradation or/and crosslinking reactions depends on the polyolefin structure. In case of EPM and EPDM it is believed that crosslinking and chain scission are competing mechanisms and their relative effects depend on the copolymer composition i.e. the relative amount of ethylene and propylene sequences [13, 14-16]. Loan [17] found out that using only peroxide results in poor crosslinking of EPDM and EPM. Machado et al. [13] studied the rheological behavior of PP, PE and EPM in a twin extruded monitored along the barrel, they observed that the degree of crosslinking/branching and/or degradation in EPM depends essentially on the ethene/propene ratio, on the original molecular weight of polymer and on the amount of peroxide used.

The present study aims to make a comparative study on degradation/crosslinking of EPM and EPDM processed in a batch mixer with and without peroxide. The effect of rotor speed, temperature and peroxide amount was investigated. Rheological measurements were used to monitor the chemical changes (crosslinking/branching or degradation).

## EXPERIMENTAL

### Materials

EPDM rubber (K2340A: 53 wt.% ethylene and 6 wt.% ENB;  $M_w = 150$  kg/mol; Mooney viscosity (1+4) at 125°C: 25) and the EPM rubber (K3200A: 49 wt.% ethylene;  $M_w = 150$  kg/mol; Mooney viscosity (1+4) at 100°C: 51) were supplied by DSM Elastomers BV. Cumyl hydroperoxide (80 %;  $M = 84,16$  g/mol) were supplied by Acros and used as received. The half time of the peroxide at 200 and 300°C are 260 and 0.73 s.

### Processing

No special precautions against the presence of oxygen were taken. Both EPDM and EPM without and with peroxide (0.05 and 0.1 phr) were processed in a batch mixer

(Haake Rheomix 600 OS; 69 ml) using two different temperatures (200 and 300°C) and screw speeds (80 and 150) were used. After 25 minutes the rotors were stopped and the all material was collected.

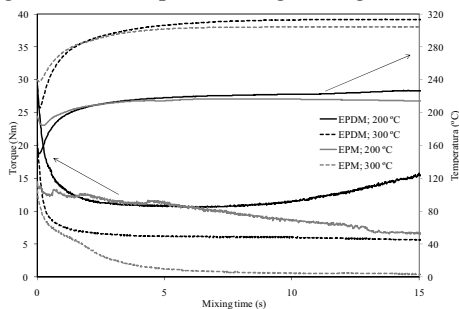
## Materials Characterization

Oscillatory rheological measurements were carried out using a Rheological Stress Tech HR, rotational rheometer using parallel-plate geometry. The gap and diameter of the plates were 1 mm and 25 mm, respectively. Isothermal frequency sweeps from 0.01 and 100 Hz at 200°C were performed. For each material, a stress sweep was carried out from 0.5 to 5000 Pa at frequencies of 1 and 10 Hz to determine the linear viscoelastic regime. The discs were prepared by compression molding at 200°C under a press of 30 tons. In case of very low viscous samples which are liquid at room temperature it was not possible to do discs and samples were place directly in the rheometer. Rheological measurements were not performed on samples presenting high crosslink degree since they do not soften.

Gel content determinations were performed using approximately 300 mg of the collected samples, with were placed in 80  $\mu\text{m}$  mesh stainless cages and immersed in cyclohexane under gentle stirring during 48 h at room temperature. The solvent was refreshed once after about 24 h. After removal of the cyclohexane, samples were dried in a vacuum oven for 12 h at 100°C with nitrogen purging and weighed again.

