MODIFICATION OF PROPYLENE-ETHYLENE COPOLYMERS BY REACTIVE EXTRUSION

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Abstract: The rheological properties of commercial propylene-ethylene copolymers were modified by reactive extrusion. A dialkyl peroxide was used as initiator of the controlled degradation reaction of the starting polymers. The experiments were carried out in a twin screw extruder at different peroxide concentrations, temperatures, and screw speeds. Gel permeation chromatography was used to estimate the molecular weight distribution of the original and modified copolymers. It has been observed that the estimated molecular weight of the copolymers tends to decrease with the increase in peroxide concentration at all extrusion conditions studied. The linear viscoelastic properties of all the polymers were evaluated at different temperatures and frequencies in a rotational rheometer. Both the viscous and the elastic properties decrease with augmenting peroxide concentration. The rheological behavior of the materials is strongly affected by the global ethylene content of the copolymers. The scanning electron microscopy study did not reveal a significant difference between the morphology of the unmodified and the modified blends for a given composition of the original copolymers. In all the cases the microstructure is composed of a finely dispersed phase of ethylene-propylene copolymer within a continuous polypropylene phase.

INTRODUCTION

Propylene-ethylene copolymers (PEC) based on new catalyst systems and polymerization technologies have been recently introduced in the market (Ref. 1). They are a complex mixture of propylene homopolymer, poly-(propylene-co-ethylene) and polyethylene. These copolymers have relatively large molecular weights and broad molecular weight distribution

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which make their processing difficult due to the high melt viscosity and elasticity. To improve the flow properties it is necessary to reduce their molecular weight. The aim of this work is to obtain information on the phenomenon that occurs during the modification of the propylene-ethylene copolymers by reactive extrusion. This method has been used commercially for many years to modify polypropylene homopolymers (Refs. 2-6). It takes advantage of the random chain scission process of the polymer molecules initiated by free-radicals generated by the decomposition of organic peroxides that are added to the polymer during the extrusion process. As a consequence of the reactive extrusion, the resulting polymer has lower molecular weight, narrower molecular weight distribution, lower viscosity, and better processing properties.

In this study we analyze the effect of processing conditions and peroxide concentration on the molecular weight distribution, the melt rheological properties and the microstructure characteristics of PECs.

EXPERIMENTAL

Two commercial copolymers having a global ethylene content of 2.8% (PEC1) and 16.4% (PEC2) were used in this study. They were supplied by Petroquímica Cuyo S.A. in the form of pellets. The 2,5-dimethyl (2,5-bisterbutyl) peroxy-hexane (DDTBP) was used as initiator of the degradation process. The resin pellets were impregnated with a diluted solution of peroxide to give a final concentration on weight base of 200, 400 and 600 ppm, after removing the solvent.

The reactions were carried out in a Göttfert, 35 mm, counter-rotating twin screw extruder. The temperature in all the extruder sections was controlled to obtain isothermal operation at 197, 207 and 217°C. Experiments were performed at constant screw rotational speed of 20 and 60 rpm which give mass flow rates of approximately 6 and 18 kg/h, respectively.

Gel permeation chromatography (GPC) was used to estimate the molecular weight distribution and the average molecular weights of the original and the modified copolymers. The analysis was carried out in a Waters-150-C ALC-GPC equipped with a set of 10 μm PLG-gel columns from Polymer Laboratories having nominal porous size of 10^6, 10^3 and 500 Å. The solvent used was 1,2,4-trichlorobenzene (TCB) at 140°C. The molecular weights of the PECs were estimated by standard calibration with polystyrene samples of narrow molecular weight distribution and using Mark-Houwink coefficients for polystyrene and polypropylene in TCB. This procedure does not provide absolute molecular weight measurements but it is useful to analyze the relative change in molecular weights and molecular weight distribution

of the polymers.

Part of the original and the processed materials were molded into sheets of approximately 0.2 cm thick using a thermostatized hydraulic press. Discs of 2.5 cm diameter were cut from the sheets to examine the dynamic properties of the melts. A rotational rheometer from Rheometrics (RDA-II) was used for this purpose in the parallel plate mode. Measurements were made in small-amplitude oscillatory shear flow (Ref. 7). The dynamic storage and loss moduli, $G'(\omega) = \omega\eta''(\omega)$ and $G''(\omega) = \omega\eta'(\omega)$ respectively, were determined in the linear viscoelastic range of strain. Frequencies were ranged from approximately 5×10^{-3} up to 500 s^{-1}, and temperatures from 187 to 227 °C.

