

Structure Modification of Isotactic Polypropylene through Chemical Crosslinking: Toughening Mechanism

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ABSTRACT: Reversibly crosslinked isotactic polypropylene (iPP) was prepared in the presence of dicumyl peroxide. The effects of the peroxide oxy-radicals in the melt were investigated in relation to the modification of the polymer. The dynamic rheology analysis of the crosslinking process was carried out by using a plastograph. The crosslinking reaction was evaluated by the Monsanto method. The resulting structure of the modified samples was studied by means of differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), microhardness, and mechanical properties. The degree of crystallinity of the modified iPP, derived

from DSC and WAXS, remains almost unchanged, i.e., the crystalline structure is unaffected, though the lamellar thickness slightly decreases. The impact strength of the crosslinked iPP is greatly improved with reference to that of the unmodified material. A transition from brittle to ductile behavior appears in the modified iPP for all the crosslinking agents studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2968–2976, 2007

Key words: reactive blending; crosslinking; interpenetrating networks; ductile–brittle transition

INTRODUCTION

Branched crosslinked interpenetrating polymer networks present improved properties, such as higher melt strength and better processability, than their linear counterparts. These are important characteristics for the preparation of fibers and materials capable of being processed by blow molding.¹ In addition, crosslinked polyethylene (PE) is widely used in the wire and cable coating, and in the preparation of heat shrinkable materials.^{2,3}

PE is an easily crosslinking polymer, which is prepared by means of an organic peroxide capable of creating radicals by a decomposition reaction, or by irradiation with different doses of electron beam.^{4,5} On the contrary, isotactic polypropylene (iPP) has been considered until very recently as a noncrosslinkable polymer. This is due to the fact that, if iPP is either irradiated, or subjected to the action of a peroxide, the β -scission degradation process predominates over the crosslinking mechanism. Nevertheless, in the last year, new methods to achieve the crosslinking of the iPP have been developed.^{1,6}

The present study deals with an innovative method that allows the preparation of reversibly crosslinked iPP.⁷ This method, with slight variations, can be used to obtain crosslinked blends of PP and low or high density PE, copolymers of iPP or their blends with elastomers. In addition, the polymers to be crosslinked can be freshly prepared, recycled, restored, etc. The reversible crosslinking reaction is the newest method developed to obtain modified polyolefins. As it is well known, polymer modification contributes to the development of new materials or blends, especially attractive from the recycling and environmental point of view. On the other hand, polyolefins (particularly, PE and polypropylene) represent the major part of the total thermoplastic materials consumed.

The materials intervening in the crosslinking process are as follows: iPP, an organic peroxide, sulfur (S), an accelerator (or a mixture of them), and potassium persulfate. The so-called “crosslinking agent” is constituted by the peroxide, sulfur, and accelerator. The mixing process used is the extrusion method. However, all other processes of transformation used for thermoplastics, i.e., blow, injection, or compression molding, could also be useful for the subsequent industrial use. Therefore, this kind of modified polymers can be used to manufacture different articles.

The principle of the crosslinking mechanism is to create macroradicals and cause them to act immediately on sulfur before the reaction of termination

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TABLE I
Sample Composition

Sample	Polymer	Peroxide content (%)	Sulfur content (%)	Accelerator content (%)
iPP	iPP	–	–	–
1	iPP	0.2	0.2	0.05 (TMTD)
2	iPP	0.4	0.4	0.1 (TMTD)
3	iPP	0.2	0.2	0.05 (TMTM)
4	iPP	0.4	0.4	0.1 (TMTM)
5	iPP	0.2	0.2	0.05 (MBTS)
6	iPP	0.4	0.4	0.1 (MBTS)

occurs. The crosslinking process takes place by a homolytic chemical reaction. The initiation reaction is originated by the peroxide decomposition, which gives rise to the formation of macroradicals with a very short lifetime. The sulfur atoms link the chains (coupling reaction) through the formation of a tridimensional, heat-resistant, network. The interchain bridges can be a sulfur atom, a polysulfide $-(S)_x-$, or a cyclic S-compound. Accelerators increase the sulfur activation rate. In this way, the macroradicals' formation and their coupling reaction with the sulfur takes place simultaneously, thus obtaining an optimum crosslinking degree for each formulation. The potassium persulfate increases the macroradicals' lifetime. More details are given in Ref. 7.

The composition of the blend is derived by taking into account the degree of crosslinking to be achieved. This, in turn, depends on the radical peroxide efficiency and on the activation rate. Therefore, in every experiment, it is necessary to consider the transformation temperature and the particular extrusion characteristics used.

The aims of the present study are two-fold:

- The preparation of crosslinked iPP by using different formulations, following the earlier described method.
- To examine the influence of the crosslinking process on the structural and the mechanical properties of the modified material.

