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# Compatibilization effects in the thermal degradation of blends containing SAN and EPDM polymers

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Thermal degradation of blends containing SAN and EPDM was investigated and compared with that of graft EPDM-g-SAN copolymer molecules. Characterization of decomposition products and of degradation residues was carried out in order to reveal the differences in the degradation processes. With plain mixtures of SAN and EPDM, degradation behaviour is practically additive whereas in the case of EPDM-g-SAN lower volatile products and larger chain scissions are produced. The results can be explained by considering that the degradation process is influenced by the dispersion of the blend components. In phase segregated systems very few interactions take place between the different types of polymers, whereas in the graft copolymer molecular dispersion favours reactive interactions between the structurally different components. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

The continuously growing importance of polymer blends as materials with new or improved properties is determined by the large number of combinations achievable, in terms of structures, compositions and morphologies, when different polymers are mixed together. Improvements of polymer properties, particularly the mechanical ones, are sometimes obtained at the expense of other characteristics, e.g. the stability of polymeric components towards thermal stresses or weathering conditions. The investigation of polymer blends degradation behaviour is therefore necessary in order to determine the sustainable operating conditions and durability characteristics of the materials. A variety of polymer blends has been investigated from the point of view of their stability under different degradation conditions, and the principal results have been reviewed[1-3].

The majority of polymer blends are heterogeneous systems at molecular level, where the polymeric components are incompatible with each other. Their degradation behaviour may therefore depend not only on the characteristics of the pure components, but also on the structural and morphological modifications of the blend, which will affect the eventual chemical interactions between different components. In this respect, the presence of compatibilizing agents is expected to play an important role in determining blend degradation behaviour.

Investigation of thermal degradation of blends revealed that the chemical reactions taking place in multicomponent polymer systems lead to a number of different reaction patterns, with possible interactions between the macromolecular components themselves, or with their degradation products. When no interactions at all develop, the degradation behaviour of a blend is additive with respect to

that of the pure components, as has been shown to occur in the case of polymethylmethacrylate/polystyrene (PMMA/PS) blends[4]. In some cases the chemical interactions produce destabilizing effects, leading to acceleration of degradation rates, whereas in others the resulting effect is a stabilizing one. In general, the overall behaviour depends on the balance of effects induced in the different components by the blend structure and composition. The difference in degradation temperatures between the blend components is also important in influencing the overall material stability, producing both stabilizing and destabilizing effects, according to the structures involved. For example, in blends of PS with polyvinylidene chloride (PVDC)[5], polyacrylonitrile (PAN)[5], polybutadiene (PB)[6,7], and polyphenyleneoxide (PPO)[8], the decomposition of PS component occurs at temperatures higher than that of PS alone, due to deactivation of PS macroradicals through intermolecular reactions with structural units of the second component. In blends of PS with polyethylene glycol (PEG)[9], on the other hand, PS degradation is accelerated by reaction of PS chains with the small radicals produced in the PEG decomposition.

Blends of polyvinyl chloride (PVC) with PMMA or with polycarbonate (PC) show intermediate behaviour, in that the PVC component degradation is delayed, whereas the second component undergoes acceleration of its degradation reactions[10-13].

The optimum stabilizing effect in a blend is obviously obtained when degradation rates are slowed down, or decomposition temperatures shifted to higher values, for all the blend components. This situation has been found only in a few cases, one for example being that of PVC/PS blends[5]. However, if one of the blend components is stabilized and the second one is not negatively affected, its decomposition pattern being the same in the mixture and when it is alone, it may be stated that the blend is stabilized because, on the whole, the degradation reactions will take place at a rate slower than that expected on a pure additivity basis.

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The miscibility of blend components affects the degradation stability of the systems in a non-predictable manner. In some cases increased miscibility produces stabilizing effects, and in others destabilizing ones. With heterogeneous systems, on the other hand, the blend phase structure and the presence of compatibilizers influences the thermal stability of the material because of the different interactions which may develop at the phase boundary between components.