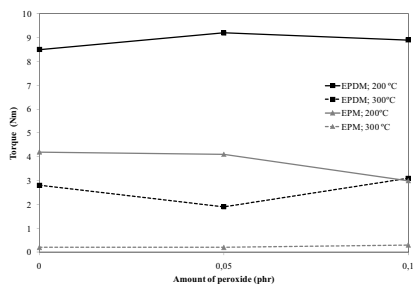
## RESULTS AND DISCUSSION

The torque behavior recorded during processing of EPDM and EPM in the absence of peroxide at different temperatures is shown in Figure 3. As it was expected, for both EPDM and EPM, an increase of temperature results in a decrease of the torque, suggesting a decrease in viscosity. For EPDM it can be observed that mixing does not allow significant changes in the torque only a slight decrease is observed, with the exception of EPDM processed at 200°C were an increase is observed. This increase of the torque value suggests that crosslinking/branching occurred. In case of EPM, while at 200°C the torque decreases along the processing time, at 300°C a pronounced decrease can be observed before 5 min. These results suggested that thermo-mechanical degradation took place during mixing and it was faster at 300°C.



**FIGURE 3.** Effect of the temperature on torque behaviour as a function of mixing time of EPDM and EPM in the absence of peroxide at a rotor speed of 80 rpm.

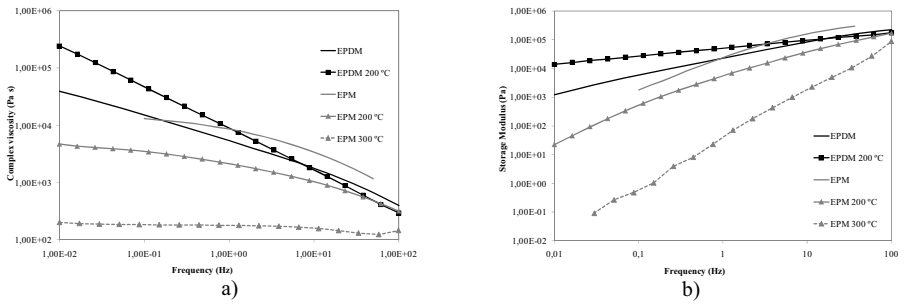
Figure 4 depicts the torque measurements at the end of mixing as a function of peroxide concentration at 200 and 300°C and at a rotor speed of 150 rpm. At 200°C for both EPDM and EPM peroxide amount does not have a significant influence on the torque. However, a slightly decrease of torque value is observed for EPM at 200°C when the concentration of peroxide increases from 0.05 to 0.1 phr. For the same variation of peroxide amount, EPDM at 300°C shows a slightly increase of torque.



**FIGURE 4.** Effect of peroxide concentration on the final torque for EPDM and EPM at a rotor speed of 150 rpm.

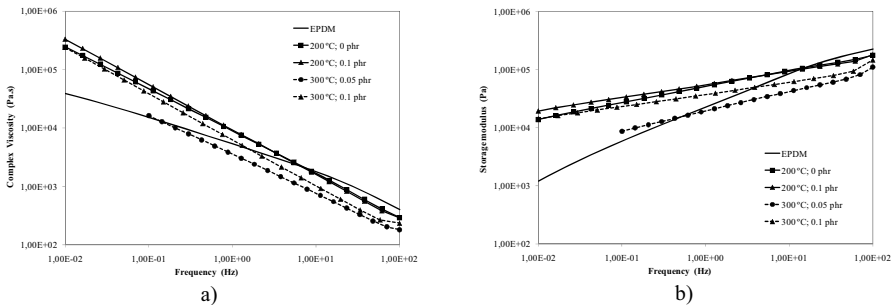
Rheological measurements were performed for the various samples produced under different processing conditions and different amount of peroxide. Samples with high crosslink levels could not be analyzed. The rheological behavior of raw materials, EPDM and EPM were also performed under the same conditions and the results were added as reference in all the Figures 5-7. As it can be seen, EPDM exhibit shear-thinning behavior over the complete range of frequencies measured while the EPM show a normal pseudo-plastic behavior, with a Newtonian plateau at low frequencies and shear thinning behavior at higher frequencies.