EXPERIMENTAL

Materials

The materials used in this investigation were the following:

- iPP Sabic-Vestolen 9000-67404: supplied by Chemische Werke Hüls, Germany.
- Dicumyl peroxide (96% activity): supplied by Norax.
- Sulfur (S) (vulcanizing agent for rubber): supplied by Wuxi Huasbeng Chemical Additives Factory, China.

Potassium persulfate: supplied by Innochem, Belgium.

The three accelerators used were "Super accelerator 500" (tetramethyl thiuram monosulphide, TMTM); "Super accelerator 501" (tetramethyl thiuram disulphide, TMTD); and "Quick accelerator 200" (mercaptobenzothiazole disulfide, MBTS). They were supplied by Rhône-Poulenc, France.

The peroxide, the sulfur, and the aforementioned accelerators constitute the "crosslinking agents."

Blend preparation

For the preparation of the blends, the sulfur concentration was always equal to that of the peroxide. The amount of sulfur and peroxide was 0.2 or 0.4 wt %. In all cases, the accelerator was 1/4 of the sulfur and peroxide concentration. The six formulations used are shown in Table I.

The iPP, the crosslinking agent, and the potassium persulfate were first mixed in the solid state, using a small quantity of vegetable oil, to wet and improve the dispersion of the fine powder of the different components within the granules of the iPP. Thereafter, the obtained mixture was inserted into a single screw laboratory extruder (Prolabo 1989) with the following characteristics: $L/D = 20$; screw diameter = 25 mm; screw speed = 60 turns/min. The residence time was about 3 min. The temperature profile used for the three stages was feed zone = 155°C; compression zone = 180°C; homogenization zone = 200°C. The extrusion cycle was repeated twice, to achieve a homogeneous blend.

Techniques

For the dynamic rheological analysis, a Brabender-type plastograph was used. The processability of the iPP blends has been evaluated by measuring the torque (torque = moment of force) required to mix the molten components in a heated chamber at 200°C, at a rotor speed of 30 rpm. To clarify the role of each component in the blends, the torque-time evolution

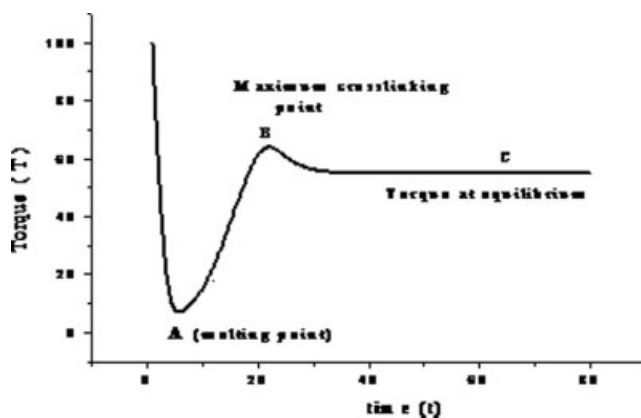


Figure 1 Typical torque–time evolution for a crosslinked polyolefin material.

was first measured for the neat peroxide, then for each couple peroxide/accelerator, and finally for every crosslinking agent, i.e., peroxide/sulfur/accelerator. Figure 1 shows a typical curve illustrating the different steps of the torque–time evolution for a crosslinked polyolefin material. In this figure, the most important and characteristic points are as follows:

- A. starting point of the melt.
- B. maximum crosslinking point.
- C. equilibrium point.

At the beginning, the polymer melts and the torque decreases to a minimum value T_A . As the crosslinking begins, the torque increases to a maximum value T_B . After that, a small decrease of torque is observed, reaching a final stable plateau at point C, usually higher than A. The logarithm of $(T_t - T_A)$ is plotted as a function of time, T_t , signifying the torque value at the time t . When the path of this curve is nearly linear, the crosslinking reaction is of 1st order and comprises the main reaction. However, this is only true for polyolefins with secondary carbons, such as PE, under the action of a peroxide.⁸

The impact strength test was carried out in a device, equipped with a control of absorption energy. Specimens were prepared by compression molding. Notched (1/10 deep) specimens were submitted to the Izod strength testing. The specimen thickness and width were 3 and 9 mm, respectively. Resiliencies a_k (J/m²) and energies of absorption (J) were determined using a hammer of 7 J. Measurements were carried at room temperature according to the ASTM D 180 norm.

The melt flow index (MFI) was measured by allowing a molten polymer to flow under fixed working conditions (load and temperature), through a standard cylindrical die (2.09 mm diameter, 8 mm length).

The MFI is defined as the weight of flow in grams per 10 min. The referred norms are ISO R 1138 or ASTM D 1238. In case of iPP, the working conditions were a load of 2.16 kg and a temperature of 230°C.

