

# Elastomeric Conducting Systems Based on Ethylene–Propylene–Norbornene Composites

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Received 8 February 2000; accepted 23 June 2000

**ABSTRACT:** This work reports the preparation and structural and electrical characterizations of composites consisting of ethylene–propylene–norbornene, polypropylene, and carbon black (CB) blends, comparing the data obtained from crosslinked and noncrosslinked samples. Structural analysis provided evidence of the reinforcing effect of CB on the properties when present in the initial system, as well as of the excellent conducting properties of CB composites. This, together with their mechanical properties and their extraordinary processing ease, makes them suited as bipolar plates in fuel cells based on polymeric electrolyte. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2136–2145, 2001

**Key words:** ethylene–propylene–norbornene; polypropylene; blends; differential scanning calorimetry; dynamomechanical analysis; impedance spectroscopy

## INTRODUCTION

Fuel cells<sup>1–4</sup> are devices capable of converting the chemical energy stored in a fuel, generally in the form of hydrogen, into electric energy through electrochemical reactions. The performance level achieved by these devices may surpass 50%. Actually, these fuel cells consist of a series of unit cells, separated one from the other by bipolar plates to allow gas diffusion.

There exist several types of fuel cells, classified according to their operating temperature and the type of electrolyte used. In the automotive industry, however, the most promising fuel cells are based on polymeric electrolytes, due to their low operating temperature (60–80°C), their high energy density as related to their weight and volume, and their high performance (around 60%), with the additional advantage that they do not

have any mobile parts, which reduces the noise level to a minimum during operation.

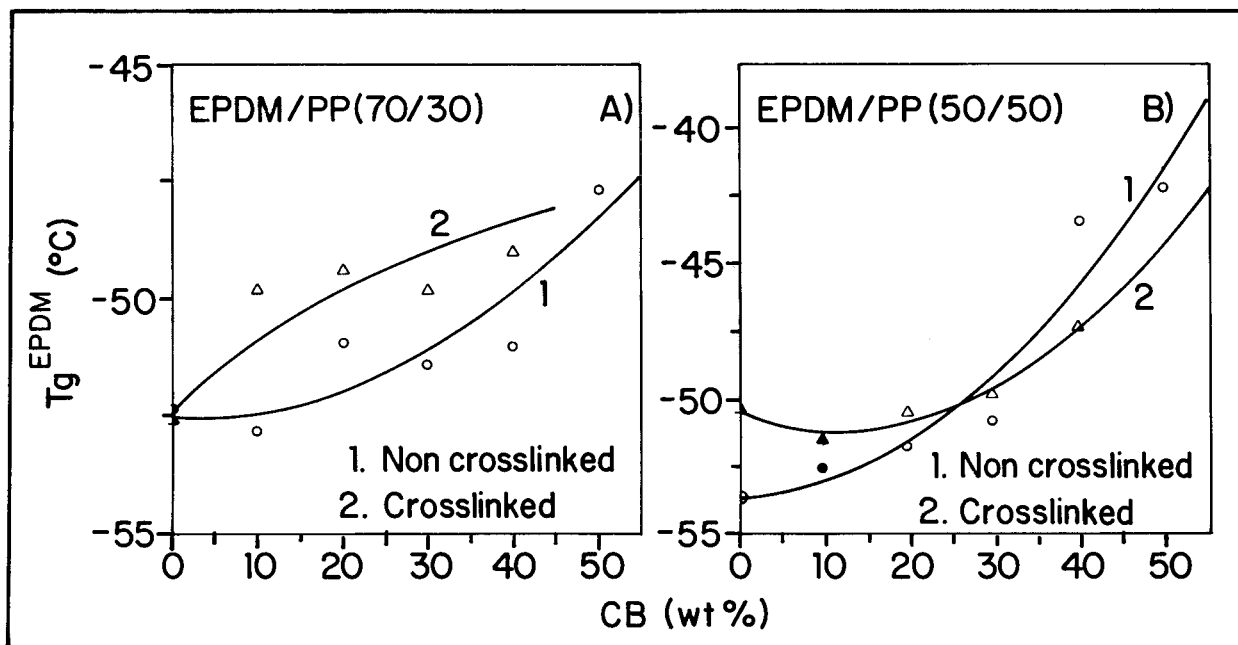
One of the most important components of a fuel cell are the bipolar plates.<sup>5–9</sup> At present time they are manufactured from raw graphite. But due to the drawbacks deriving from this material, in the near future projects to replace it by other materials will be implemented with the purpose of making these plates more feasible from a functional and economic point of view. In this work we develop a material, based on polymers and capable of replacing graphite. It is a polymeric composite possessing high electron conducting properties, good thermomechanical properties, and excellent chemical stability; above all, it is a low cost product.

At the present state of the art the successful obtention of these systems (polymeric composites filled with conducting additives) depends on the adequate choice of the polymeric host. Contrary to the predominant opinion some years ago, the polymeric matrix is not only the network supporting the filler. Moreover, it plays an essential role in many other aspects conditioning the perfor-

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Contract grant sponsor: Regional Government of Madrid.

