Study of iPP Crosslinking by Means of Dynamic and Steady Rheology Measurements

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ABSTRACT: The crosslinking of isotactic polypropylene (iPP) using crosslinking agents (CAs) based on a peroxide/sulfur/accelerator system is a very attractive new method that has been reported recently. The present work deals with the study of the dynamic rheological behavior of iPP during and after the crosslinking process. The influence of the CA concentration and the processing temperature T on the rheological behavior of the iPP was analyzed. The kinetics of the crosslinking reaction was established using the technique described by G. A. Harpell and D. H. Walrod. This reaction is found to be of order one. At $T = 180°C$, the crosslinking reaction was faster. By varying the crosslinking agent content, different crosslinking degrees of iPP, expressed by the corresponding gel content, are achieved. On the other hand, the modified polypropylene exhibits an unexpected viscosity-shear rate pattern, which describes the reverse crosslinking reaction mainly occurring by the opening of the bridges of the new interpenetrating network (IPN) formed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3184–3191, 2012

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INTRODUCTION

The procedures developed in the past for the crosslinking of polyolefins (POs) were mainly focused on polyethylene (PE).[1,2] Indeed, crosslinked PE is widely used in industrial scale (manufacture of wire and cable coatings, heat shrinkable films, etc.). Nowadays, the attention is shifting to the crosslinking of polypropylene (PP). This could generate modified PP with new and interesting morphologies, and thus fulfill the requirements for newer applications. This shift towards PP-based materials is explained for two reasons: (a) the market of this polymer is still expanding and (b) new procedures to successfully prepare branched and crosslinked PP, as well as its blends,[3–9] have been developed during the last years. In some of these new methods, a peroxide, together with a furan or bismaleimide-based coagent, is used as crosslinking promoter.[8] Other authors use polyfunctional monomers, as tri-methylolpropane triacrylate (TMPTA),[4,6] trimethylolpropane trimethacrylate (TMPTMA),[5,7] triallyl cyanurate (TAC),[6] or others as crosslinking agents.[9]

It is well known that isotactic polypropylene (iPP) cannot be crosslinked neither by the classical irradiation methods nor by the use of oxy radicals of peroxides. This is due to the fact that when iPP is either irradiated or subjected to the action of any oxy radical of peroxide, the β-scission degradation process predominates over the crosslinking mechanism.

On the other hand, other PO materials (such as PE, isotactic polybutene (iPB), etc) exhibit a limiting crosslinking degree. To overcome this limit, a new generation of thermoplastic elastomers (TPEs) and thermoplastic olefin (TPO) materials have been obtained by blending the POs with elastomers such as ethylene-propylene rubber (EPR), ethylene-propylene-diene monomer (EPDM), styrene-butadiene rubber (SBR), etc, sometimes in the presence of peroxides.[10] The properties thus obtained are considerably improved and these blends could meet new applications.

A new method for reversibly crosslinking the iPP has been recently developed in our laboratory.[11–14] This method opens up a very practical way for obtaining modified iPP materials that could exhibit TPE and TPO behavior. The basis of this innovative method is to create very active macroradicals through the homolytic reaction of a peroxide and, then, transform them to less active complex

macroradicals based on the sulfur component, to develop some coupling instead of scission reactions. The first relevant point of this crosslinking process is that it can be achieved in an easy way with all types of thermoplastics processing techniques (such as extrusion, injection molding, or calendering). The second aspect is that this process is performed very quickly, in one step, involving no significant extra expenses. This method could be considered as a new tool for controlling the melt strength of iPP. At the same time, it offers the possibility to overcome the restrictions for using the iPP in some industrial processes, such as the vertical blow molding (as applied to PE materials), or the fabrication of hot water pipes, or some types of tubes and pipes using spiral dies.[15,17]

Using this method, the crosslinking degree of iPP can be controlled by adjusting the crosslinking agent content.[11,12] Our crosslinking agents consist of the combination of dicumyl peroxide (DCP), sulfur, and tetramethyl thiuram disulfide (TMTD) as accelerator/inhibitor. The action of the three components to achieve the crosslinking reaction is complementary. Peroxide contents as high as 10% (w/w) can be used, while the crosslinking process is still carried out successfully.