The microhardness of samples was measured at room temperature, using a Leitz tester equipped with a square-based diamond indenter.⁹ The H -value was derived from the residual projected area of indentation according to $H = kP/d$.² In this expression, d is the length of the impression diagonal in meters, P is the contact load applied in N, and k is a geometrical factor equal to 1.854. Loads of 0.25, 0.5, 1, and 2 N were used. The loading cycle was 0.1 min. Eight to 10 indentations were made on each sample, and the results were averaged.

Thermal analysis was performed in a Perkin-Elmer differential scanning calorimeter (DSC)-7, in a N₂ atmosphere. The temperature range studied was 40–220°C. The heating rate was 10 or 20°C/min. Typical sample weights were 5–10 mg. The crystallinity measured by calorimetry, α_{DSC} , was derived from the melting enthalpy obtained by DSC using the following expression: $\alpha_{DSC} = \Delta H_m / \Delta H_m^\infty$, where ΔH_m and ΔH_m^∞ are the experimental melting enthalpy and the melting enthalpy for an infinitely long crystal, respectively.

The wide-angle X-ray scattering (WAXS) study was performed using a Seifert diffractometer (reflection mode). The working conditions were as follows: voltage: 40 kV; intensity: 35 mA; angular range: 5–30° (2 θ); scan rate: 0.01°/s; slits: 0.3, 0.2. The crystallinity α_{rX} of every sample has been calculated as the relation of the area corresponding to the crystalline peaks to the total area of the diffractogram.

RESULTS

Dynamic rheological analysis

A torque–time rheometer was used to study the unmodified iPP sample as well as the modified samples, with the peroxide and the couple peroxide/accelerator, respectively. Experimental results of torque–time evolution [Fig. 2(a)] show that the torque of iPP in the presence of peroxide is lower than that of pure iPP. This is due to the attack of the peroxide radicals, particularly at the tertiary carbons of iPP, which are the more reactive sites, to form macroradicals by disproportionation or by cyclization of the end groups, i.e., the peroxide provokes the scission of the iPP chains. However, the torque of the iPP with the couple peroxide/accelerator is lower than that of pure iPP, but higher than that corresponding to the iPP plus peroxide. It is clear that the couple peroxide/accelerator presents a different effect. In this case, a controlled scission takes place, because the accelerator decreases the peroxide efficiency (the