*Journal of Applied Polymer Science*, Vol. 79, 2136–2145 (2001)  
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**Figure 1** DSC analysis:  $T_g^{\text{EPDM}}$  as a function of CB concentration: (A) EPDM/PP (70/30) and (B) EPDM/PP (50/50).

mance of the end material: It influences particle interconnectivity (percolation); it provides for electrical conductivity through a tunnel-type mechanism in the event of deficient percolation; it tolerates the incorporation of large amounts of additive with no deterioration of its mechanical properties, thus potentially favoring both, the conductor mechanisms and the dimensional stability of the resulting composite.

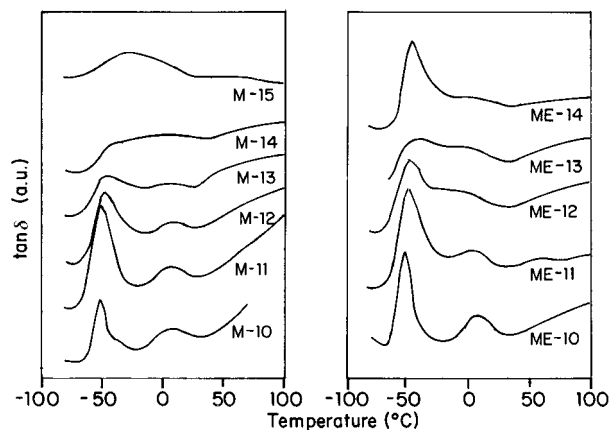
In this research ethylene-propylene-norbornene (EPDM) and polypropylene (PP) blends were used,

incorporating varying amounts of carbon black. The composites thus obtained are characterized from a microstructural ( $T_g$ , crystallization kinetics, etc.) and electrical point of view in order to know their suitability to be used as bipolar plates in polymer fuel cells.

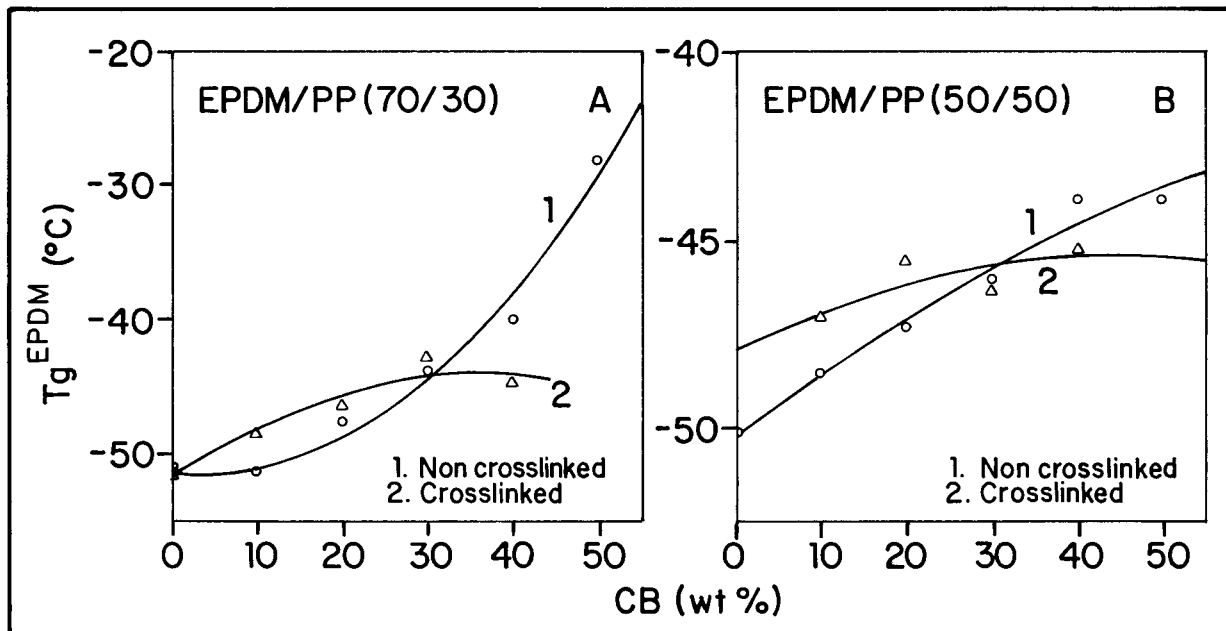
## EXPERIMENTAL

EPDM terpolymer containing 46.5% ethylene, 50% propylene, and 3.5% norbornene was Dutral Ter 054E from Enichem. Isotactic PP was IS-PLLEN PP-050 supplied from Repsol Químicas and carbon black was Black Pearls 2000 supplied by Cabot.

Blends were prepared in a Rheomix 600-Haake with Banbury type rotors at 175°C blending temperature. They were carried out with the simultaneous incorporation of the EPDM and PP into the blending camera; carbon black was incorporated after PP was melted; blending time was roughly 12 min. The crosslinked samples were carried out following the same procedure, but incorporating several curing agents: ZnO (5%), stearic acid (1%), tetramethylthiuram disulphide (TMTD) (1%), 2,2'-Dibenzothiazyl disulphide (MBTS) (0.5%) and sulfur (2%). Blending time was 20 min.