All the reactions take place simultaneously, mainly in the molten state and under high shearing rates. They need short working times to be completed, i.e., only 3 min in case of the slowest kinetic rate. These working conditions are considered to be very relevant for industrial applications. It is evident that the composition of the crosslinking complex is very important, since each component has not only specific characteristics, but also plays a specific role, depending on its content and its type (this is more clearly observable for the peroxide component). Given compositions of the crosslinking complex have to be set to balance between the two active components, i.e., peroxide and sulfur, and to result in higher crosslinking degrees.[12]

On the other hand, the performance of the processing equipments and the shearing involved on them are also important factors to consider. However, in all cases the crosslinking can be achieved. In addition, for the same formulation and concentration, the crosslinking degree will be higher in the case of using a twin screw extruder than with a single screw extruder due to the high shear involved. Therefore, the life time of the macro radicals is a crucial step. The reaction mechanism is very complex. Nevertheless, in what follows we will try to give a brief description of it.

As it was previously explained,[11,12] the crosslinking process takes place by a homolytic chemical reaction. After the attack of oxy radicals produced by the DCP decomposition to form the macroradi-cals, the active tertiary carbon sites of the iPP chains will react with the complex of the sulfur component to transfer the radicals into a less reactive component (macroradical–sulfur complex). The role of the accelerator (TMTD) is to increase the sulfur activation rate. The reaction is statistical and in random manner, and depends on the weight fraction and the ratio of the components, and on the shearing and thermodynamical conditions involved. All those different parameters and factors govern the final chemical and architectural structure. In addition to that, the continuous shearing will maintain the macro radicals in life and the crosslinking reaction will take place as far as the material is still in the molten state, but the partial destruction will replace the combination reaction for longer shearing times, and finally the overall long bridges between the long chains of iPP will be formed.

A similar morphological structure description is offered in.[18] The modular connection of the bridged units may finally lead to multiple-bridged three-dimensional structures with larger cavities surrounded by bridges. Our system of reversible crosslinking reaction could fulfill properly the 3-dimensional structures mentioned by other authors.[3,19] Thus, it could include some of the following well known binding types: reversible covalent bonds, e.g., disulfide bonds; coordinative bonds; hydrogen bonds; electrostatic bonds between permanent dipoles; charge-transfer interactions; and Van der Waals interactions, etc.

In fact, we are dealing with a very complex system that includes, among others, the oxy radicals of the peroxide and the sulfur/accelerator system; thus, different reactions take place, as, i.e., the sulfur-based vulcanization and the reversible crosslinking reaction, which affects the tertiary, secondary, and primary carbon of the macromolecular chains. The complex structures generated in our process could be considered as similar to the ones originated in the reversible diamine crosslinking of polyimide membranes.[20] Also, the structures originated by the Diels–Alder reaction behave in a similar way,[21] i.e., formation of labile covalent bonds, which are stable at low temperature (in the solid state), but disappears at high temperature (in the molten state).

Improved rheological characteristics are among the enhanced properties obtained by the crosslinking of the iPP. In the present article, we present the results obtained in the dynamic and steady rheological study of the new crosslinking process applied to iPP.

Therefore, the aims of this work are as follows:

1. To apply the dynamic rheological analysis (DRA) and the steady-state rheological technique to the study of the crosslinked iPP.

TABLE I
Sample Composition for Different Peroxide, Sulfur, and Accelerator Content

Sample code	iPP (%)	DCP content (%)	S content (%)	TMTD content (%)
PP0	100	–	–	–
PP1	100	0.5	0.5	0.125
PP2	100	2	2	0.5
PP3	100	5	5	1.25
PP4	100	10	10	2.5

2. To investigate the influence of the crosslinking agent content and the processing temperature T on the rheological properties of the crosslinked iPP.
3. To evaluate the crosslinking degree achieved for each composition and processing temperature.

