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Melts

Lewis Acid Initiated Melt Reactions of Polystyrene and EPDM Rubber

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SUMMARY

In order to obtain high impact polystyrene (PS), experiments have been performed on coupling of EPDM rubber and PS in the mixing chamber of a HAAKE plastograph. Lewis acids were added to the melt and the torque increase observed by their addition proved that chemical reactions take place in the system. During the reaction, the rubber proved to be more active, it became crosslinked and/or it was coupled with the PS molecules. Only a small fraction of the PS present coupled to the rubber molecules. No significant degradation process could be detected. Mechanical properties (tensile modulus and strength) improved during the reaction. This can be interpreted by the increased solubility of the coupled rubber molecules in the continuous PS phase.

INTRODUCTION

During the last years, we intensively studied the melt reactions of PS and EPM or EPDM rubbers in the mixing chamber of a Brabender plastograph. In these studies, $AlCl_3$ was used as Lewis acid. In the case of PS, degradation and double bond formation occurs, followed by molecular weight increasing reactions [1-3]. In the melt reaction of EPDM rubber, also crosslinking of the double bonds originally present was observed.

During the $AlCl_3$ initiated reaction of PS with EPM or EPDM rubbers, all the above mentioned reactions, i.e. grafting, degradation, crosslinking, etc. take place at the same time. The type and amount of the polymers and the quantity of the $AlCl_3$ present determine the relative rates of the reactions. These parameters should be changed in a way that the coupling of the different polymers be the dominating reaction.

The effect of the type of the Lewis acid on the cationic melt reactions of PS and EPDM rubber has been investigated as well [4]. It was established that the acidity of the Lewis acids has a considerable effect both on the process and on the properties of the final products. It was demonstrated that among the Lewis acids investigated, the $NaCl \cdot AlCl_3$ double salt has the best initiating effect. The greatest number of crosslinks was formed and the smallest extent of the degradation was observed in the reactions of this double salt.

The aim of our present investigation was to establish those reaction conditions which are favorable to the coupling, and unfavorable to the degradation of the macromolecules involved.

EXPERIMENTAL

The PS investigated was Krasten 144 ($\bar{M}_n = 104 \cdot 10^3$ Czechoslovakia). The EPDM rubber was an ethylene/propylene/ethylidene-norbornene terpolymer (BUNA AP 447, FRG) with ~7 double bonds/ 1000 carbon atoms. The $NaCl \cdot AlCl_3$ double salt was prepared from equimolar components, its melting point is 152°C.

The melt reactions of polymers were performed in the Rheomix 600 mixing chamber of the HAAKE Rheocord EU 10V (HAAKE Inc., USA). The reaction conditions were:50 ml charge volume, 150°C, 50 rpm.

PS and EPDM were homogenized for 10 min, then the double salt was added in a sealed polyethylene bag. After reaching the maximum torque, the melt was mixed for an additional 20 min. Torque and temperature were recorded as a function of time.

From the reaction products, 1 mm thick plates were prepared by compression moulding at 190°C. From the plates tensile specimens were cut and tested at 50 mm/min elongation rate.

Infrared spectra of the foils pressed from the mixtures (190°C) were also measured. Extraction of the samples with petrolether, a good solvent for rubber and bad for PS, was performed for 48 hours. The insoluble fraction was extracted for another 48 hours with methyl-ethyl-ketone (MEK) which dissolves only PS. The amount of the insoluble fraction was measured. Also the amount of the materials obtained by precipitation of the soluble fractions into methanol, was determined. Infrared spectra were measured both on the MEK insoluble fraction and on the methanol precipitates of the soluble fractions.

RESULTS

Different mixtures of PS, EPDM and $NaCl \cdot AlCl_3$ were prepared. The rubber content of the mixtures varied between 10 and 80, the amount of $NaCl \cdot AlCl_3$ between 1 and 10 mass percent. By selecting the mixture compositions, the aim was to cover the above concentration regions as much as possible. Reference mixtures were also prepared with the same composition but without Lewis acid.