**Figure 2** Dynamomechanical spectra of different samples measured at 5 Hz.



**Figure 3** DMA analysis:  $T_g^{\text{EPDM}}$  as a function of CB concentration: (A) EPDM/PP (70/30) and (B) EPDM/PP (50/50).

**Table I** Crystallization Kinetic Parameters Through DSC Measurements

Samples	Composition (% wt)		$T_c$ (K)	$T_m$ (K)	$n$	log $K$ ( $\text{min}^{-n}$ )
	EPDM/PP	CB				
M-00	70/30	0	401	439.4	2.57	-2.148
			402	439.4	2.57	-2.340
			403	439.1	2.57	-2.756
			404	439.4	2.73	-3.326
M-01	70/30	10	401	437.9	2.59	-1.182
			402	438.4	2.76	-1.543
			403	438.6	2.71	-1.791
			404	439.0	2.71	-2.074
M-02	70/30	20	401	438.0	2.68	-0.981
			402	438.0	2.65	-1.147
			403	438.5	2.67	-1.405
			404	438.5	2.72	-1.700
M-03	70/30	30	403	438.0	2.44	-1.247
			404	438.0	2.44	-1.496
			405	438.5	2.35	-1.680
			406	438.5	2.39	-1.935
M-04	70/30	40	403	437.6	2.08	-1.143
			404	437.6	2.10	-1.374
			405	437.6	2.26	-1.730
			406	438.1	2.23	-1.928
M-05	70/30	50	403	435.7	2.40	-1.756
			404	436.2	2.06	-1.648
			405	436.3	2.32	-2.264
			406	436.2	2.36	-2.523

**Table II Crystallization Kinetic Parameters Through DSC Measurements**

Samples	Composition (% wt)		$T_c$ (K)	$T_m$ (K)	$n$	log $K$ (min <sup>-n</sup> )
	EPDM/PP	CB				
M-10	50/50	0	401	438.4	3.03	-2.235
			402	438.8	2.95	-3.393
			403	438.8	3.13	-2.938
			404	438.7	2.68	-2.728
M-11	50/50	10	402	438.8	2.60	-1.115
			403	438.8	2.81	-1.468
			404	439.3	2.81	-1.717
			405	439.3	2.86	-2.025
M-12	50/50	20	403	439.2	2.61	-1.386
			404	439.7	2.66	-1.656
			405	439.7	2.78	-2.006
			406	439.7	2.75	-2.187
M13	50/50	30	404	438.5	2.57	-1.631
			405	438.5	2.53	-1.790
			406	439.0	2.56	-2.025
			407	439.0	2.78	-2.570
M-14	50/50	40	404 <sup>a</sup>	437.0	2.23	-1.452
			407	438.1	2.32	-1.719
			408	438.4	2.24	-1.825
			409	439.	2.30	-2.116
M-15	50/50	50	404 <sup>a</sup>	435.9	2.34	-1.142
			406	436.4	2.13	-1.453
			407	436.9	2.07	-1.552
			408	436.9	2.10	-1.778

<sup>a</sup> extrapolated values.

Sheets of 10 × 10 cm were conformed in a Collins press at 200 kg · cm<sup>-2</sup> and 180°C temperature.

Mechanical experiments were performed under standard conditions using an Instron mod. 4301, at room temperature (25°C); the deformation rate was 10 mm s<sup>-1</sup>. The modulus and elongation at break were determined with the help of a noncontacting video extensometer. The tensile modulus  $E$  was determined from the slope of the initial part of the stress vs. strain curve.

The dynamic mechanical measurements were conducted in a dynamic mechanical thermal analyzer MKII from Polymer Laboratories at 5, 10, and 30 Hz in the temperature range 133–413 K and at a rate of 2 K min<sup>-1</sup>.

Differential scanning calorimetry (DSC) thermograms were recorded at a heating rate of 5°C/min. Isothermal crystallization and melting behavior were followed using a Perkin-Elmer DSC-7 differential scanning calorimeter. Samples were melted at 373 K for 10 min and then quenched (350 K/min) to the desired crystallization temper-

ature. Melting temperatures were obtained by heating the crystallized samples at 10°C/min.

Conductivity measurements were carried out using a Hewlett-Packard Model 4192A impedance analyzer coupled to a computer, in the frequency range of 10<sup>-2</sup> to 10<sup>4</sup> kHz over the temperature range of 30 to 110°C.