EXPERIMENTAL

Materials

The materials used in this investigation were the following:

- Isotactic polypropylene (iPP) Sabic-Vestolen 9000-67404: supplied by Chemische Werke Hüls, Germany.
- DCP (99% activity): supplied by Acros, Belgium.
- Sulfur (S) (vulcanizing agent for rubber): supplied by Wuxi Huasbeng Chemical Additives Factory, China.
- The accelerator used was: "Super accelerator 501. (TMTD); supplied by Rhodia., France.
- The peroxide, the sulfur, and the accelerator constitute the "crosslinking agent" (CA).

In all the compositions, the sulfur concentration was always equal to that of the peroxide. The accelerator was [1/4] of the sulfur and peroxide concentration. The sample composition is indicated in Table I.

Techniques

Dynamic rheological analysis

The crosslinking reaction is evaluated by using DRA in a Brabender plasticorder. The method developed by Harpell and Walrod[17] was used to determine the kinetics of the crosslinking reaction. The processability of the iPP blends was evaluated by measuring the torque (torque = moment of force) required to mix the molten components in a heated chamber under fixed conditions, i.e., temperature, time, and rotor speed. This is a very useful equipment to distinguish the crosslinking behavior of iPP from that

of other PO materials. iPP presents particular torque–time curves at constant rotating rotors speed, at least compared to those of the most popular PO material: PE.

Figure 1 (torque variation as a function of time) reports the different rheological behavior of crosslinked PE and iPP in the presence of crosslinking agents and peroxide. Here, t_A and t_B are the times corresponding to the polymer melting point and the maximum crosslinking degree, respectively. In this plot, curve 4 illustrates the scission degradation behavior of iPP in the presence of the peroxide. The torque decreases to a slightly lower value than the corresponding to the melting point A (T_A) for long rotating times. As a reference, the crosslinked behavior of PE in the presence of peroxide is shown (curve 2). Here, it is observed that the curve reaches a maximum crosslinking torque value T_B and thereafter remains constant. This is due to the fact that the primary and secondary carbon atoms of the backbone of most of the PO materials prevent the scission degradation reaction, and the crosslinking reaction is favored. On the other hand, curve 3 characterizes the behavior of the unmodified iPP. Finally, curve 1 shows the particular torque variation of iPP in the presence of crosslinking agents. This behavior can be described as follows:

At the beginning, the iPP melts and the torque decreases to a minimum value T_A (point A) which describes the transformation from the solid to the molten state. At this point, the iPP and the crosslinking agents start to interact and the crosslinking reaction begins, while the torque increases until it reaches the maximum value T_B (point B). After that, a partial decrease of the torque is observed. This slight decrease, which is specific for the iPP, is attributed to the partial destruction of the network formed. Then, a leveling off takes place with an almost constant torque T_C value at the point C, usually higher than T_A. The T_C value depends on the crosslinking agents' content and efficiency.
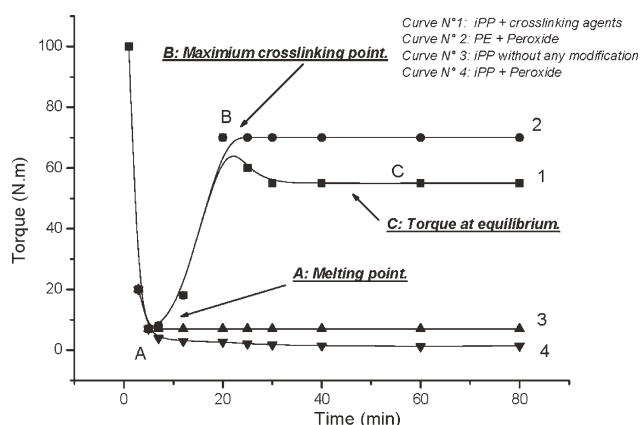

Figure 1 Crosslinking rheological behavior of iPP and PE.

