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# Cationic Reactions in the Melt

## 3. Grafting Polystyrene onto Ethylene-Propylene Co- and or-Terpolymers

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## SUMMARY

Reactions in the melt between polystyrene and ethylene propylene co- and terpolymers were studied in the presence of anhydrous $AlCl_3$ using the mixing chamber of a Brabender Plastograph as the reactor. Various concurrent reactions have been identified, i.e., grafting, degradation, crosslinking, etc., the rates of which depend on the nature of the polymers and of the $AlCl_3$ added. Grafting is extensive, 40-50%, and the composition of the grafts is close to that of the charge.

## INTRODUCTION

Friedel-Crafts reactions of ethylene-propylene copolymers (EPM) with polystyrene (PSt) in solution gave PSt-g-EPM grafts (CARRICK 1970). The characteristics of these grafts were studied by BARENSTEN and HEINKES (1973, 1974) who established that although the grafts do not act as blending agents they can be used as impact modifiers. According to BARAMBOIM et al. (1979) reactions of polyethylene and Lewis acids (LA) in the melt result in a variety of products by various chemical reactions. The method can be used to produce polymers with new, advantageous characteristics (BARAMBOIM and PINYAEV 1978).

According to our investigations the reaction of PSt with Lewis acids leads to the formation of double bonds, which in turn lead to higher molecular weight products (PUKÁNSZKY et al. 1981). Polyolefin terpolymers containing double bonds (EPDM rubbers) react readily (crosslink) under the influence of Lewis acids (PUKÁNSZKY et al. 1982). The rate of crosslinking and the characteristics of the products depend on the amount and type of diene in the terpolymer.

Since we have demonstrated that PSt and EPDM rubbers react with Lewis acids in the melt, we continued our investigations with the aim of coupling these polymers by Lewis acid and thus producing new graft copolymers with potentially useful characteristics.

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## EXPERIMENTAL

Materials, equipments and techniques used have been reported (PUKÁNSZKY et al. 1981, 1982). In addition to unsaturated polymers (EPDM), a chlorinated ethylene-propylene copolymer (Cl-EPM, prepared from Epcar 306, tertiary chlorine content 1.15 wt%) was also examined to investigate the effect of tertiary chlorines. Reaction conditions were 150°C, 50 rmp, 65g charge (88 wt% PSt and 12 wt% polyolefin). Lewis acid was added after homogenization of the two polymer components (after 10 min.).

The product was dissolved in toluene, precipitated into n-hexane and the insoluble part was extracted with methylethylketone (MEK) for 24 hours. The composition of the soluble fractions was determined by $^1$H-NMR spectroscopy (Varian T-60 NMR Spectrometer).

## RESULTS AND DISCUSSION

### Evaluation of torque vs. time curves

The overall trends of the torque vs. time curves are similar to those described and discussed before (PUKÁNSZKY et al. 1981a,b). Degradation of a small part of the material upon the addition of $AlCl_3$ causes fast drastic decrease of the torque which is followed by a homogenization process. After homogenization, the torque rapidly increases again. Reactions take place during and after homogenization. Although the characteristics of the degradation are the same for all polyolefin/PSt pairs, the behavior of the melt during the later phases of the reaction is much affected by the structure of the olefin component in the rubber.

The torque vs. time curve of EPM/PSt mixtures is shown in Figure 1. The torque does not increase above the initial level, i.e., degradation is the most important reaction.

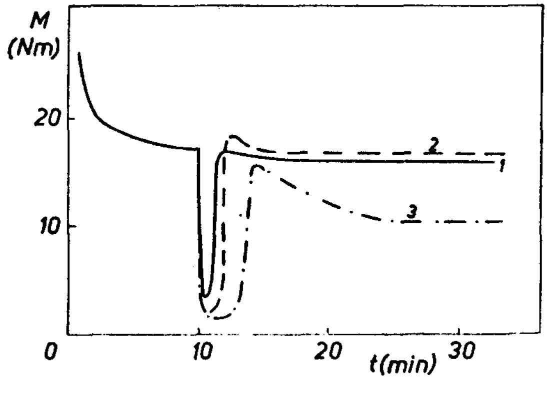

Figure 1. Torque vs. time curves of the melt reaction of EPM. PSt mixture 1: 0.093 g; 2: 0.150 g; 3: 0.295 g $AlCl_3$

R EPDM/PSt and V EPDM/PSt mixtures behave similarly. In both cases the torque which is related to the molecular weight, increases above the initial level after homogenization (Figures 2 and 3). The extent of this molecular weight increase depends on the type of polymer and amount of $AlCl_3$ used. Evidently chemical coupling and not physical effects cause the torque to increase. After a maximum the torque decreases again due to polymer degradation by the $AlCl_3$.