With AES blends, which are systems formed by ethylene propylene-diene (EPDM) rubbers dispersed into a glassy matrix of a styrene-acrylonitrile (SAN) copolymer, containing also SAN molecules grafted onto the EPDM rubber (EPDM-g-SAN) which act as compatibilizing agents between the two immiscible components, it has been shown that, during thermal degradation either in inert atmosphere or in oxidative conditions, chemical interactions between EPDM and SAN develop more easily within the graft copolymer molecules[14,15]. In thermo-oxidative degradation the process is controlled by the higher reactivity of EPDM chains in the graft copolymer, which induces an earlier starting of degradation reactions in the other parts of the blend[15].

In this paper are reported the results obtained in comparing the thermal degradation in the absence of oxygen of AES, i.e. of a compatibilized SAN/EPDM blend, of the graft copolymer EPDM-g-SAN, and of plain mechanical mixtures of SAN and EPDM. The investigation has been made through characterization of decomposition products and degradation residues, in order to elucidate the reactions taking place in the blends, and the mechanism of the process.

## EXPERIMENTAL

### Materials

AES was a mixture of SAN copolymer (24 wt% acrylonitrile), EPDM (ethylene 60%, 5-ethylidene-2-norbornene 9%), and EPDM-g-SAN graft copolymer (57% EPDM, 43% SAN). The weight composition of AES was: 60% SAN, 9.5% EPDM, 29.5% EPDM-g-SAN, 1% gel fraction.

An EPDM/SAN mixture, with the same ratio of components as in the graft copolymer, was prepared by dissolving in chloroform appropriate amounts of the two components.

### Degradation and characterization

Thermal degradation experiments were performed under high vacuum in a TVA apparatus[16], with temperature programming at 10°C/min heating rate, or isothermally at selected temperatures.

The volatile products formed in the degradation were condensed with liquid nitrogen, and analysed by GC (Carlo Erba, Fractovap 4160) coupled with a Perkin-Elmer 1710 FTi.r. spectrometer, or by GC-MS (Hewlett-Packard 5890). Oligomers and chain fragments (high boiling fractions: HBF) condensing in the degradation tube at the exit of the oven were quantitatively removed by dissolving in chloroform.

Structural analysis on HBF and polymer residues obtained from the thermal treatments was performed by FTi.r. Samples were in the form of films cast from chloroform solutions.

Molecular characterization was carried out by size

exclusion chromatography (SEC) in tetrahydrofuran at 1 cm³/min flow rate. The instrumental system was a Waters M45 pump, a Rheodyne 7010 injection valve with 150 μl injection loop, and an ERMA 7510 differential refractometer. Three PL gel columns (Polymer Labs), $10^5$ + $10^4$ + $10^3$ porosity and 5 μm particle size were used for separations. Chromstar PC based software (Bruker) was employed for data acquisition.

## RESULTS AND DISCUSSION

The TVA traces obtained from thermal degradations under vacuum with temperature programming up to 500°C, heating rate 10°C/min, of the AES blend, and of its principal components SAN and EPDM, are reported in *Figure 1*. SAN decomposition produces one rate curve only, with peak maximum at 420°C, due to the compounds volatile at room temperature and condensed in the liquid nitrogen cooled trap. EPDM, on the contrary, gives two curves: the larger peak is due to the evolution of total volatile products, whereas the smaller one is given by permanent gaseous products, such as hydrogen and methane, which are not condensed at the liquid nitrogen temperature. The temperature of maximum volatilization rate is 465°C for the main peak, and 475°C for the non-condensable gases. The AES blend has two rate curves, like EPDM, with peak temperatures near to 440 and 450°C.