## RESULTS AND DISCUSSION

### Glass Transition Temperature Analysis ( $T_g$ )

Glass transition temperature was determined by means of two different techniques: DSC and dynamomechanical analysis (DMA). A single  $T_g$  was observed to appear in all cases by DSC analysis, which corresponded to the  $T_g$  of EPDM. No other transition could be assigned to PP incorporated into the blend up to a maximum amount of 50%. The low sensitivity of DSC in the detection of this type of transition in semicrystalline polymers is

**Table III Crystallization Kinetic Parameters of Crosslinked Samples Through DSC Measurements**

Samples	Composition (% wt)		$T_c$ (K)	$T_m$ (K)	$n$	$\log K$ ( $\text{min}^{-n}$ )
	EPDM/PP	CB				
ME-00	70/30	0	402	438.7	2.29	-1.335
			403	439.2	2.34	-1.589
			404	439.7	2.46	-1.941
			406	440.9	2.55	-2.517
ME-01	70/30	10	404	439.0	2.19	-1.347
			405	439.0	2.13	-1.550
			406	439.0	2.24	-1.897
			407	439.3	2.13	-1.981
ME-02	70/30	20	403	437.9	2.41	-1.746
			404	437.9	2.29	-1.764
			405	437.9	2.23	-1.989
			406	437.9	2.29	-2.322
ME-03	70/30	30	401	436.4	2.06	-1.376
			402	435.9	2.14	-1.691
			403	436.4	2.03	-1.781
			404	436.4	2.22	-2.178
ME-04	70/30	40	404	434.6	1.81	-1.357
			405	434.6	1.90	-1.422
			406	435.1	1.81	-1.490
			407	435.3	1.84	-1.786

to be held accountable for the absence of a second transition.

The effect of carbon black (CB) concentration on the samples containing 30 or 50% PP can be seen in Figure 1. In Figure 1(A) the effect of CB content on  $T_g$  is compared for all samples with a 30% PP portion, as well as the additional effect exerted on the  $T_g$  by crosslinking these samples. In the 30% PP samples a gradual decrease of  $T_g$  is observed, when CB content is increased. By the same token and as expected, for one and the same CB concentration,  $T_g$  diminishes noticeably, which is attributable to the difficulty of positional chain movements in networked systems. This behavior is not observed when examining the same effects in the 50% PP samples [Fig. 1(B)], although a certain  $T_g$  decrease is observed when incrementing the CB content, similar to the effect recorded for the 30% PP samples. For high CB content, the  $T_g$ 's of the noncrosslinked samples are surprisingly higher than for the crosslinked materials.

DMA appears to be a considerably more sensitive technique than DSC in the detection of glass transitions. Figure 2 shows, by way of illustration, the dynamomechanical spectra of some samples measured at 5 Hz.

At 70% EPDM concentration in the composite,  $T_g$  is difficult to detect; even with this technique, there appears not a single transition for the noncrosslinked samples at any of the experimental frequencies. In the case of the crosslinked samples the transition is visualized with difficulty, but in most cases the temperature value could be determined.

Figure 3 shows the effects of CB on the  $T_g$  of EPDM for the blends EPDM/PP (70/30) and EPDM/PP (50/50). The behavior patterns are similar to those observed with DSC analysis. The only difference consists of a generalized downward shift of  $T_g$  toward a lower range for all the samples tested and, in some cases, especially in the noncrosslinked EPDM/PP (70/30) samples at high CB concentrations, the drop is spectacular.

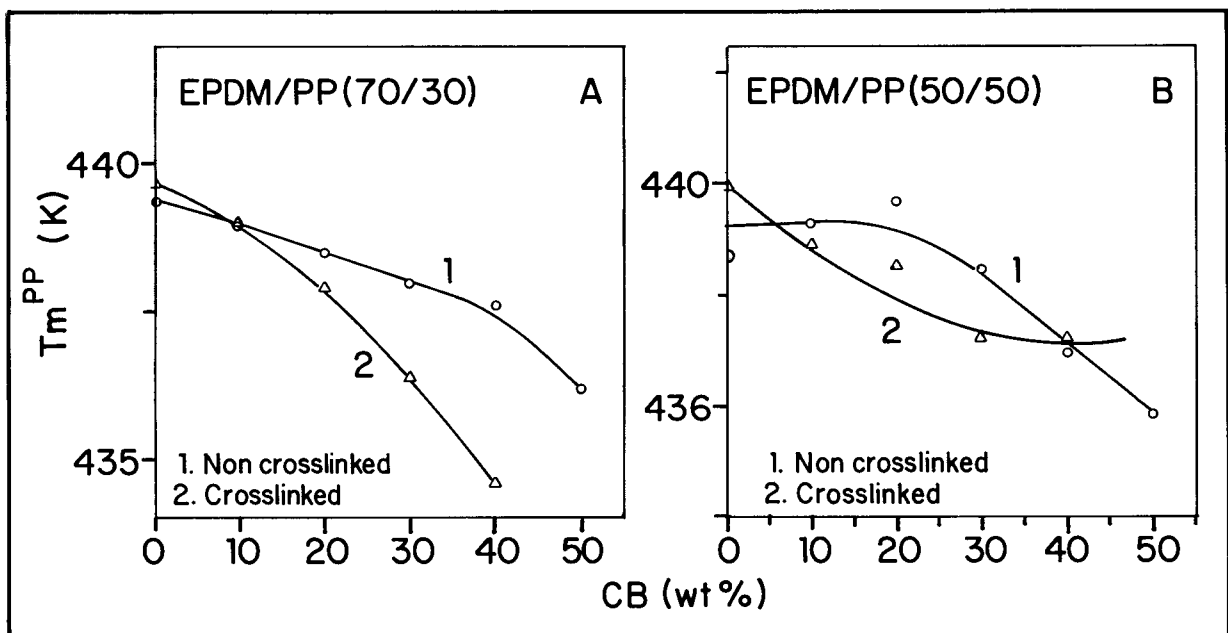
From the DSC and DMA data commented on, it becomes evident that CB acts like a polymeric plasticizers for the EPDM/PP blends, the respective  $T_g$ 's shifting to lower ranges, with increasing CB content. Doubtlessly this effect favors the processing of the composites.