Fig. 1. shows typical torque vs. time and temperature vs. time curves obtained during the melt reaction. On the torque vs. time curve, three distinct stages can be distinguished:

- A: fusion and mixing of the components. The temperature and the torque reach a constant value (T_o, M_o).
- B: addition of the Lewis acid. After the momentary decrease of torque, which is caused by the small lubricating effect of the molten Lewis acid, there is a sharp torque increase resulting from the coupling reactions initiated by the double salt.
- C: after reaching a maximum (M_{max}), the torque approaches its final value (M_{final}). At the maximum, there is an equilibrium between the chemical reactions causing molecular weight (viscosity) increase and the homo-

genization of the mixture of the products and of the unchanged materials.

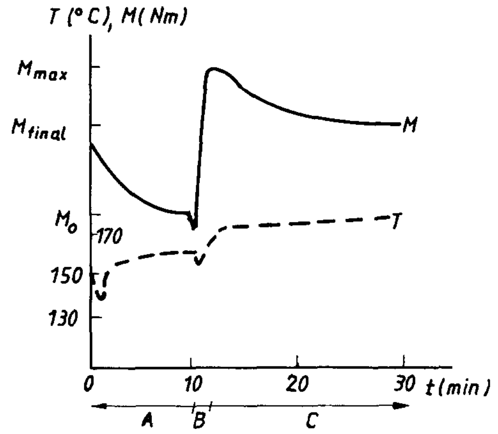

Figure 1. Torque and temperature vs. time curves of LA initiated PS/EPDM melt reaction

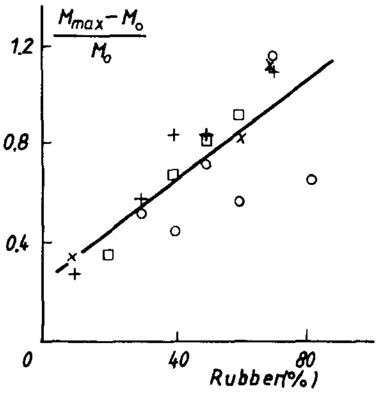

Figure 2. Relative torque maximum vs. initial rubber content

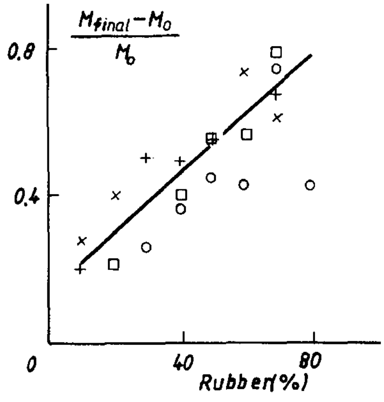

Figure 3. Relative final torque vs. initial rubber content

o:0.5-1.0; □:1.5-2.0; +:2.5-3.0; x:3.5-4.0 g Lewis acid. Symbols are the same in Fig. 2-8.

Figures 2 and 3 represent the $(M_{max}-M_o)/M_o$ and $(M_{final}-M_o)/M_o$ values as a function of the initial rubber content, respectively. It can be established that

- with increasing rubber content, the relative torque values increase. This is due to the fact that with increasing EPDM rubber content, the amount of double bonds also increases, which results in higher extent of coupling,
- at a given rubber content, increasing amount of the Lewis acid causes - to a certain extent - the increase of the

torque. This also can be explained by increased coupling. However, when the double salt is present in excessive quantity, degradation processes become dominant.

The fact, that the addition of the Lewis acid significantly increases the torque, proves that chemical reactions take place in the system. Also the extraction experiments support this statement: after the reaction, a part of the material cannot be solved either in petrolether or in methyl-ethyl-ketone.

As we have resumed in the introduction, several types of Friedel-Crafts reactions must be considered during the preparation of the mixture:

- coupling of rubber and PS molecules by grafting;
- degradation of rubber or PS;
- crosslinking via double bonds present in the rubber or formed during degradation;
- self-alkylation of PS molecules;
- isomerisation, etc.