When SAN and EPDM are mixed together in appropriate amounts, an equivalent EPDM/SAN blend is obtained with the same composition of the EPDM-g-SAN graft copolymer present in the AES system. In *Figure 2* the TVA traces are reported for the two cases. EPDM-g-SAN gives a curve similar to AES, whereas the EPDM/SAN mixture presents two stages in the formation of the total volatile products, partially superimposed and with peak temperatures located at *ca.* 425 and 465°C, in fair agreement with the peak temperatures of the two separate blend components. The lower traces, due to non-condensable gases, have peak temperature 475°C, like in EPDM, showing that permanent
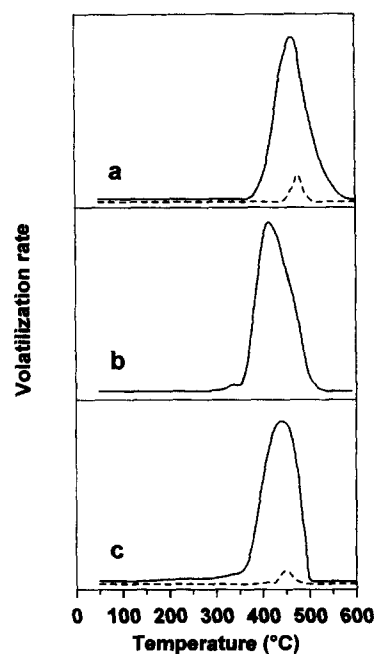
Figure 1 TVA curves of AES (a), SAN (b) and EPDM (c). Total volatiles: ———. Permanent gases: - - -
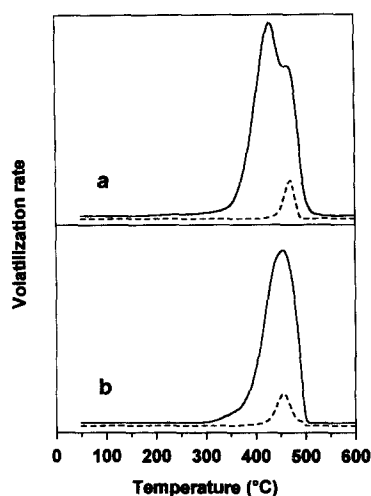
**Figure 2** TVA curves of EPDM/SAN mixture (a) and of EPDM-g-SAN copolymer (b). Total volatiles: ———. Permanent gases: - - -

gases are originated from decomposition of the rubbery part. This is also confirmed by the relative peak intensities of these gases, in *Figures 1 and 2*, which appear to be related to the different contents of EPDM.

The condensable volatile products obtained from the different samples were analysed by GC coupled with $F$Ti.r. The main products formed in EPDM decomposition were ethylene and propylene, together with lower amounts of branched hydrocarbons both aliphatic and olephinic in nature. From SAN degradation, styrene and acrylonitrile were the main products, together with minor amounts of aromatic compounds such as toluene, ethylbenzene and α-methyl styrene.

The same volatile compounds produced in the degradation of EPDM and SAN were also obtained in the decomposition of AES, of EPDM/SAN mixtures and of the EPDM-g-SAN graft copolymer, without any evidence of formation of products with different structures.

HBFs produced in the thermal degradation of the different samples, and condensed at the outlet of the oven, were collected and characterized by elemental analysis, $F$Ti.r. and SEC. Nitrogen contents of the HBFs obtained from total degradation of the separate components, of AES, and of the EPDM/SAN mixture, can be compared in *Table 1* with the values of the starting polymers. Such values reflect the acrylonitrile content, and it is seen that only in the HBF of the graft copolymer is a significantly lower amount of nitrogen containing units present, in comparison with the starting polymer. The structural differences between initial samples and their HBFs were revealed by $F$Ti.r. spectroscopy. As an example, the i.r. spectra of EPDM-g-SAN and of its HBF are reported in *Figure 3*, where the large decrease in the spectrum of HBF of the absorption characteristics of aromatic and nitrile structures may be seen.

The SAN content in the starting samples and in HBFs may be quantified through the ratio between the 2238 cm$^{-1}$

**Table 1** Acrylonitrile contents determined by $F$Ti.r. in initial samples compared with those of the chain fragments produced in thermal degradation of AES, EPDM/SAN blend and EPDM-g-SAN copolymer

| $A_{2238}/A_{1377}$ | AES | EPDM/SAN | EPDM-g-SAN |
|---|---|---|---|
| Initial | 0.57 | 0.42 | 0.41 |
| HBF | 0.55 | 0.24 | 0.13 |

absorbance, corresponding to −CN stretching, and that at 1377 cm$^{-1}$, due to −CH$_3$ symmetrical bending and used as an index of EPDM content. Such values are reported in *Table 1* for AES, for the EPDM/SAN mixture and for the EPDM-g-SAN graft copolymer. Whereas practically no change is found in AES, acrylonitrile content is about one half in HBF of the mixture of polymers, and less than one third in the graft copolymer. The above results show that in the contemporary complete degradation of SAN and EPDM chain fragments and oligomeric species deriving from EPDM chains predominate, and that this phenomenon is increased when the two polymers are linked together, as in the graft copolymer.