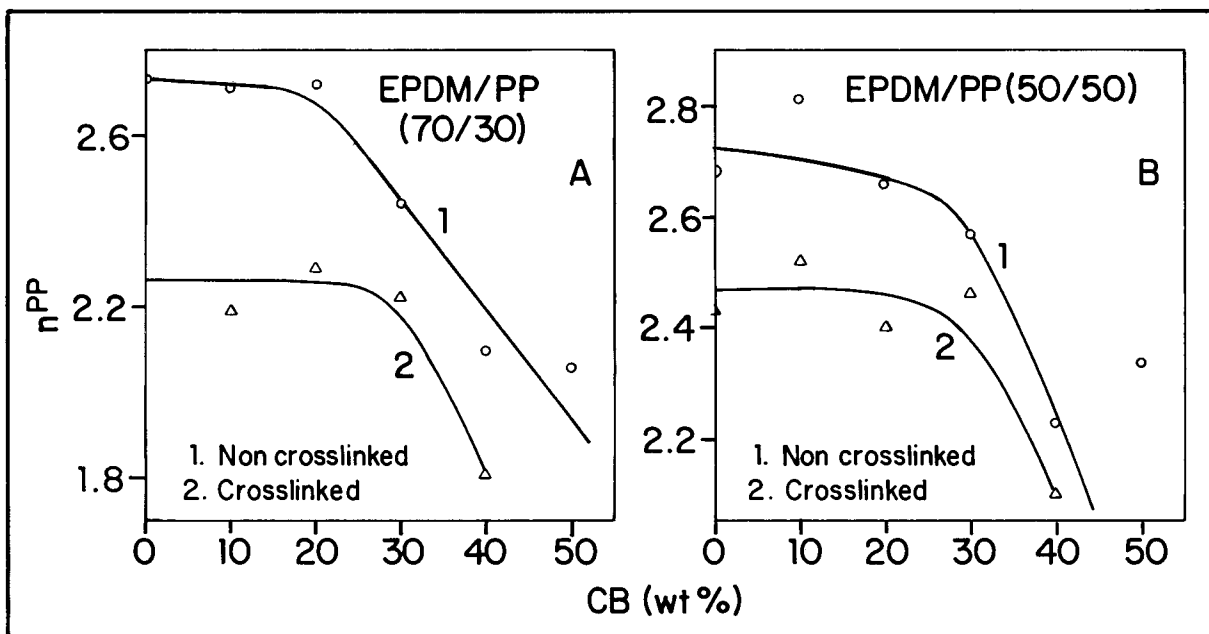
#### Isothermal Crystallization Kinetic

Tables I–IV compile the kinetic parameters of isothermal PP crystallization for the samples un-

**Table IV** Crystallization Kinetic Parameters of Crosslinked Samples Through DSC Measurements

Samples	Composition (% wt)		$T_c$ (K)	$T_m$ (K)	$n$	$\log K$ ( $\text{min}^{-n}$ )
	EPDM/PP	CB				
ME-10	50/50	0	404	440.0	2.43	-1.528
			405	440.0	2.42	-1.538
			406	440.6	2.53	-1.880
			407	440.9	2.45	-2.050
ME-11	50/50	10	402	438.4	2.49	-1.145
			403	438.4	2.49	-1.403
			404	438.9	2.52	-1.662
			405	439.4	2.61	-2.022
ME-12	50/50	20	402	438.0	2.37	-1.399
			403	438.0	2.53	-1.779
			404	438.5	2.40	-1.863
			405	438.5	2.31	-1.957
ME-13	50/50	30	401	437.2	2.43	-1.325
			402	437.2	2.44	-1.596
			403	437.2	2.51	-1.918
			404	437.2	2.46	-2.090
ME-14	50/50	40	402	436.7	2.19	-1.193
			403	437.2	2.18	-1.317
			404	437.2	2.10	-1.488
			405	437.5	2.17	-1.739