From the above curves, it is clear that the crosslinking of the iPP shows an original and new torque–time behavior, which characterizes a particular rheological behavior.

The experimental protocol used consists on testing four crosslinking concentrations with the iPP at three different processing temperatures, and at a constant rotating rotors speed. The CAs are composed of sulfur and peroxide in the same weight percent, plus the accelerator (in [1/4] of the sulfur or peroxide percent). The composition of the samples is indicated in Table I. The total mass of CA is added in different weight percents (from 0.5 to 10 wt % of sulfur and peroxide) to the iPP in the solid state before to be mixed onto the closed chamber of a Brabender mixer at 170, 180, and 190°C for a continuous rotating time equal to 20 min at 60 turns/min.

Gel content measurement

Since no normalized procedure for the gel content measurement in crosslinked iPP is found in the literature, we used the ASTM D 2765 norm by analogy to the crosslinked PE, though working at a temperature of 130°C. We consider this norm as a very useful starting point to set the working conditions described above. However, in using this alternative method, it should be mentioned that the values obtained may be different from those obtained by a normalized method. The temperature of the immersed polymer is above the crystallization temperature and below the melting point of iPP. In addition, we have taken into account the period necessary to achieve first, the complete dissolution and then, the gel formation in the iPP samples. Before the gel content measurements were performed, the specimens were cut into small pieces with the surface-to-volume ratio as large as possible. Then, 0.2–0.5 g of crosslinked iPP were weighed and then immersed in the extracting solvent (xylene) at a constant temperature $T = 130°C$ for 4 h. After the extraction, the samples were removed and weighed after drying. These working conditions are similar to the ones used by other researchers.[5,8] By following this procedure, the gel content[5,8] as well as the swelling ratio[22] of the crosslinked iPP can be determined.

Steady-state study

This rheological study was performed with a rheometer MCR500 from PHYSICA (frequency from 10^{-4} to 10^2 Hz) using plate–plate geometry with two diameters: 25 and 50 mm. This instrument is controlled by a computer through software US2000 to process and analyze the results. A variety of frequency range and temperature control systems can be changed easily at any level, in no time with this
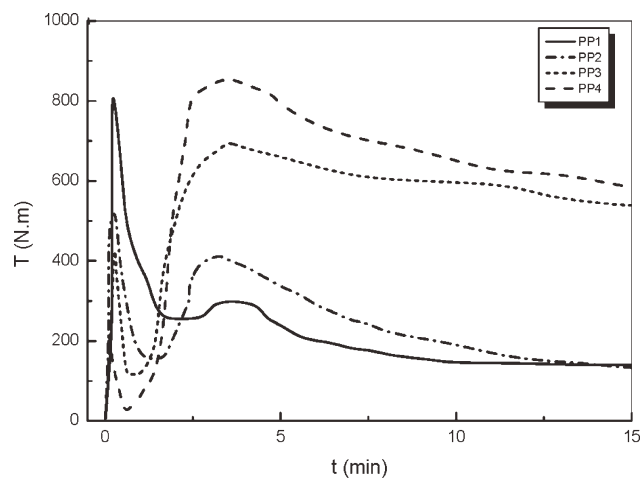

Figure 2 Torque–time evolution for the different samples at $T = 190°C$. For sample composition, see Table I.

rheometer. The measurements (permanent regime, rotation mode) were performed at a shear rate from 10^{-3} to 10^3 s^{-1} in the temperature range 180–220°C.

RESULTS AND DISCUSSION

Influence of crosslinking time

The kinetics of the crosslinking reaction was established using the Harpell and Walrod technique.[17]

Figure 2 clearly illustrates the crosslinking step from T_A to T_B for the different samples at a temperature $T = 190°C$. All the torque–time curves shown in Figure 2 are similar to the curve 1 described in Figure 1. Figure 2 also shows that this crosslinking step is strongly dependant on the composition. As the weight percent increases, the T_B torque value increases, and the crosslinking time t_B necessary to reach the point B is shorter. Thus, one can conclude that the viscosity increases with the crosslinking degree, thus giving rise to an increase in the T_B torque value.