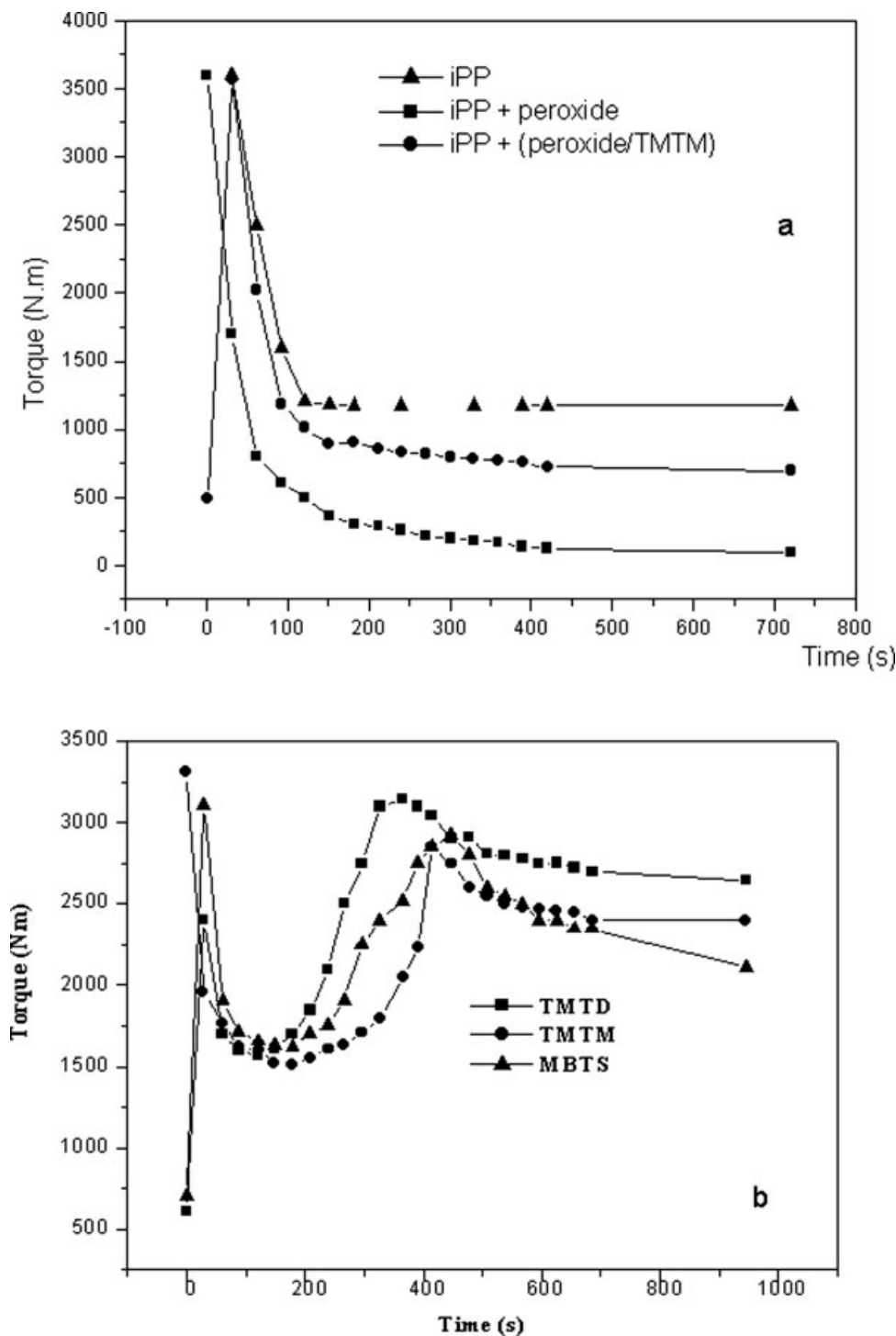


Figure 2 (a) Effect of the peroxide and the couple peroxide/accelerator TMTM on the torque–time evolution of iPP. (b) Effect of the accelerator type on the torque–time evolution of iPP in the presence of different crosslinking agents (peroxide/sulfur/accelerator).

accelerator could then be considered as inhibiting or slowing down the action of the peroxide).

Consequently, with the decrease of the torque in the presence of peroxide, there is a decrease of the molecular weight (M_w). It has been shown that the higher is the peroxide concentration [P], the lower is

the M_w obtained.¹⁰ Such a result, not shown here, has also been observed in a MFI study on iPP as a function of the peroxide content. With the couple peroxide/accelerator, a smaller decrease in the MFI, as compared to that observed with only the peroxide, is observed. Therefore, in this case, controlled

TABLE II
Microhardness and Impact Strength of Isotactic Polypropylene Normal, and Crosslinked by Using Different Agents

Sample	H (MPa)	Impact strength (J/m^2)
iPP	89	4.47
1	78	19.40
2	72	15.91
3	79	24.47
4	70	18.25
5	88	30.94
6	81	19.79

Samples are as in Table I.

scission reactions are thought to occur. The M_w of the resulting material is controlled by the accelerator concentration related to, both, the concentration and the activity of the peroxide. However, the weight fraction of the accelerator should not exceed that of the peroxide. By using 1/4 weight concentration of the peroxide, which is the common weight fraction used in this study, a constant torque value, and a moderate increase of MFI values compared to those shown by the iPP-peroxide formulations, are obtained.¹¹

Furthermore, the combination of the peroxide and sulfur agents shows no important effect on the peroxide activity. Because the accelerator also has an activation effect on the sulfur, the combination of the sulfur, the peroxide, and the accelerator gives rise to the crosslinking reaction [Fig. 2(b)]. Here, it can be seen that the torque–time evolution follows the typical shape shown in Figure 1 for a crosslinked polyolefin material. Using the Monsanto method, developed by Harpell and Walrod,⁸ it is possible to evaluate how the crosslinking reaction occurs. Figure 2(b), additionally, shows the effect of the different accelerators used when the three components (peroxide/sulfur/accelerator) are added. It is to be noted that the T_B values (T_B = maximum torque, corresponding to the maximum crosslinking degree) are not so different for the three accelerators used. The maximum degree of crosslinking (maximum T_B) takes place at a shorter time for TMTD and at a longer time for MBTS. These results are strongly related to the activity temperature of each accelerator. The most interesting aspect here is that the macroradicals of the iPP chains present a very long lifetime.

Mechanical properties

Data concerning the impact strength and the microhardness of the samples are collected in Table II. All samples show hardness values slightly lower than that of initial iPP, except sample 5. The hardness of

this sample is almost identical to that of iPP (see Table II, column 2). None of the samples included in this study showed any elastic recovery. From the plot of the microhardness versus the yield stress of the modified samples (not shown here), one obtains $H/\sigma_y = 2.8$. Additionally, for all crosslinked samples, a linear relationship (not shown here) between the Young's modulus E and the hardness H , $E/H = 15.6$, is obtained.