**Figure 4** DSC analysis:  $T_m^{PP}$  as a function of CB concentration: (A) EPDM/PP (70/30) and (B) EPDM/PP (50/50).

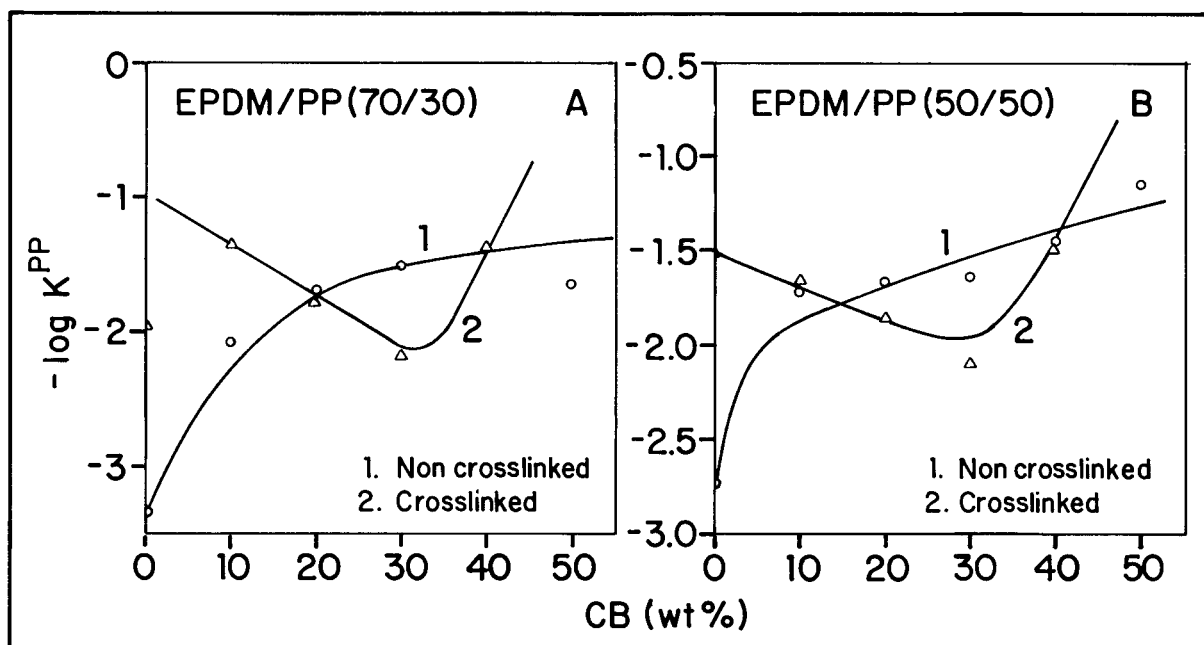


**Figure 5** Avrami's exponent of PP as a function of CB concentration: (A) EPDM/PP (70/30) and (B) EPDM/PP (50/50).

der investigation, data obtained from the Avrami<sup>10</sup> equation. Figures 4–6 show the effect of CB concentration on the different parameters.

Figure 4 shows the melting point variation of the PP portion contained in the samples as a

function CB concentration for the two families, i.e., EPDM/PP [70/30; Fig. 4(A)] and EPDM/PP [50/50; Fig. 4(B)]. In all cases the melting point is observed to drop with increasing CB portion in the sample, the drop being considerably more



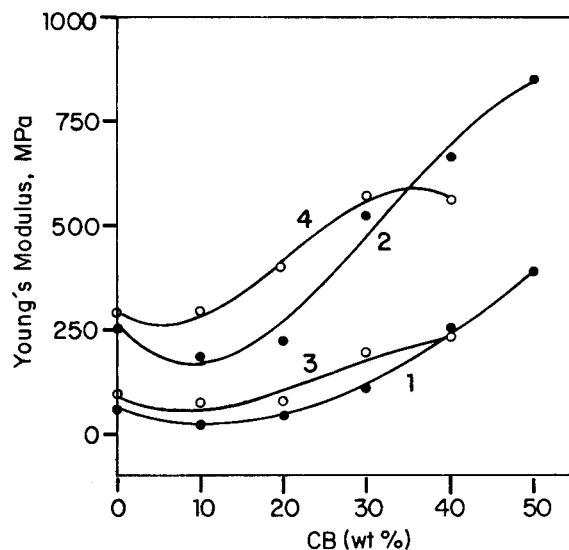
**Figure 6** Crystallization rate constant of PP as a function of CB concentration: (A) EPDM/PP (70/30) and (B) EPDM/PP (50/50).



prominent for the crosslinked samples, as opposed to the noncrosslinked materials with the same CB concentration. This behavior confirms the plasticizing effect exerted by CB on the polymer host, as previously inferred from  $T_g$  analysis, commented on above. The difference in the behavior of one and the other family under study, i.e., composites with 30 and 50% PP, respectively, are negligible, which allows for the conclusion that the value of PP content does not affect the  $T_m$  of the material.

Figure 5 illustrates the effect exerted by CB on Avrami's exponent  $n$ , i.e., on the growth geometry of the PP spherulites in the polymeric matrix, comparing the 30 to the 50% PP family. In both families the effect proves similar. In a first stage, at low CB concentration (below 20%), the growth geometry remains constant for both the crosslinked and noncrosslinked samples, in order to give rise to a second stage, where growth diminishes inversely proportionate to increasing CB concentration. During the first stage the growth geometry is fundamentally tridimensional for both families. In the second stage, however, there occur, simultaneously, tridimensional and bidimensional growth mechanisms, which generate low Avrami exponent values, mainly due to the high CB concentration, physically inhibiting crystal growth. Crosslinking also has an influence on both stages, due to the constraints it puts on chain mobility, as evidenced, for the same CB concentration, by the higher  $n$  values of the noncrosslinked samples.