Figure 3 illustrates the influence of the temperature on the crosslinking time t_B for the different compositions studied. It is shown that, for all the compositions, the crosslinking time is shorter at $T = 180°C$, i.e., the intermediate temperature. Based on these results, it seems that the processing temperature governs the crosslinking time t_B, and the sample composition has only a little influence on it. However, there is a nonlinear dependence between the working temperature and the crosslinking time. For this reason, it is not possible to determine the activation energies by using this method. It should be also mentioned that any other system compared to the present formulations could show a different behavior. This depends, to some extent, on the accelerator used. This uncertainty is due to the complexity of our crosslinking reaction. The kinetics of this
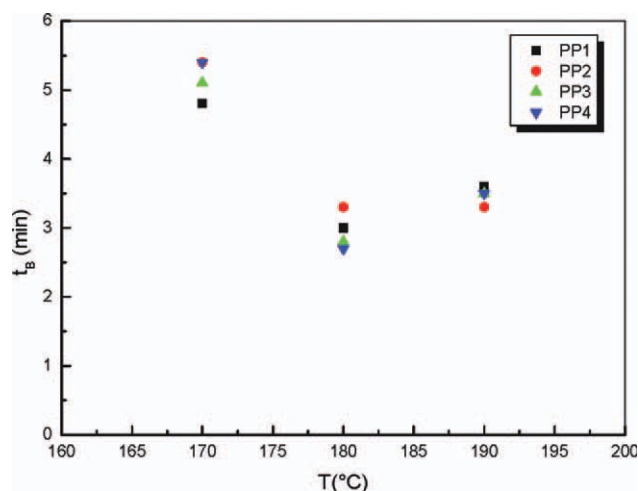
Figure 3 Maximum crosslinking time t_B as a function of temperature for the different samples. For sample composition, see Table I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction is strongly related to the amount of active macro radicals involved, thus depending somehow on the accelerator used.

Figure 4 shows the evolution of the torque T_B value as a function of the peroxide content for the three temperatures studied. At $T = 170°C$ and $T = 180°C$ the crosslinking behavior for the different peroxide contents is similar. Therefore, the crosslinking kinetic process is identical, but the T_B is somewhat delayed at the lower processing temperature $T = 170°C$. Concerning the behavior of the different formulations at $T = 190°C$, the curve is nearly linear as compared to the two other working temperatures. This could be related to the increasing reaction kinetics or to a transition of the crosslinking mechanism. Another reason could be the competition between the crosslinking
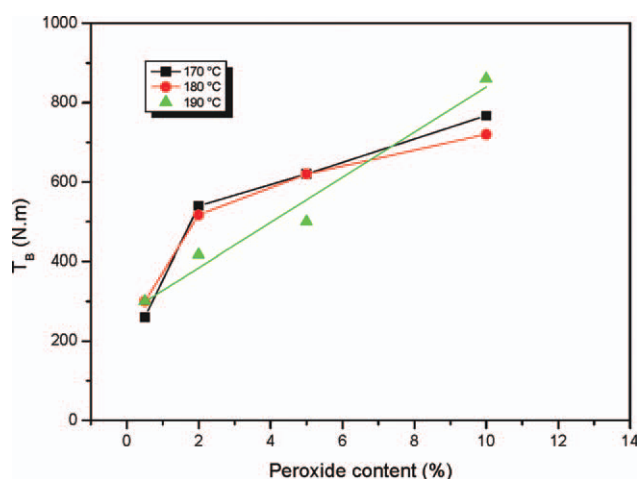