Samples of all the extruded materials were cut to analyze their morphology. They were fractured in two halves at liquid nitrogen temperature. Contrast between the continuous matrix and the dispersed phases was obtained by selective extraction of the soluble material. One half of each fractured sample was placed in hexane at room temperature for 24 h and then dried to remove the solvent. Micrographs of the fractured surfaces of the untreated and the hexane-treated halves were obtained using a Jeol 35 CF scanning electron microscope (SEM). The analysis was done using a voltage of 5 kV and with an incident beam that was perpendicular to the surface.

RESULTS AND DISCUSSION

Figure 1 displays the GPC traces of the original PEC2 copolymer and those of the corresponding modified materials after extrusion with different peroxide concentrations. The chromatogram of the resin extruded without peroxide is also included in this figure. These chromatograms illustrate the effect of peroxide concentration on the molecular weight distribution of PEC. An increment on peroxide concentration shifts the low elution volume tail of the distributions, i.e. the high molecular weight region, toward higher elution volumes. At the same time, the high elution volume tail, i.e. the low molecular weight region, remains practically unaffected. Similar results were obtained under all processing conditions for both copolymers.

The weight- and number-average molecular weights, Mw and Mn, were estimated from the GPC traces by standard calibration using Mark-Houwink coefficients for polypropylene in TCB. This procedure allows the estimation of relative molecular weight parameter which is helpful for the qualitative comparison of the copolymers in terms of the compositional changes of species with different molecular structure. Table 1 includes, as an example, the relative Mw and Mn results obtained for copolymers processed at 60 rpm and 217 °C. To

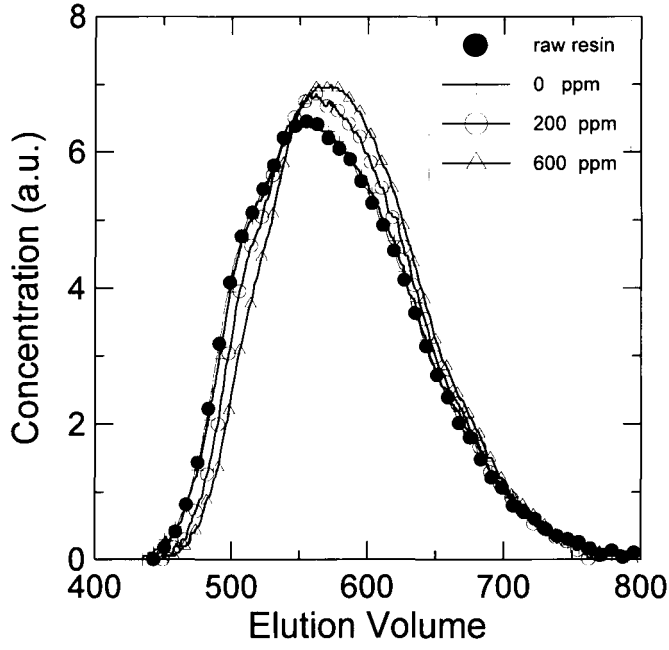


Figure 1. GPC traces of the original PEC2 copolymer and of the modified materials processed at 60 rpm and 217°C with different peroxide concentrations

Table 1. Estimated molecular weights of the polymers modified at 60 rpm and 217°C

	PEC1		PEC2	
Peroxide concentration	Mw	Mn	Mw	Mn
raw resin	201000	53500	298000	69000
0 ppm	199000	50000	297000	67000
200 ppm	190000	53000	243000	68000
400 ppm	162000	46000	232000	61000
600 ppm	164000	45000	210000	61000

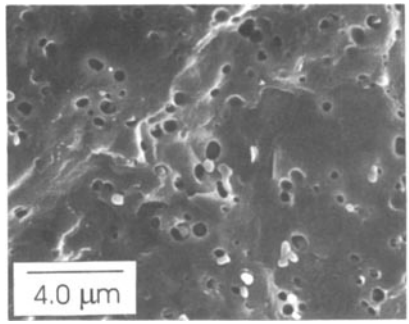
analyze the possible degradation effect of the shear flow that exists inside the extruder, both copolymers were also extruded without the addition of peroxide under all the processing conditions. These experiments were classified as runs with 0 ppm peroxide concentration. From these tests, no significant changes were observed in the molecular weight of the polymers. This result implies that the copolymers are not noticeably affected by the processing conditions and that all the molecular weight modifications are due to the addition of the reactive peroxide.