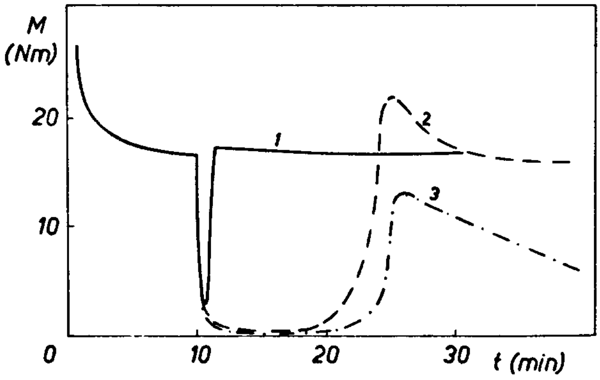

Figure 2. Torque vs. time curves of the melt reaction of R EPDM with PSt 1: 0.097 g; 2: 0.428 g; 3: 0.717 g $AlCl_3$

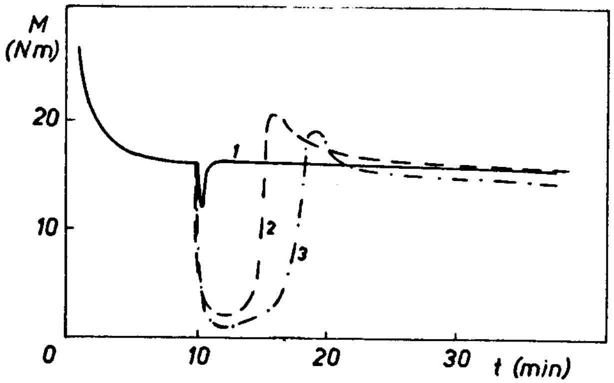

Figure 3. Torque vs. time curves of the melt reaction of V EPDM with PSt 1: 0.075 g; 2: 0.295 g; 3: 0.522 g $AlCl_3$

The Cl-EPM/PSt system behaves similarly (Figure 4). After homogenization the torque increases above the initial level and passes through a maximum. The extent of the degradation is, however, somewhat smaller than in case of R and V EPDM. In the

Cl-EPDM/PSt system HCl is evolved indicating that reactions involving the labile tertiary chlorine atoms occur.

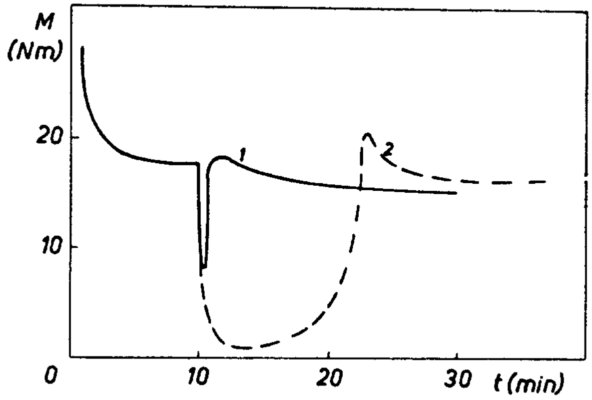

Figure 4. Torque vs. time curves of the melt reaction of Cl-EPM with PSt 1: 0.023 g; 2: 0.221 g $AlCl_3$

The behavior of the N EPDM/PSt mixture is somewhat different from those described above. Thus the increase in the torque is more pronounced (Figure 5). This is surprising because the number of double bonds per macromolecule is the lowest in this polymer. Evidently the structure of the diene component plays an important role in determining the rheology of the melt. The N EPDM/PSt system is very sensitive towards degradation: very severe degradation occurs already upon the addition of moderate amounts of $AlCl_3$. Other polyolefin/PSt mixtures start to degrade significantly only with $AlCl_3$ amounts about twice as high. The reason for this behavior is not clear though it is in agreement with former findings on the behavior of N EPDM (PUKÁNSZKY et al., 1982).

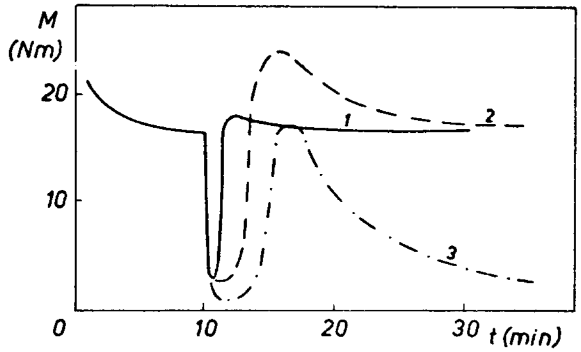

Figure 5. Torque vs. time curves of the melt reaction of N PDM with PSt 1: 0.099 g; 2: 0.205 g; 3: 0.454 g $AlCl_3$

## The effect of the amount of $AlCl_3$

Various reactions take place in the system at the same time, e.g., grafting, degradation, alkylation of the aromatic ring, crosslinking, isomerization. All mixtures exhibit a maximum in the $m = M_{max}/M_o$ vs. $AlCl_3$ amount curves (Figure 6; $M_{max}$: maximum torque after homogenization; $M_o$: torque at $AlCl_3$ addition). In the case of EPM (i.e., a saturated copolymer) this maximum is insignificant. With increasing amounts of $AlCl_3$ degradation becomes dominating in EPDM systems also and only small m values are reached.