Figure 4 Maximum crosslinking torque value T_B as a function of the peroxide content for different working temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
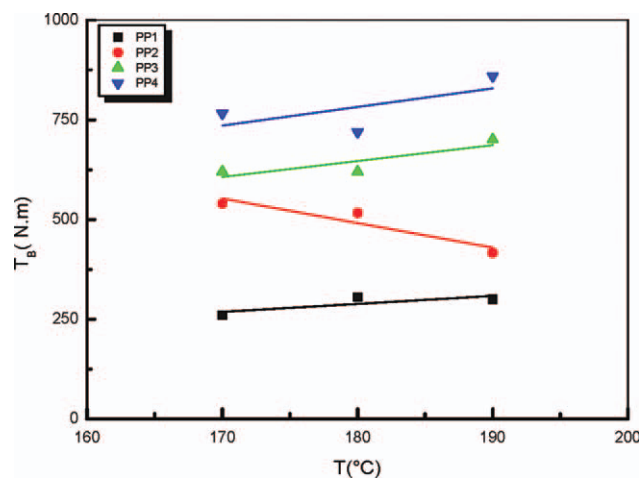
Figure 5 Maximum crosslinking torque value T_B as a function of temperature for the different samples. Sample composition is indicated in Table I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and the scission reactions, as indicated in Ref. [23]. At the equilibrium, the system shows the predominant crosslinking reaction. This is more evident for the two working temperatures of 170 and 180°C.

Figure 5 illustrates the maximum torque values T_B as a function of the working temperature T for the different samples. The sample PP1 represents the most common case, whereas in case of sample PP2 a negative deviation is shown. A positive deviation is also shown for the other two formulations. In all cases the variation is quite small according to the slope of the curves, and the effect is relative, though sensitive.

The torque–time curves obtained from the thermographs have been analyzed by using the Monsanto method, developed by Harpell and Walrod.[17] The variation of log $(T_B - T_t)$ as a function of time is used to calculate the crosslinking reaction constant K. Figure 6(a–d) shows the evolution of log $(T_B - T_t)$ as a function of the crosslinking time and temperature for each sample. From this figure it can be seen that this evolution is linear in all cases. The behavior of all the compositions is quite similar for the three working temperatures. The different slopes mean that all of them follow a first order exponential law having different kinetics. On the other hand, it is noticed that the PP1 sample presents lower torque T_B values and longer t_B times. This is due to the fact that when the crosslinking agent content is lower, the number of macroradicals involved is smaller, and the crosslinking reaction step is slower.