Similar conclusions are obtained from SEC analysis of the HBFs. In *Figure 4* are reported the chromatograms of the fractions recovered from the separate blend components, from the EPDM/SAN mixture and from the graft copolymer. Curves (a) and (b), relative to EPDM and SAN respectively, show two characteristic fragment distributions, centered at different elution volumes. From EPDM degradation a mixture of fragments with relatively
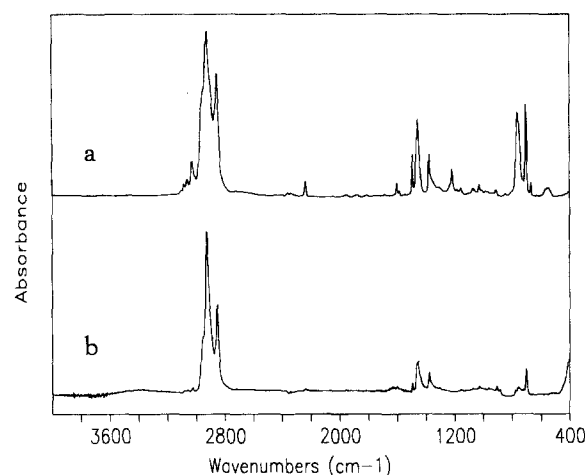


**Figure 3** $F$Ti.r. spectra of EPDM-g-SAN (a) and of high boiling fraction (b) formed in complete thermal degradation under vacuum
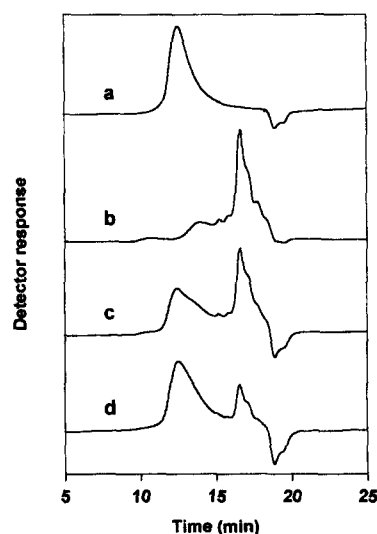


**Figure 4** SEC chromatograms of high boiling fractions obtained from complete thermal degradation of EPDM (a), SAN (b), EPDM/SAN (c) and EPDM-g-SAN (d)

high molecular weight is produced, which is responsible for the broad peak eluting with maximum at 12.5 min. The HBF of SAN, on the other hand, contains oligomers having lower molecular weights whose main components, formed by depolymerization reactions, are dimers and trimers[17]. The trimer with two styrene and one acrylonitrile unit (molecular weight 261) is responsible for the peak eluting, in chromatogram (a) of *Figure 4*, at *ca.* 17 min[18]. The chromatograms of the fractions derived from AES, EPDM/SAN and EPDM-g-SAN appear to be formed by the superimposition of the two different distributions, the first at lower retention times, due to fragments arising from decomposition of the rubber part and the second, at higher retention times, having the characteristic shape produced by SAN oligomers[18]. It also appears that the HBF obtained from the graft copolymer (*Figure 4d*) contains a higher proportion of fragments from EPDM.

The fractional areas of species eluting between 10 and 15 min retention times may be used as a rough measure of the products formed by the degradation of the EPDM part. The values are 19% in the case of AES, 27% in EPDM/SAN mixture, and 57% in the EPDM-g-SAN copolymer. The largest compositional difference is again found between the simple mixture of EPDM and SAN and the graft copolymer. It is therefore evident that the different behaviour is not induced by the chemical composition, which at the beginning is the same. The main difference between the two polymer systems is their morphology: in the mechanical mixture the immiscible EPDM and SAN molecules are more segregated, whereas in the graft copolymer the level of dispersity is higher, and there is a much larger number of heterocontacts between the two components. When the temperature increases, SAN fractions start to degrade first, with production of radicals. If such radicals are in close contact with EPDM molecules, as they must be in the case of the graft copolymer, they will easily deactivate through hydrogen transfer from EPDM. The macroradicals therefore formed on the rubber will induce chains scission of the EPDM molecules, and the overall degradation will then take place at temperatures lower than that of pure EPDM molecules. The higher number of EPDM chain scissions, induced by the radicals formed on the SAN units, will produce higher amounts of the oligomeric species and fragments forming the HBF.