Figure 5 shows the effect of the processing temperature on EPM and EPDM using a rotor speed of 80 rpm in the absence of peroxide. EPDM processed at 200°C presents higher viscosity and elasticity at low frequencies, increasing shear thinning, which suggests that crosslinking/branching took place during mixing. These results are in agreement with the gel content value, which was 60 % at 200°C. EPDM sample processed at 300°C present a gel content value of 95 %, consequently rheological measurements could not be performed. Nevertheless, the results obtained by both techniques show that under these processing conditions crosslinking/branching of EPDM increases with temperature. A different behavior can be observed for EPM, which shows a decrease of the viscosity and elasticity as the temperature increases. At 300°C the EPM viscosity becomes too low, the Newtonian plateau enlarges to high frequencies and the elasticity presents values below 1 at low frequencies. Thus, under these processing conditions and in the absence of peroxide, an increase of temperature decrease the viscosity and elasticity of the EPM, this can be associated with higher chain scission.



**FIGURE 5.** Effect of processing temperature on rheological behavior of EPDM and EPM (80 rpm without peroxide).

The rheological behavior of EPDM samples prepared with different amounts of peroxide at different temperatures and rotor speed of 80 rpm is shown in Figure 6. An increase of complex viscosity and elasticity at low frequencies can be observed in all cases, suggesting that crosslinking/branching were the main reaction occurring under the conditions used. However, due to the shear thinning behavior, the slope of complex viscosity curves increases and at medium and high frequencies, the viscosity becomes smaller than the original EPDM. In general, crosslinking occurs and the viscosity of the modified EPDM is quite similar and independent of the temperature and the amount of peroxide used.



**FIGURE 6.** Effect of peroxide concentration on the rheological behavior of EPDM.

Figure 7 shows the results of rheological measurements of EPM samples prepared with a rotor speed of 80 rpm at different temperatures and with different amounts of peroxide. At 200°C complex viscosity and elasticity decreases and the lowest values were obtained when 0.05 phr of peroxide was added. Thus, increasing the amount of peroxide to 0.1 phr result in an increase of viscosity and elasticity, suggesting that crosslinking/branching also occur for EPM under certain conditions. Degradation is significantly improved by increasing the temperature to 300°C and it is almost independent of peroxide amount, in fact at this temperature the same level of degradation is achieved with and without peroxide. These results are in agreement with the gel content measurements, since gel content values below to 2 % were obtained for all EPM samples.

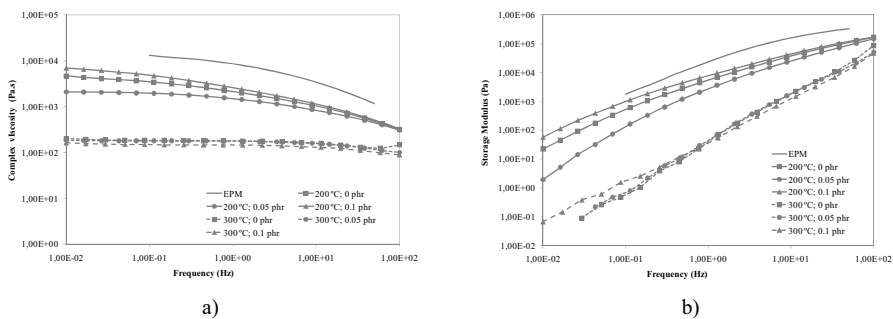


FIGURE 7. Effect of peroxide concentration on the rheological behavior of EDM (rotor speed at 80 rpm).

## CONCLUSIONS

EPDM processed at 200 and 300°C shows an increase of viscosity and elasticity at low frequencies and an increase of the shear thinning behavior, which evidence that crosslinking/branching prevails over degradation. However, the balance between crosslinking/branching and degradation is a result of a complex interrelationship between peroxide amount, processing temperature and rotor speed.

Degradation always occurs for EPM and it is mainly enhanced by increasing the temperature. Although the rheological measurements suggest that crosslinking/branching also occurs, degradation is the main reaction, as a consequence gel content is close to 0 % for all EPM samples obtained at different processing conditions and using different amounts of peroxide.

The above results suggest that crosslinking/branching occurs in the diene group of EPDM, since the ethene/propene ratio is quite similar (47 and 51 % of propene for EPDM and EPM, respectively) and the molecular weight of the elastomers is the same.

## ACKNOWLEDGMENTS

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