The last kinetic parameter to be assessed was the crystallization rate constant of the PP component in the different composites. As can be seen in Figure 6, there exists behavior parallelism, when comparing the 30% PP family to the 50% one. But there exist also appreciable differences, which come to light when comparing the effect of CB concentration within one and the same sample family. This unusual behavior can be explained in terms of a combined inhibition-induction effect, i.e., crystalline spherulite growth is inhibited due to the presence of a high CB percentage in the blend, a phenomenon accompanied by massive crystalline nucleus formation on the CB surface from the matrix of the composite, motivated by the weak PP crystalline nucleus formation energy on carbon substrates. Thus high CB concentrations will trigger high concentrations of nuclei on the CB surface, and hence an apparent crystallization rate increase. In this case CB could be described as a material favoring PP nucleus formation on its surface.

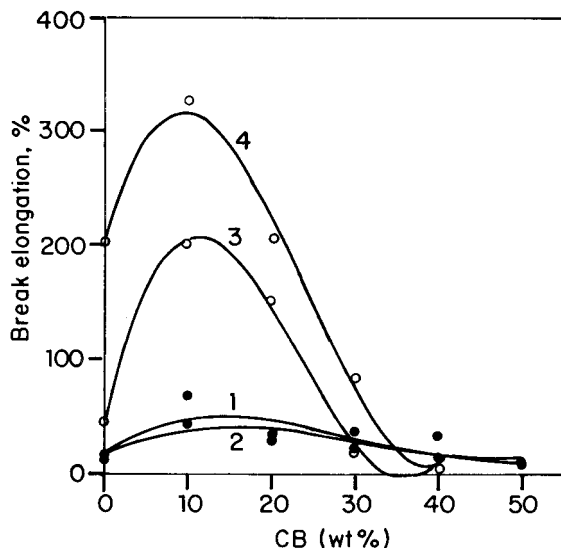


**Figure 7** Young's modulus as a function of CB concentration. 1 and 3: EPDM/PP (70/30); 2 and 4: EPDM/PP (50/50). Solid circles represent noncrosslinked samples and open circles represent crosslinked samples.

### Mechanical Properties

The physical properties of the EPDM/PP/CB composites were determined for two polymer ratios and different filler portions, as well as for crosslinked and noncrosslinked samples of these compositions. Figure 7 shows Young modulus variation as a function of CB content for composites with the following EPDM/PP ratios: 70/30 and 50/50. Graphs 1 and 2, relating to the composites in which the rubber phase has not undergone crosslinking, show similar responses for the two series. The increment produced in the 50/50 series has to be attributed to the higher PP content, which confers greater stiffness to the material. The moduli show increases for the crosslinked rubber phases, in good agreement with the fact that a crosslinked rubber phase already possesses some elastic properties. Thus, for the crosslinked samples the moduli increase with filler content, until an optimal filler portion is reached, from which the properties diminish. Both the EPDM/PP (70/30) series and the (50/50) family present the Young modulus peak between 30 and 40 pph CB. The carbon black exerts its reinforcing effect preferably on the rubber phase, and the increase in the Young moduli is to be assigned to the increase in the filler (hydrodynamic effect), as well as to the CB/elastomer interactions, and most importantly, to the crosslinking of the rubber phase, which converts the sample into an elastic material.





**Figure 8** Break elongation as a function of CB concentration. 1 and 3: EPDM/PP (70/30); 2 and 4: EPDM/PP (50/50). Solid circles represent noncrosslinked samples and open circles represent crosslinked samples.

The remaining mechanical properties are to be analyzed on these same lines of argument. Figure 8 shows the variation of breaking stress as a function of filler content. The slight differences between graphs 1 and 2 should be attributed exclusively to the PP content increase. In contrast, the crosslinked composites react in quite a special way. The increase in break strength at low CB concentration is remarkable, as compared to the respective noncrosslinked composites. The two crosslinked series present a peak between 10 and 20 pph CB. Most of the rubbers, when reinforced by a carbon black filler and crosslinked, will develop an optimum filler volume, from which the rubber matrix becomes less ductile with the respective decline in mechanical properties.

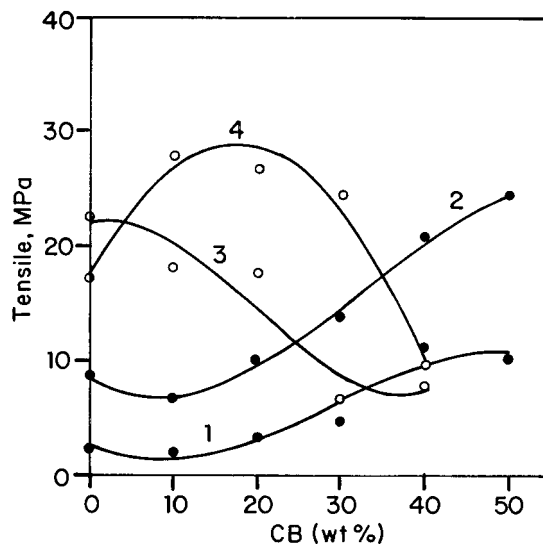
The continuous and unimpaired increment in breaking stress as a function of filler content in the noncrosslinked materials, can be explained by the fact that the rubber phase floats, as a result of the stress applied (as it is not crosslinked) and hence allows for higher breaking stresses due to the hydrodynamic effect.