Figure 3 shows the influence of the crosslinked structure on the impact strength for notched specimens at room temperature. The effect of the different crosslinking agents and of the different weight fractions on a_k is apparent. The histogram clearly shows that the modified material reaches higher impact strength values than those of the raw material. In particular, the impact strength for sample 5 (iPP with a 0.05% of MBTS added) is as high as $30.94 J/m^2$, i.e., about 7 times the value of unmodified iPP ($4.47 J/m^2$, see Table II, column 3). Also, it is noteworthy that the iPP raw material presents a brittle fracture behavior, whereas the different crosslinked iPP samples present a ductile fracture behavior^{12–14}. For instance, compare Figures 4(a) (unmodified iPP) and 4(b) (iPP with a 0.05% of MBTS added). The other crosslinked samples behave similarly.

Differential scanning calorimetry

From the calorimetric study, it is seen that the crosslinking process gives rise to a new, low temperature peak, not appearing in the nonmodified iPP. For instance, compare Figure 5(a) (the thermogram of

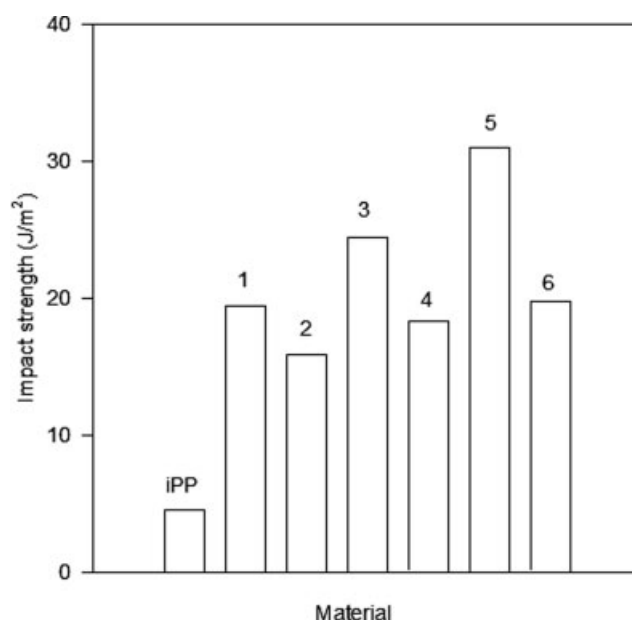


Figure 3 Impact strength for the unmodified iPP and for the crosslinked samples. Sample composition is indicated in Table I.

the nonmodified iPP) with Figure 5(b,c) (the thermograms obtained on samples 5 and 6, i.e., crosslinked iPP prepared with 0.05 and 0.1% of MBTS, respectively). The new peak, indicated by an arrow, is probably caused by the presence of PE chains, eventually originated by the action of the peroxide and potassium persulfate on some of the tertiary carbon atoms of the iPP. Table III includes the melting temperatures (T_m) corresponding to the different peaks of every sample. The thermodynamic crystal size l_c has been calculated for each maximum, from the Thomson–Gibbs equation:

$$T_m = T_m^0 [1 - (2\sigma_e / \Delta H_m^\infty l_c)] \quad (1)$$

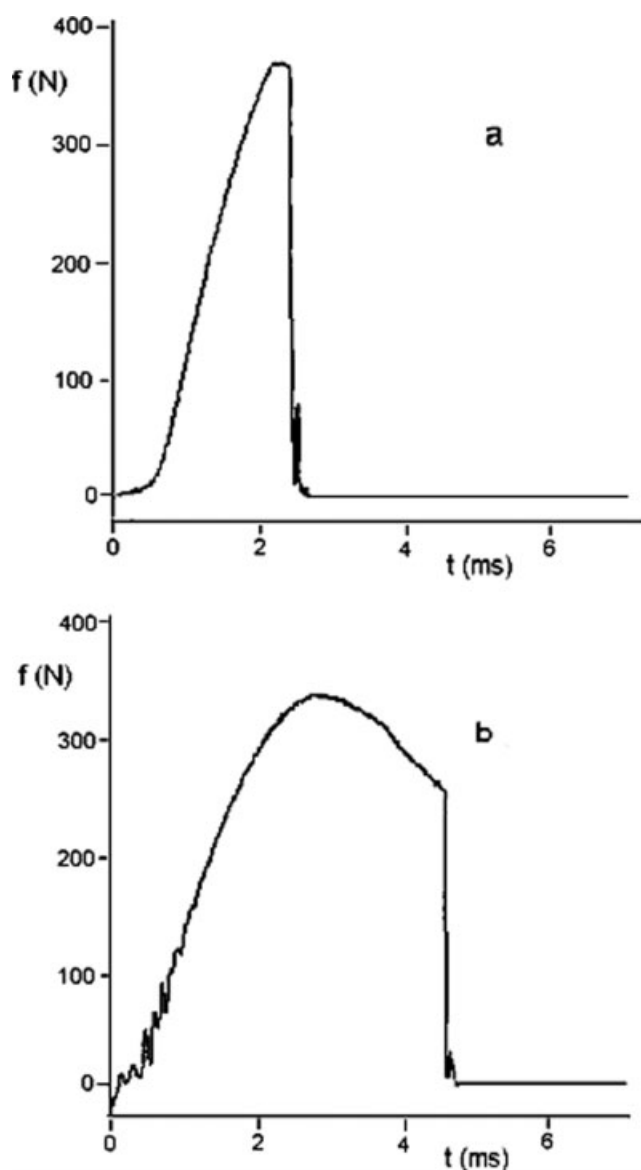


Figure 4 Plot showing the fracture behavior of (a) unmodified iPP; (b) sample number 5 (See Table I).

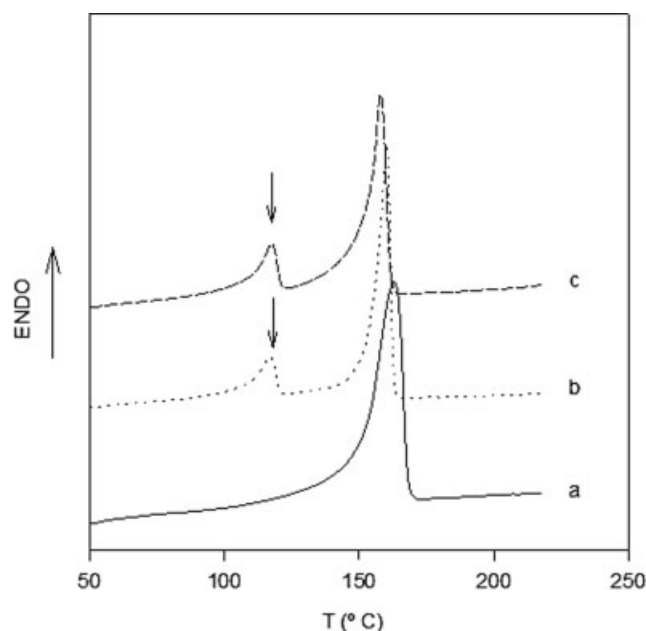


Figure 5 Thermograms of (a) unmodified iPP; (b) sample number 5; (c) sample number 6 (see Table I).

where σ_e is the surface free energy and T_m^0 is the equilibrium melting point of each component. The l_c values, the melting enthalpies ΔH_m , and the crystallinities α_{DSC} for both PP and PE are also included in Table III. In this calculation, we have used the following values: for the iPP, $\Delta H_m^\infty = 207.33 \text{ J/g}$,¹⁵ $T_m^0 = 460.7 \text{ K}$,¹⁵ and $\sigma_e = 100 \text{ erg/cm}^2$;¹⁶ for the PE, $\Delta H_m^\infty = 293.86 \text{ J/g}$ ¹⁵ and $T_m^0 = 414.6 \text{ K}$.¹⁵ For the surface free energy of the PE, we have taken $\sigma_e = 79 \text{ erg/cm}^2$.¹⁷ However, this σ_e value is probably an upper limit. In fact, according to our results, σ_e on linear PE samples depends on the molecular weight. Thus, for PE samples studied in Ref. 17, the surface free energy varies between 79 and 91 erg/cm^2 .¹⁷ On the other hand, the melting point found in our work for the first maximum appearing in the thermograms of the crosslinked samples is 117–118°C. This is a relatively low value, suggesting that the PE originated during the crosslinking process has a low molecular weight and/or is not linear, but branched.

X-ray diffraction study

The WAXS patterns taken for the nonmodified and crosslinked samples show the characteristic reflections of the monoclinic α -form of isotactic PP (Fig. 6).¹⁸ By comparing the diffractogram of the original iPP [Fig. 6(a)] with that of the crosslinked sample number 6, prepared with a 0.1% of MBTS [Fig. 6(b)], it is seen that the crosslinking process affects mainly the relative intensity of the first and second diffraction peaks. The other crosslinked iPP

TABLE III
Melting Points T_{m1} and T_{m2} from DSC; Crystal Thickness Values l_{c1} and l_{c2} Derived from the Melting Points; Melting Enthalpies ΔH_1 , ΔH_2 , and ΔH_m Total and Crystallinity Values α_{DSC} and α_{rX} Derived from the DSC and WAXS