The different behaviour between degradation of the SAN/EPDM blend and that of the graft copolymer has been further pointed out by performing isothermal treatments under vacuum, at selected temperatures, where polymer residues and degradation products have been collected and analysed.

Polymer weight losses and the quantities of products formed in the degradation of the two systems at 350°C for treatment times up to 3 h are shown in *Figure 5*. The initial volatilization rate of the graft copolymer (*Figure 5b*) is lower than that of the blend (*Figure 5a*); the weight loss at the end of the treatment is also lower. In both cases the quantity of volatile products is lower than the high boiling fractions. Analysis by GC-MS of the volatile products showed that from the SAN/EPDM blend the main compounds which are formed are the monomers (styrene and acrylonitrile) and oligomers arising from the degradation of the SAN part. From the same treatment of EPDM-g-SAN a larger number of volatile compounds is obtained, styrene still being the main product, together with a variety of aromatic and nitrilic mixed structures, and compounds produced by decomposition of the rubber part.

Confirmation that the degradation patterns of SAN/EPDM blend and of the graft copolymer molecules are different emerges from *F T*i.r. and SEC results on the HBFs and on the polymeric residues obtained after the treatments at different times. The infrared spectra of SAN/EPDM blend residues show a decrease of the SAN content with increasing heating time. In *Figure 6* the i.r. spectra of the blend and of the residue after 2 h treatment are shown: in the residue absorptions due to SAN structures are almost absent, whereas the spectral features of EPDM remain practically unchanged. Under these conditions low molecular weight fragments from EPDM chains were not produced, as can be seen from the fact that the i.r. spectra of the HBFs obtained from blend treatments showed exclusively absorptions related to SAN structures.

In the residues from degradation of the graft copolymer, even after the longest treatment (3 h), SAN related absorptions are still present, as can be seen in *Figure 7*, whereas the spectra of the HBFs show the presence of an absorption at 1377 cm$^{-1}$ deriving from the EPDM part of the graft copolymer. It may therefore be concluded that at temperatures below weight loss due to EPDM molecules
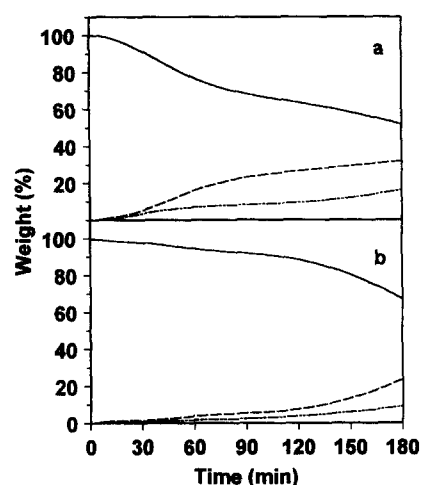


**Figure 5** Weight losses and amount of products formed as a function of time in the degradation under vacuum at 350°C of: (a) EPDM/SAN; (b) EPDM-g-SAN. Weight loss: ——; high boiling fractions: - - -; volatile compounds: — - - —
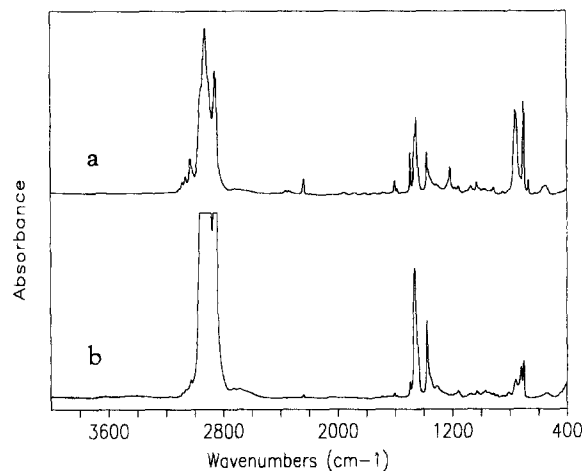


