

Cationic Reactions in the Melt

2. The Effect of Lewis Acids on the Ethylene-Propylene Co- and Terpolymers

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SUMMARY

The effect of Lewis acids on various ethylene-propylene co- and terpolymers has been investigated in the mixing chamber of a Brabender Plastograph at 180°C. Fast degradation of the polymers was observed upon the addition of Lewis acids. Terpolymers containing unsaturations undergo crosslinking: the structure of the third monomer (diene) determines the rate of crosslinking and the characteristics of the crosslinked materials.

INTRODUCTION

The aim of this research is the preparation of graft copolymers with ethylene-propylene copolymer backbones carrying polystyrene branches using cationic reactions in the melt. After having completed our investigation on the effect of various Lewis acids (LA) on polystyrene melts (PUKÁNSZKY et al. 1981), we have turned our attention to the exploration of the effect of Lewis acids on ethylene-propylene copolymers (EPM) and terpolymers (EPDM).

Earlier investigations showed that the degradation mechanism of saturated hydrocarbon polymers by LA's is essentially identical in solution (FRANK 1963, CARRICK 1970, PAPIRER et al. 1975) and in the melt (BARAMBOIM et al. 1979, PUKÁNSZKY et al. 1981). Some of the degradation products contain double bonds. Unsaturated polymers (polydienes) undergo cyclization reactions (PAPIRER et al. 1975). The reactions of carbocations arising during the degradation may be used for polymer modifications (CARRICK 1970, PAPIRER et al. 1975, GRASSIE and GILKS 1973, KRAKOVYAK et al. 1976).

Investigations of polystyrene/LA reactions showed that higher molecular weight products may be formed by the cations

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in the system reacting with unsaturations that arose during degradation (PUKÁNSZKY et al. 1981). Therefore, we decided to study the effect of LA's on ethylene-propylene terpolymers containing different types and amounts of dienes in the melt.

EXPERIMENTAL

The ethylene-propylene co- and terpolymers were used as supplied by the manufacturer. Table I shows their compositions and molecular weights. The experimental equipment and methods has been reported (PUKÁNSZKY et al. 1981). Reaction conditions were slightly different, i.e., 180°C, 50 rpm and 40 g charge, from those used with polystyrene.

RESULTS AND DISCUSSION

The general characteristics of torque vs. time curves obtained were similar to those observed in case of polystyrene (PSt; PUKÁNSZKY et al. 1981). The degradation of a small part of the polymers (fast drastic decrease of the torque) upon the addition of the LA was observed. The length of the minimum torque phase t_h (homogenization, i.e., mixing and diffusion of the low molecular weight degradation products with the rest of the melt), as well as the extent of crosslinking depends on the amount and structure of the diene in EPDM.

TABLE I

Source, composition and molecular weight of ethylene-propylene co- and terpolymers

| Trade Name | Epcar 306 | Nordel 1440 | Royalene | Vistalon 6505 |
|----------------------------|-------------|--------------------|--------------------|--------------------------------|
| Abbreviation | EPM | N EPDM | R EPDM | V EPDM |
| Manufacturer | BF Goodrich | Du Pont | Uniroyal | Exxon |
| Diene | - | 1,4-hexa- diene | dicyclo- penta- | 2-ethylidene- -5-norbornene |
| Composition (wt %) | | | | |
| Ethylene | 69 | 44 | 49 | 46 |
| Propylene | 31 | 52 | 46 | 45 |
| Diene | - | 4 | 5 | 9 |
| $\bar{M}_n \times 10^{-3}$ | 43 | 19 | 47 | 65 |
| $\bar{M}_w \times 10^{-3}$ | 121 | 220 | 390 | 275 |
| \bar{M}_w/\bar{M}_n | 2.8 | 11.6 | 8.3 | 4.2 |

Three stages can be distinguished in the torque vs. time curve of EPM: a) fast degradation followed by homogenization,

b) slow degradation, and c) molecular weight increase (Fig. 1). The last phase, however can be observed only when more than 1.4 wt% AlCl_3 was added to the melt. In the case of PSt, the molecular weight increased already with 0.3 wt% AlCl_3 and t_h strongly increased with increasing amounts of LA (because of the increase of the amount of the low molecular weight fraction). In the case of EPM, t_h passes through a maximum as a function of the amount of LA added (Fig. 2). Evidently the initial degradation mechanism and/or physical processes are different with PSt and EPM.