Sample	T_{m1} (°C)	l_{c1} (nm)	ΔH_1 (J/g)	T_{m2} (°C)	l_{c2} (nm)	ΔH_2 (J/g)	ΔH_m total (J/g)	α_{DSC} total	α_{rX}
iPP	—	—	—	163.2	19.2	114.1	114.1	0.55	0.48
1	118.4	9.6	30.3	158.5	16.1	82.3	112.7	0.50	0.39
2	117.7	9.3	31.2	157.8	15.7	81.6	112.8	0.50	0.41
3	118.6	9.7	33.7	159.9	16.9	83.3	117.0	0.52	0.42
4	117.6	9.3	25.2	158.6	16.4	75.4	100.5	0.45	0.40
5	117.7	9.3	30.1	160.8	17.5	96.5	126.5	0.57	0.42
6	118.4	9.6	30.2	158.8	16.3	84.3	114.5	0.51	0.42

Samples are as in Table I.

samples behave similarly. All crosslinked samples exhibit crystallinity values α_{rX} slightly lower than that of the unmodified iPP. Table III includes α_{rX} data for all the samples (column 10). These data show a linear correlation (not presented here) with respect to the hardness values of the samples.

From a closer inspection of the WAXS patterns of the crosslinked material, one observes a new, small intensity reflection appearing at 23.85° (2θ). See, for instance, Figure 6(b), corresponding to the crosslinked sample with a 0.1% of MBTS, in which the reflection is indicated by an arrow. This new reflection, not appearing in the original iPP [Fig. 6(a)], could be associated to the (200) planes in PE.¹⁹ In addition, the (111) reflection of the original iPP, at 21.03° (2θ), in the crosslinked material is slightly shifted toward higher angles, and nearly coincides

with the peak (110) of PE at 21.55° (2θ)¹⁹ [compare Fig. 6(a,b)]. It is also noteworthy that the results, obtained in the FTIR study of these samples (not shown here), confirm the presence of ethylenic chains in the modified iPP. For instance, the occurrence of a band at 720 cm^{-1} is attributed to the ethylenic chains induced during the crosslinking process. This band, usually appearing in the range of $750\text{--}720\text{ cm}^{-1}$, is characteristic of the “rocking” mode of the $-(\text{CH}_2)_n$ -sequences when $n \geq 4$.²⁰ In addition, at 650 cm^{-1} , a new band appears. This band could be due to the “stretching” mode of the $-\text{C}-\text{S}-$ groups, thus being directly related to the bridging chains created in the crosslinked material.²¹

DISCUSSION

From the results shown in Figure 2(b), it can be seen that the equilibrium torque value T_C and also the difference between the maximum torque T_B and the equilibrium torque T_C values are different for each accelerator type. According to the technique of Harpell and Walrod,⁸ in the torque–time curves, the activation energy of the crosslinking has always been calculated between T_B and T_A . However, it is noteworthy that our present study is the first one which shows the decrease from T_B to T_C . This result can be explained as follows: The long macroradicals’ lifetime shown in Figure 2(b) might be due to the high continuous shearing involved. Therefore, the fast initial crosslinking reaction should result in a high degree of crosslinking, which later undergoes a partial destruction by the high shearing developed just before the equilibrium takes place. The crosslinking degree is determined at the equilibrium torque value T_C , because at this stage there is a stable equilibrium for very long processing times. This is because a stable torque value involves a stable viscosity. Consequently, one reaches a stable crosslinking degree during a longer time (~ 15 min), which corresponds to 5 times the extruder cycle time. Accordingly, a reversible crosslinking reaction

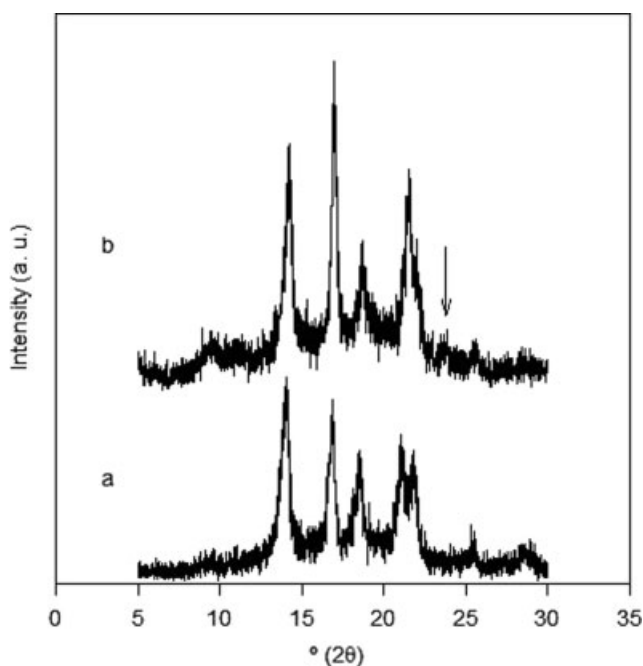


Figure 6 WAXS diagrams of (a) unmodified iPP; (b) sample number 6 (see Table I).

will not affect the overall crosslinking degree, even for a multirepeated processing cycle. The overall network formed will be stable. More details are reported in the patent.⁷ This is also an important result from the industrial point of view, because the pumping and shearing involved in a single screw extruder does not provide the same crosslinked iPP as in a twin-screw extruder device.