**Figure 6** *F T*i.r. spectra of EPDM/SAN (a) and of blend residue after 120 min degradation at 350°C (b)
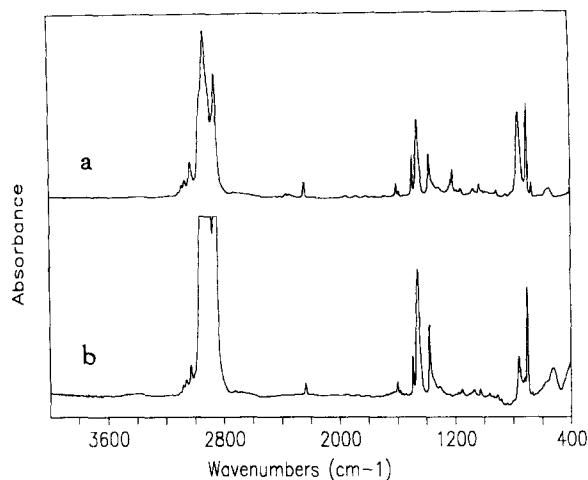
**Figure 7** Comparison of *FT*i.r. spectra of EPDM-g-SAN (a) and of residue after 180 min degradation at 350°C (b)
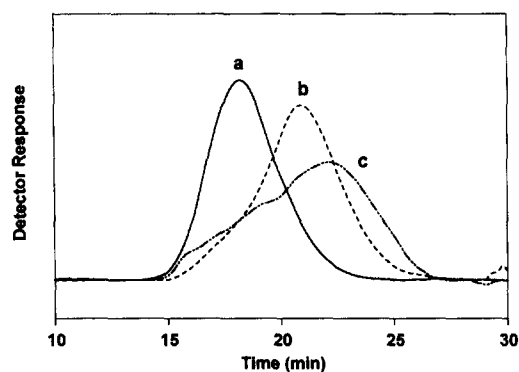


**Figure 8** SEC curves of SAN/EPDM blend before (a) and after degradation at 350°C for 60 min (b) and 180 min (c)
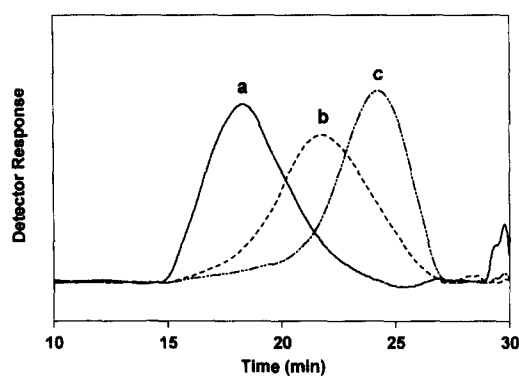


**Figure 9** SEC curves of EPDM-g-SAN before (a) and after degradation at 350°C for 60 min (b) and for 180 min (c)

decomposition, degradation of SAN/EPDM blend is practically limited to the SAN depolymerization, whereas in the same conditions the rubber part of the EPDM-g-SAN molecules is already affected by decomposition reactions.

All the residues obtained from the treatments at 350°C from the SAN/EPDM blend as well as from the graft copolymer were completely soluble and were studied by

SEC. In *Figure 8* the chromatogram of the initial SAN/EPDM blend is reported, together with those of the residues at 350°C after 60 and 180 min heating. A molecular weight decrease is seen to have occurred in the degraded samples, and this has taken place in the EPDM component as well, which is the only one present in the residue at 180 min. The same effect of molecular weight decrease can be seen from the results of *Figure 9*, relative to the EPDM-g-SAN residues. In this case the molecules still contained SAN structures, even at the longer treatment time. A comparison between *Figures 8* and *9* shows that more chain scissions took place in the graft copolymer than in the blend.

## CONCLUSIONS

The thermal degradation of blends containing SAN and EPDM molecules is influenced by the level of phase dispersion between these two non-compatible polymers. When the two components are mixed at a molecular level, as in the EPDM-g-SAN molecules, radical transfers from one structure to the other are favoured. As a result, chain scissions increase and the amount of low molecular weight volatile compounds decreases. This could be explained by the reduction of SAN chains depolymerization, together with a contemporary increase of chain scissions in EPDM molecules.

## ACKNOWLEDGEMENTS

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