The maximum of the m vs. $AlCl_3$ amount curves is inversely related to the number of double bonds in the macromolecule. Alkylation and crosslinking compete and with an increaseing concentration of double bonds crosslinking becomes increasingly favorable. Crosslinking, however, occurs within the rubbery phase so that the torque of the mixture does not change significantly.

Cl-EPM behaves similarly to the EPDM rubbers. However, not only the tertiary but also the secondary chlorines may participate in graft formation.

## Analysis of the products

Since various reactions take place in the mixing chamber, the products are also diverse. The composition and molecular weight of the grafts cover a wide range. Fractionation of the crude products was carried out by extraction with MEK (see Experimental).

The results of fractionation studies are listed in Table I. The samples were selected for fractionation at $AlCl_3$ amounts and reaction times which gave maximum amounts of graft, i.e., at the maxima of the m vs. $AlCl_3$ amount curves in Figure 6. The composition of the grafts was calculated by using the composition of the soluble fractions as determined by NMR. The hexane-soluble fraction contained some very low molecular weight PSt fragments (PUKÁNSZKY et al. 1981).

Table I shows that the EPM/PSt system did not yield graft. The N and R EPDM rubbers and Cl-EPM gave 40-50% graft, and the compositions of the grafts were close to that of the charge.

In the case of V EPDM the high double bond content resulted in extensive crosslinking of the rubber component; only ∿12 wt% graft has formed the rubber content of which was twice that obtained with the other materials. Crosslinks in the rubbery phase of the graft are advantageous for impact modification: slightly crosslinked rubbers exhibit higher impact strength than uncured rubbers (PAUL and NEWMAN 1978).

## CONCLUSIONS

Numerous competitive reactions take place in reactions in the melt of ethylene-propylene co- and terpolymers with PSt: grafting, degradation, crosslinking, etc. The amount of added $AlCl_3$, the type, concentration and structure of the functional

TABLE I

Table I. Composition of melt reaction products

| Polyolefin | $AlCl_3$ (g) | Hexane soluble* (wt%) | PSt (%) | MEK soluble** (wt%) | PSt (%) | MEK insoluble*** (wt%) | PSt (%) |
|---|---|---|---|---|---|---|---|
| EPM | 0.144 | 12.8 | 0 | 87.2 | 100 | - | - |
| N EPDM | 0.205 | 4.6 | 39.7 | 42.5 | 100 | 52.9 | 82.6 |
| R EPDM | 0.435 | 12.8 | 53.3 | 42.7 | 97.6 | 44.5 | 87.5 |
| V EPDM | 0.249 | 5.1 | 49.9 | 82.7 | 92.6 | 12.2 | 73.1 |
| Cl-EPM | 0.358 | 12.9 | 57.2 | 43.8 | 96.6 | 43.3 | 88.5 |

* unreacted polyolefin and low molecular weight polystyrene

** polystyrene and low molecular weight graft

*** graft copolymer

groups in the rubber determine the rate of the reactions and the amount and characteristics of the products. Significant extent of grafting occurred in most cases. Inhomogeneous mixing (due to the presence of a rapidly decomposing fraction) complicates the evaluation of the processes.

According to these experiments cationic melt reactions of polymers may produce valuable new materials in a convenient way. Further experiments must be carried out to optimize reaction conditions and to evaluate the properties of the products obtained.

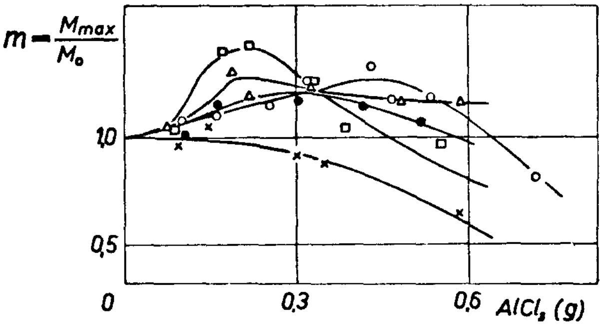

Figure 6. Relative maximum torque as a function of $AlCl_3$ concentration -x-x-x-: EPM; -o-o-o: R EPDM: -□-□-□-: N EPDM; -●-●-●-: V EPDM; -Δ-Δ-Δ-: Cl EPM

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