All the modified resins show molecular weights lower than the mother polymers under every processing condition. The relative molecular weights decrease with an increase in the concentration of peroxide. These results suggest that main chain scission is the dominant reaction in the reactive extrusion of these copolymers.

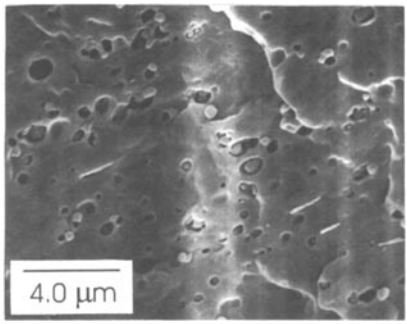
It is known that the components of these copolymers separate into distinct phases (Ref. 4). The morphology is characterized by a dispersed phase and a continuous phase. The continuous phase, called matrix, consists of a propylene-rich polymer while the dispersed phase is formed by an ethylene-rich polymer phase surrounded by a rubber-like interface where the polymer may have different proportions of both monomers. The final properties of these resins depend in great extension on the amount, size, and distribution of the dispersed phase (Ref. 4). The last two factors are controlled by the processing conditions and the flow properties of the individual components of the mixture.

The micrographs shown in Fig. 2 correspond to fracture surfaces of samples treated with hexane. They were chosen as example to illustrate the microstructure observed in these copolymers. The components separate into distinct phases, a matrix and a discrete dispersed phase. This is true for the original copolymers and the modified resins. The extraction of part of the elastomeric interface produces a fracture-surface with many dispersed cavities. The part of the dispersed phase corresponding to the ethylene-rich polymer, can be distinguished as spheroid-shaped particles lying on the surface or placed inside the cavities. The density of the dispersed phase is higher in PEC2 than in PEC1 which can be expected from the global ethylene concentration of these materials. The size of the dispersed phase coincides with that observed in a typical reactor polymerized rubber-modified polypropylene (Ref. 4). The dimension of the largest particles is about 1μm long. The SEM study suggests that the reactive extrusion process does not alter significantly either the average particle size or the homogeneity of the particle distribution within the matrix. No evidence was found of a dependence of the microstructure with the processing conditions, i.e. temperature and flow rate.

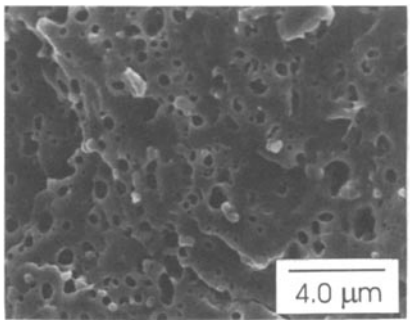
The elastic and viscous moduli $G'(\omega)$ and $G''(\omega)$ or, equivalently, the viscous and elastic



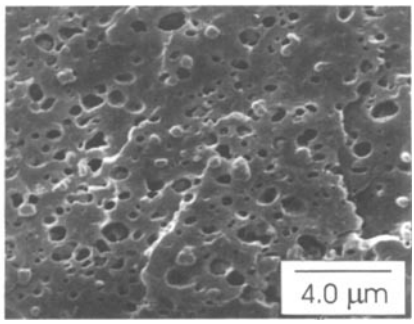
PEC1 - Extruded with no peroxide



PEC1 - Extruded with 600 ppm



PEC2 - Extruded with no peroxide



PEC2 - Extruded with 600 ppm

Figure 2 - SEM images of fractured samples of the copolymers extruded with no peroxide and with 600 ppm peroxide concentration

parameters $\eta'(\omega)$ and $\eta''(\omega)/\omega$ (Ref. 7), of the original copolymers and of all the processed materials were measured at five different temperatures between 187 and 227°C. From these data, master curves of dynamic parameters at 187°C were obtained as a function of the frequency. Good superposition of the results was obtained in all the cases except for the PEC1 data at the higher frequencies ($\omega > \sim 70\ s^{-1}$), where a gradual dispersion of the data with temperature was observed. This effect, which is typically found in the time-temperature superposition of blends, was not observed in the PEC2 polymers in the frequency range covered by this study.

Figure 3 shows the master curves of the linear viscoelastic parameters at 187°C obtained for both copolymers and the modified materials at 60 rpm and processing temperature of 197°C.