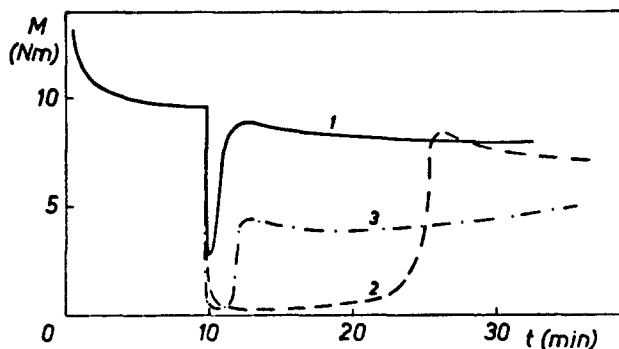


Figure 1. Torque vs. time curves of the melt reaction of EPM with AlCl_3 1: 0.130 g; 2: 0.35 g; 3: 0.54 g AlCl_3 .

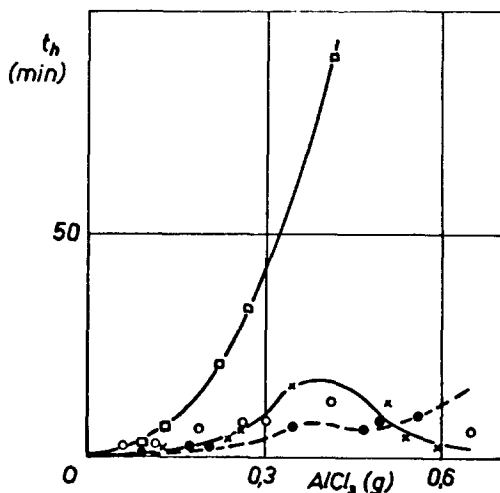


Figure 2. Homogenization time as a function of the amount of AlCl_3 -x-x-x-: EPM; -o-o-o-: R EPDM; -□-□-□-: N EPDM; -●-●-●-: V EPDM.

Figure 3 shows the torque vs. time curve of the N EPDM terpolymer. In contrast to EPM, after homogenization the torque raises above the initial level. This phenomenon indicates crosslinking that is most likely due to the presence of double bonds in N EPDM. Although EPM showed some molecular weight increase during the post-homogenization phase, the torque never reached the initial level.

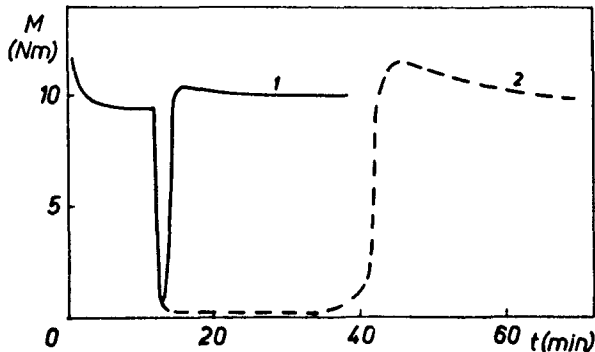


Figure 3. Torque vs. time curves of the melt reaction of N EPDM with AlCl_3 , 1: 0.110 g; 2: 0.285 g AlCl_3 .

A further important difference is that with N EPDM t_h does not exhibit a maximum (Fig. 2). This indicates that the scission products formed from N EPDM and EPM are different.

The torque vs. time curves of R EPDM (Fig. 4) are similar to those of N EPDM. With small amounts of AlCl_3 added the torque rapidly increases (Curve 2), but decreases when the amount of AlCl_3 reaches ~ 0.65 g. The product obtained in experiment 3 was powdery (and not a melt as in the case of Curve 2). On account of the relatively large amount of AlCl_3 used crosslinking is rapid and crosslink density is high so that the product crumbles even at a relatively low torque. The t_h versus AlCl_3 curve of R EPDM exhibits a maximum (Fig. 2).

V EPDM behaves similarly to R EPDM. The torque/time curve suggests crosslinking and the maximum torque (M_{max}) decreases above ~ 0.23 g AlCl_3 (Fig. 5). In experiments associated with Curves 2 and 3 powdery products were obtained. This is probably due to secondary crosslinking between the particles (see torque increase at the end of Curve 2) caused by the high double bond content of V EPDM. The t_h vs. AlCl_3 curve does not exhibit a maximum (Fig. 2).

Bu_2SnCl_2 does not induce chemical reactions in the ethylene-propylene co- and terpolymers, it has only a lubricating effect on these polymers.

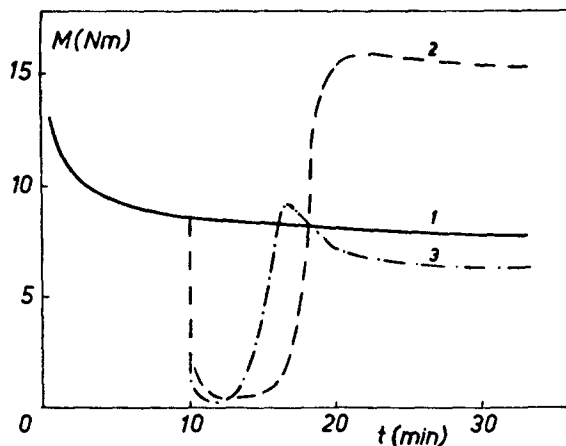


Figure 4. Torque vs. time curves of the melt reaction of R EPDM with AlCl_3 1: 0 g; 2: 0.404 g; 3: 0.6 g AlCl_3 .