Informations about the reactions can be obtained from the extraction results and from the infrared spectra of the products.

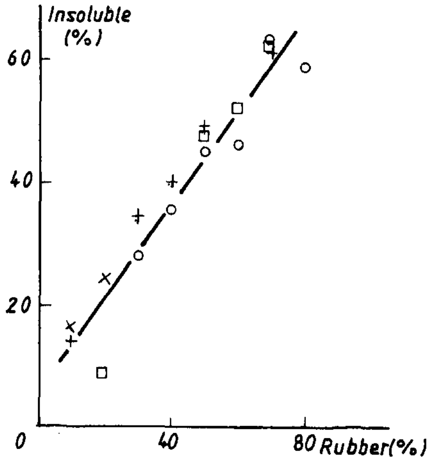

Figure 4. Relative amount of the insoluble fraction vs. initial rubber content

Figure 4 represents the relative amount of the fraction insoluble both in petrolether and MEK, as a function of the rubber content of the initial mixture. It can be observed that the quantity of the insoluble residue increases with increasing rubber content and it practically does not depend on the amount of the Lewis acid added.

In Fig. 5 and 6, the amount of the PS and rubber, respectively, incorporated into the insoluble product, is plotted as a function of the initial composition. These values were calculated from the amount of the unreacted PS and rubber which remained soluble in the adequate solvent during the extraction. (The results obtained from infrared spectra are in good aggreement with those of the extraction.)

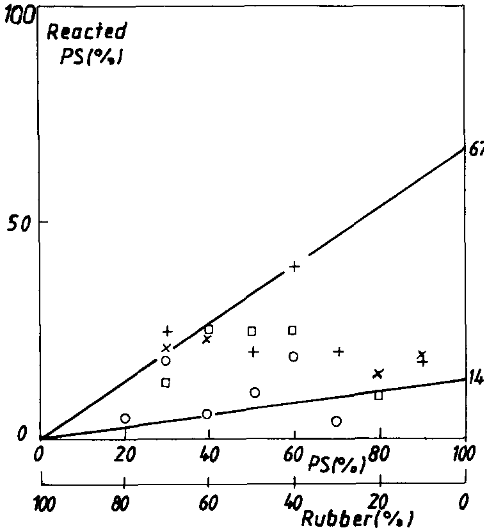

Figure 5. Amount of the reacted PS vs. initial PS content

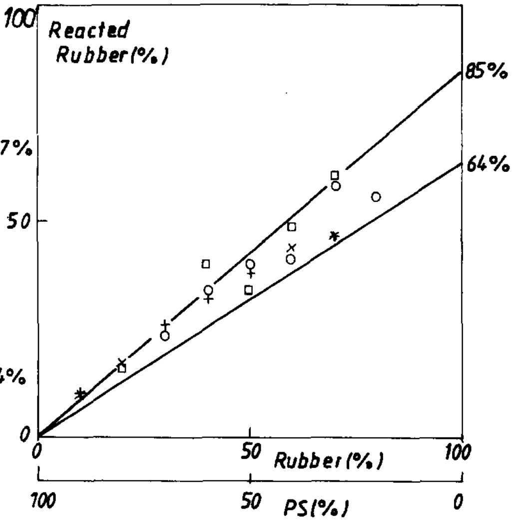

Figure 6. Amount of the reacted rubber vs. initial rubber content

It is obvious from Fig. 5 that the amount of the reacted PS varies between wide limits (~14-67 percent) and depends only slightly on the PS content of the mixture. In general, the effectiveness of coupling increases somewhat with increasing amount of the Lewis acid.

It can be seen from Fig. 6 that the amount of the rubber incorporated into the insoluble part linearly increases with the initial rubber content. The amount of the incorporated rubber is relatively high as compared to PS and changes between 64-85 %. Generally, the increase of the Lewis acid concentration decreases the amount of the incorporated rubber.