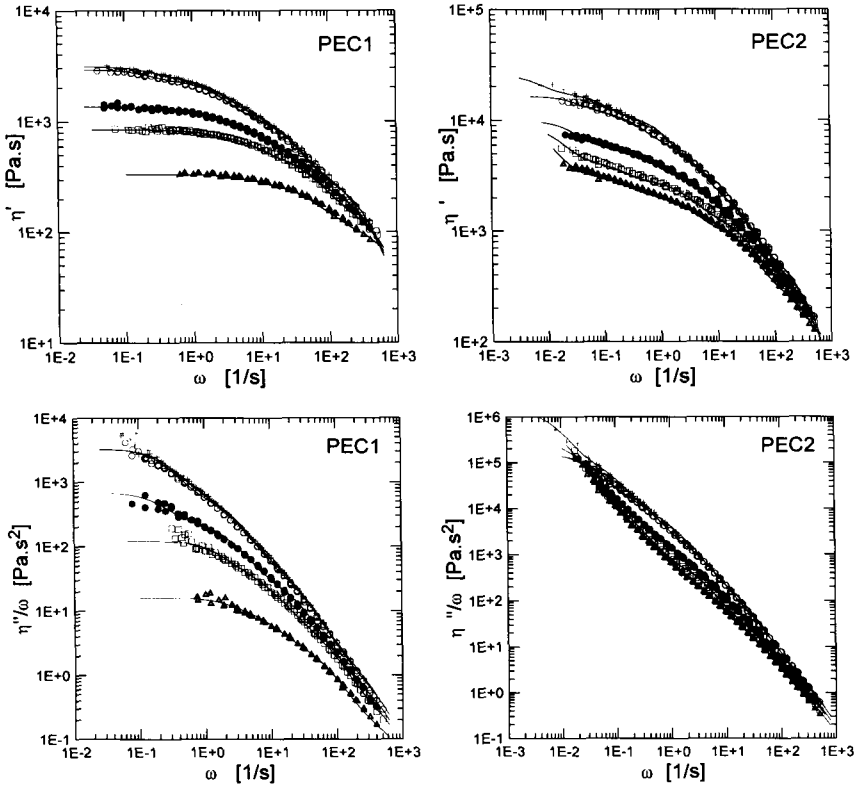


Figure 3 - Master curves of the dynamic properties η' and η''/ω of both copolymers at T=187°C. Full lines correspond to the predictions of the 4-mode Maxwell model with the coefficients shown in Fig. 4. Each plot includes data of the original polymers (+) and the extruded materials with 0 (○), 200 (●), 400 (□), and 600 (▲) ppm of peroxide.

The slightly dispersed data of PEC1 at high frequencies are not included (only the data obtained at 187°C and the smaller temperatures were plotted in this region of the spetra) to avoid confusion in the plots. Equivalent results were obtained with the materials extruded at 20 rpm and other processing temperatures. The results obtained for the extruded materials with no added peroxide are very similar to the measured data for the mother polymers. This result confirms the information obtained from the GPC measurements indicating that there is no change in the molecular structure of the copolymers caused by the extrusion itself. All the modified polymers have lower viscosity than the original copolymers in the frequency

range analyzed. Both the dynamic viscosity $\eta'(\omega)$ and the elastic parameter $\eta''(\omega)/\omega$, are found to decrease farther away from the original data of the mother polymers as the concentration of the peroxide increases. But a qualitatively different behavior is observed in both polymers. The PEC1 and the corresponding modified materials present, in the covered frequency range, the typical behavior of a melt with a monotonic decrease of both visco-elastic parameters as the frequency increases. On the other hand, PEC2 and the corresponding modified polymers present a smaller decrease with peroxide concentration at the smaller frequencies than at intermediate frequencies. Independently of the peroxide concentration used, all the materials seem to have the same viscous and elastic moduli at small and very high frequencies. The degradation affects only the response of the materials at intermediate frequencies.