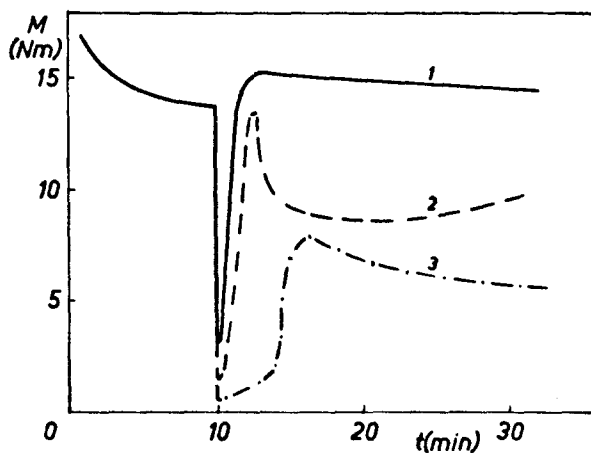


Figure 5. Torque vs. time curves of the melt reaction of V EPDM with AlCl_3 1: 0.176 g; 2: 0.231 g; 3: 0.479 g AlCl_3 .

By increasing the amount of AlCl_3 , t_h passes through a maximum (Fig. 2). Probably, mixing is more homogeneous in the presence of larger amounts of AlCl_3 in the chamber, thus the effect of initial inhomogeneities decreases. An exception is N EPDM which degrades easier than the other copolymers (Fig. 2). N EPDM may react rapidly with AlCl_3 , so that mixing does not

improve even at higher doses of LA.

The reactions of EPM and PSt are very similar: after degradation only a small increase of molecular weight can be observed. In EPDM rubbers crosslinking becomes important. Figure 6 illustrates the effect of the composition by plotting $m = M_{max}/M_0$ relative torque (M : torque at the addition of LA, M_{max} : maximum torque after homogenization) against the amount of $AlCl_3$ added. In the case of EPM mainly degradation occurs ($m \leq 1$) whereas with the unsaturated EPDM rubbers crosslinking dominates ($m \geq 1$).

Table II shows the number of double bonds per macromolecule and the amount of $AlCl_3$ which is necessary to reach the maximum of the m vs. $AlCl_3$ curves (Fig. 6). Evidently, when the double bond content is higher, a smaller amount of $AlCl_3$ can cause the same level of crosslinking.

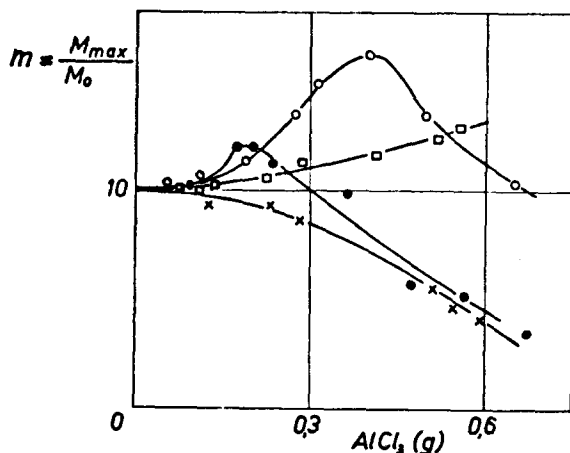


Figure 6. Relative maximum torque as a function of $AlCl_3$ concentration. -x-x-x-: EPM; -o-o-o-: R EPDM; -□-□-□-: N EPDM; -●-●-●-: V EPDM.

TABLE II

Estimated double bond content of EPDM rubbers and $AlCl_3$ concentration at the maximum of the M_{max} (Fig. 6)

| Polymer | Double bond/molecule | $AlCl_3$ (g) |
|---------|----------------------|--------------|
| N EPDM | 8.6 | >0.7 |
| R EPDM | 17.8 | 0.41 |
| V EPDM | 48.8 | 0.18 |

The nature of the crosslinks influences the rheological properties of the crosslinked material. The N EPDM contains a linear diene and gives rise to relatively long and flexible crosslinks; M_{\max} increases continuously with increasing amounts of $AlCl_3$ and the maximum of the m vs. $AlCl_3$ curve (Fig. 6) is out of the range studied. The EPDM rubbers that contain cyclic dienes lead to more rigid crosslinks so that mechanical breakdown (crumbling) takes place at lower crosslink densities.

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