The data derived from the structural study seem to indicate that the crosslinking process originates a slight decrease in the crystallinity and microhardness of the samples. Furthermore, from the DSC, WAXS, and IR results, it is clear that crosslinking gives rise to the appearance of a certain amount of PE (25–29%). The generation of the ethylenic chains could be explained as follows: The oxy-radicals of the peroxide might eventually attack the tertiary carbons of the iPP. In this case, the alcoholates provided by the peroxide or the peroxodisulfate would stabilize these tertiary carbons through formation of double bonds (intermediate reaction), which may react with the hydrogen H atom of the methyl side groups.

The working conditions used are sufficiently strong as to permit the attack of this hydrogen atom. This is a very stable atom, and one needs a very high energy to abstract it. Nevertheless, the entropy involved in this process is also high. The process would finally lead to the formation of branched ethylenic chains. These chains are thought to be responsible for the melting peak appearing at 117–118°C in the thermograms of the modified iPP.

In addition, the slight decrease in the hardness of the modified material (see Table II) can be due to a combination of several effects:

- a. A decrease in crystallinity of the modified samples (see Table III, columns 9 and 10).
- b. The smaller crystal thickness shown by the crosslinked iPP (see Table III, column 6).
- c. The appearance of a 25–29% of a crystalline population (probably due to the new branched PE chains), with smaller hardness values than those of pure iPP.

From the study of the mechanical properties of the samples, the obtained value of $H/\sigma_y = 2.8$ is quite close to that predicted by the Tabor relation, $H/\sigma_y = 3.0$.²² Previous investigations carried out in our laboratory on melt-crystallized PE indicate that the Tabor relation is obeyed when the strain rate in the tensile tests is comparable to that employed in the hardness tests.²³ In our samples, the value found for $E/H = 15.6$ is higher than that obtained by Struik²⁴ and Flores et al.²⁵ i.e., $E/H = 10$.

The crosslinking process is thought to be responsible for the improvement of the impact strength (see

Fig. 3 and Table II, column 3) in the modified samples. The six formulations, based on the different accelerators with the two compositions (0.2% and 0.4% by weight) related to the matrix, show a synergistic effect on a_k .

According to the foregoing, the structure of the modified iPP could be considered as a combination of rubber-like and crystalline thermoplastic components. The earlier results also indicate that crosslinking takes place at a higher scale than crystallite formation. This assumption fits well with the results obtained. Thus, the more the bridges are formed (higher crosslinking degree), the higher is the ductile behavior (the rubber-like behavior). This transformation from a brittle to a ductile behavior in the modified material is extremely important. As pointed out in the introduction, the bridges present in the modified iPP, basically originated by the sulfur component, act as linking agents of the olefin macrochains involved.

The influence of the accelerator type on the reactive blend to form a network has a direct effect on the impact fracture. The mode of dispersion of the different components and the network architectural structure are factors that can be properly adjusted, to obtain blends with lower values of residual stress. As it has been reported before, a ductile behavior is accompanied by a decrease of the interfacial tensions due to the high mobility chains.²⁶ The brittle–ductile fracture transition of iPP is usually promoted, either by blending the iPP with EPDM or EPR, or with a 6–7% of LDPE, when a peroxide is added.^{27–31} Within this context, the high impact strength iPP does not need to be blended, to become a ductile material.

There is a great flexibility in the formulation of the crosslinking agents, so that many combinations are possible. In fact, one has just to find a compromise between the selected crosslinking agent and the characteristics of the processing device. Another advantage of the new crosslinking method described earlier is the possibility of recycling the crosslinked samples a number of times. The samples can be repeatedly melted and used again, which is an important aspect when one compares these products with conventional elastomers. In summary, the reversibly crosslinked iPP is an innovative material from the mechanical point of view. In addition, the reactivity of crosslinked iPP overcomes the problem of recycling. This is another aspect that will probably improve the wide using range of this material.

CONCLUSIONS

1. The new method developed for the reversible crosslinking of iPP gives rise to a promising ma-

terial with improved impact strength, comparable to that shown by conventional elastomers.

2. The crosslinking process originates a transition from brittle to ductile behavior in the modified iPP.
3. The crystallinity and the micromechanical properties of the crosslinked iPP are slightly lower than those the unmodified material. The microhardness decrease is attributed to the combined effect of a crystallinity decrease, the occurrence of smaller crystals in the modified iPP, and the appearance of a low fraction (25–29%) of PE crystals.

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