The greater reactivity of the rubber can be explained with the higher activity of its double bonds. In many cases, in particular when small quantity of Lewis acid is added, the product consists of crosslinked rubber containing no or only low amount of PS.

The torque vs. time curves and the analysis of the reaction products shows that the double bonds of the EPDM elastomer have a high reactivity and they can easily be crosslinked by the addition of a small amount of Lewis acid. The amount of reacted EPDM depends only slightly on the Lewis acid content (Fig. 6). The PS, on the contrary, reacts slowly but the amount of reacted PS increases with the Lewis acid content (Fig. 5). While EPDM crosslinks readily, PS mostly participates in coupling reaction; this is indicated by the fact that the PS content of the insoluble product increases with increasing rubber concentration (Fig. 5).

The mechanical properties of the reaction products, i.e., the Young's modulus and the tensile strength, have also been investigated.

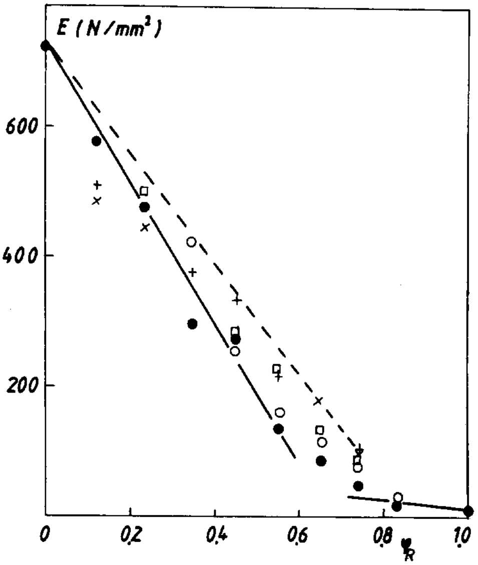

Figure 7. Young's modulus of non reacted and reacted mixtures as a function of initial volume fraction of rubber

Fig. 7 shows the dependence of the modulus on the volume fraction of the rubber in the initial mixture, according to [5]. It is clear that up to about 60 % rubber content the PS forms the continuous phase. With increasing Lewis acid and rubber content of the mixture, the modulus of the product also increases as compared to the modulus of the non reacted mixture.

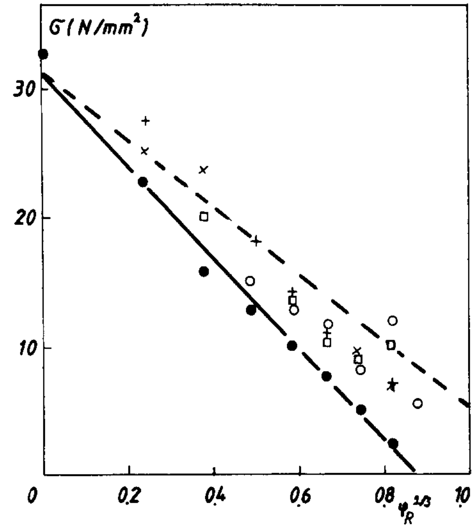

Figure 8. Ultimate tensile strength of non reacted and reacted mixtures as a function of the initial volume fraction of rubber

As shown in Fig. 8, the dependence of the tensile strength on the rubber volume fraction can well be described by the equation [6]:

$$\sigma = \sigma_o (1 - m\, \varphi_R^{2/3})$$

As a result of the reaction, the tensile strength increases i.e., the slope in the above equation decreases. The m=1.14 slope of the unreacted mixture (which is quite near to the theoretical value, m=1.21) decreases to the average value m=0.90, independently of the amount of the Lewis acid added. The higher the initial rubber content, the higher is the increase of the tensile strength.

The results of the tensile test can well be interpreted by the coupling of the rubber and PS molecules. The extent of coupling increases with increasing Lewis acid and rubber content. Assumingly, the solubility of the elastomer particles in the continuous PS phase increases as a result of the coupling. Increased solubility causes increased adhesion, thus the tensile strength increases too, and the phase transition occurs only at higher rubber contents.

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