To further analyze this observed effect, the master curves were fitted with the multi-mode Maxwell model (Ref. 7) using 4 and 5 modes for the family of curves of the PEC1 and PEC2 copolymers respectively. This model predicts that:

$$\eta'(\omega) = \sum_{i=1}^{N} \frac{\eta_i}{1+(\lambda_i\omega)^2} \qquad \frac{\eta''(\omega)}{\omega} = \sum_{i=1}^{N} \frac{\eta_i\lambda_i}{1+(\lambda_i\omega)^2} \qquad \textbf{(1)}$$

where λ_i and η_i are the relaxation time and the zero-shear-rate viscosity corresponding to the i^{th} component of the stress. The spectra $\{\lambda_i , \eta_i\}$ of each material is obtained by fitting the experimental data in the curves of Fig. 3 to eqs. (1) using the Levenberg-Marquard nonlinear regression method. The calculated coefficients characterize the viscoelastic behavior of the materials in the range of frequencies of the rheological measurements. The number of modes was chosen to be the minimum number necessary to obtain a smooth fit of the data. The λ_i and η_i that gave the best fit are plotted in Fig. 4. In the case of PEC1, as the peroxide concentration increases, the contribution of all four modes to the viscoelastic properties of the materials decreases. This effect is stronger in the modes with larger relaxation times which may be associated to the propylene-rich polymer. An equivalent behavior is found in the PEC2 materials in the modes with relaxation time smaller than 10 s. A larger relaxation time appears in all the PEC2 materials (λ > ~1 min) which may be associated with the macroscopic structure of the blends. In this case the blends are richer in ethylene and have a larger amount of the dispersed phase than in the case of the PEC1 family of copolymers. It is interesting to notice that this larger mode has a practically constant contribution to the viscoelastic properties for all the polymers that belong to the PEC2 family.

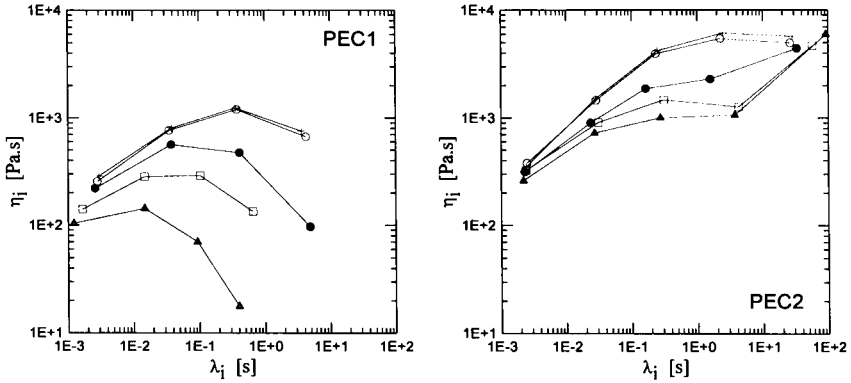


Figure 4 - Spectrum of relaxation times obtained by fitting the data of the master curves of Fig. 3 to the multi-mode Maxwell model. Each plot includes the results of the original polymers (+) and the extruded materials with 0 (○), 200 (●), 400 (□), and 600 (▲) ppm of peroxide.

CONCLUSIONS

Propylene-ethylene copolymers were modified by reactive extrusion using a dialkyl peroxide to induce their controlled degradation. Experiments were carried out in a twin screw extruder at different processing temperatures, peroxide concentrations, and screw speeds. The morphological and rheological results obtained in this study may be summarized as follows:

- Materials with narrower molecular weight distribution and lower weight and number-average molecular weights were obtained under all processing conditions with increasing concentration of peroxide. As expected, the random degradation process affects primarily the higher molecular weight molecules narrowing the low elution volume side of the GPC traces.

- The morphology of the original and the modified copolymers is very similar, as revealed by SEM. The components having different molecular structure separate into distinct phases. The microstructure is composed of a finely dispersed phase within a matrix. There are no significant differences between the original and the modified copolymers in either particle size of dispersed phase or phase distribution within the matrix.

- The modified copolymers display lower viscosity and elasticity than the original materials. The higher the concentration of peroxide used, the lower the viscoelastic parameters in the range of temperature and frequencies studied.

- The controlled degradation of the copolymers seems to have a similar effect on both PECs families at relaxation times up to 10 s. The global results of this study suggest that this behavior corresponds to the propylene-rich matrix phase. In the range of small frequencies (larger relaxation times) there are important differences in the rheological behavior of the two families of copolymers. These differences may be attributed to the contribution of the dispersed phase whose proportion is larger in the PEC2 family of copolymers.

This work will be continued with further analysis of the morphological and rheological properties of these copolymers and some others of different composition. The study of equivalent blends prepared in the laboratory with components of known structure and molecular properties is also in progress to further explore the distinct alteration of the relaxation spectra when copolymers with higher content of ethylene rich phase are modified by reactive extrusion.

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