The break behavior of the different series is shown in Figure 9. The noncrosslinked composites present low break strains, which are, in addition, similar for the whole series and unaffected by the filler content. The composites with a crosslinked rubber phase, however, show quite divergent behaviors. Crosslinked EPDM admits much stronger strain than the respective non-

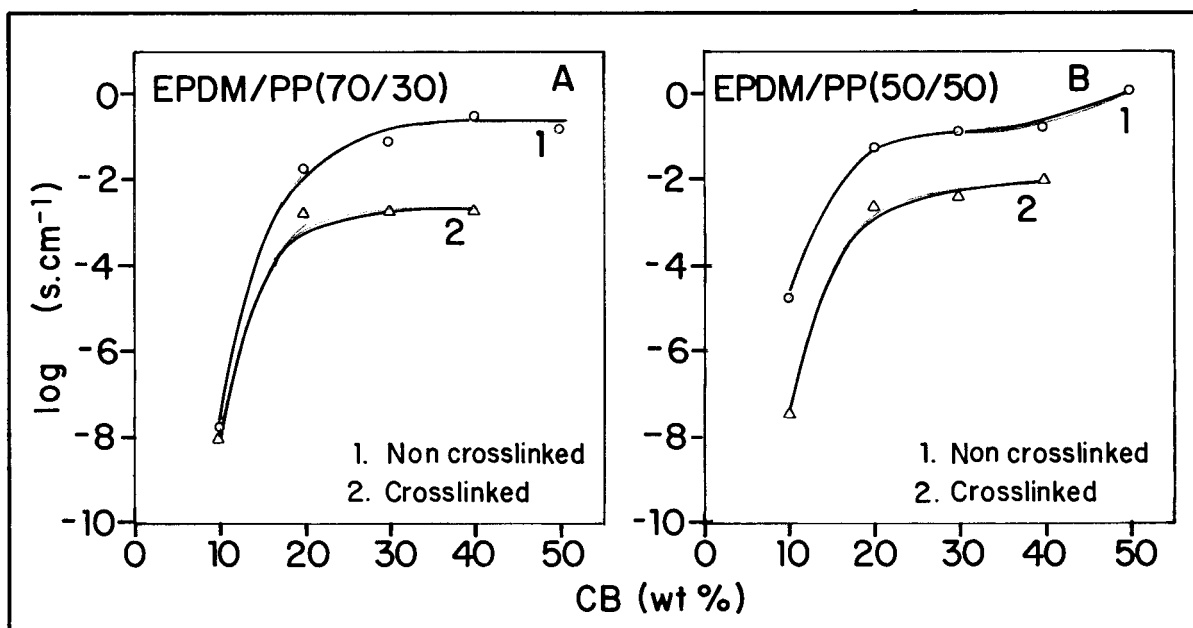
crosslinked composites, with the increases in breaking stress mentioned above.

### Electrical Properties

One of the most relevant properties that these materials must possess when they are to be employed as bipolar plates in polymeric membrane fuel cells refers to high electronic conductivity. To the purpose of determining the electrical properties of the experimental composites, they were subjected to a complex impedance spectroscopy study, as well as to the four-point method. The conductivity values obtained are shown in Figure 10, in which the two families of experimental composites are compared. For both series conductivity increases spectacularly between 10 and 20% CB, where the particle percolation peak is reached. When comparing the conductivity values achieved by the 30 and 50% PP families, the latter show fairly higher values than the series with the lower PP content. Comparison between the crosslinked and noncrosslinked samples showed that the noncrosslinked specimens reached higher conductivity values than the crosslinked ones, due to the constraints on particle movement derived from crosslinking, probably due to the effect of CB particle aggregate formation and consequentially deficient percolation.



**Figure 9** Tensile strength as a function of CB concentration. 1 and 3: EPDM/PP (70/30); 2 and 4: EPDM/PP (50/50). Solid circles represent noncrosslinked samples and open circles represent crosslinked samples.



**Figure 10** Conductivity as a function of CB concentration: (A) EPDM/PP (70/30) and (B) EPDM/PP (50/50).

## CONCLUSION

In the light of the data obtained from this research it is legitimate to conclude that carbon black affects the microstructure and the electrical properties of EPDM/PP blends containing this filler in different proportions. On the one hand, CB acts as a plasticizer of the polymer matrix (independent of the fact that the composite was crosslinked or not), shifting both the glass transition temperature and the melting point toward lower temperature ranges. This phenomenon has a direct impact on the mechanical properties of the composite, in such a way that, in the presence of CB, the processing conditions improve, as well as the mechanical properties, as compared to the behavior of CB-free systems.

By the same token, CB has an effect on the PP spherulite growth in the different composites, especially at high PP content. In addition, CB, at high concentrations, is capable of inducing crystalline nucleus formation on its surface, which motivates an apparent increase in the crystal growth rate.

Finally, the conductivity values reached and the unproblematic processing of these composites qualify them as adequate base materials in bipolar plates.

We express our sincere thanks to the Regional Government of Madrid for the funding of this project and the support provided in the implementation of this research.

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