Gel content

In the frame of this study, the gel content was measured using xylene as a solvent. This was done to determine the corresponding crosslinking degree for
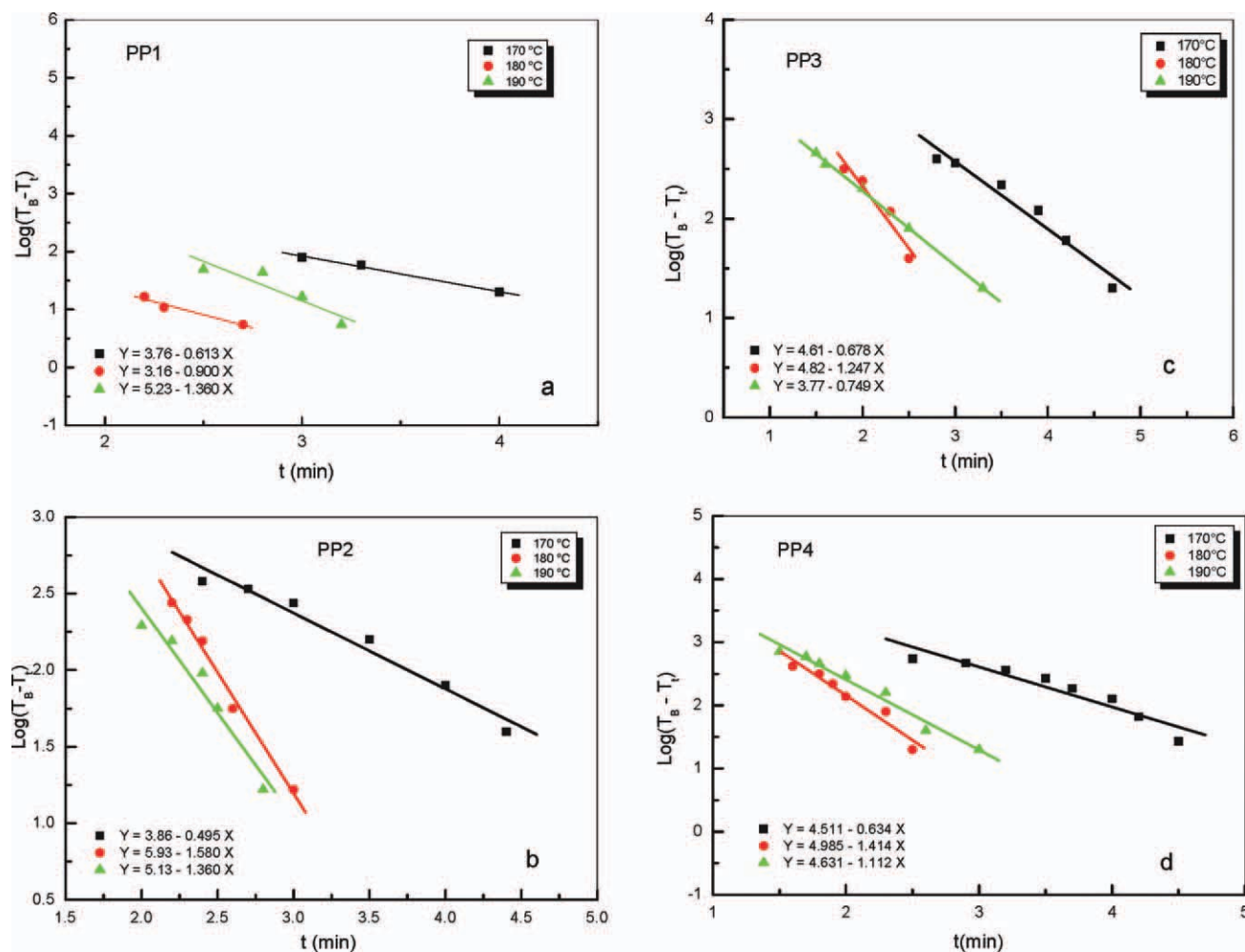
Figure 6 Log $[T_{max} - T_i]$ as a function of the crosslinking time and temperature for the different samples: (a) PP1; (b) PP2; (c) PP3; (d) PP4. See Table I for composition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the different compositions. As it was indicated above, this test was performed according to the ASTM norm D 2765. The obtained results listed in Table II clearly show that as the CA content increases, the gel content values also increase up to a value of 75%. For CA contents higher than 5% wt, no significant change in the gel content values was observed. We should point out that such results are in good agreement with those obtained by the DRA method.

Steady-state study

To have a better idea about the rheological behavior of the new material formed, steady-state viscosity measurements were performed using the parallel plates rheometer. Figure 7 shows the variation of the viscosity as a function of the shear rate for the different samples at $T = 200°C$. It is clearly seen that the viscosity decreases as the shear rate does increase; this variation follows a power-law. It is also noticed that there is a slow viscosity decrease at low shear rates

$(0.01–1 \text{ s}^{-1})$; this decrease is accentuated for intermediate shear rates (from 1 to 100 s^{-1}). At higher shear rates ($\geq 100 \text{ s}^{-1}$) the viscosity decreases again in a slower way. Thus, one can distinguish three phases of decreasing viscosity that are better observed for the higher crosslinking agent contents (samples PP3 and PP4). Table III shows the viscosity values found at two different working temperatures (180 and 200°C) for the four materials investigated. From these values, the activation energy E_a can be derived, through the Arrhenius equation, at zero gradient viscosity (η_0)[17,24]:

TABLE II
Gel Content Values for the Different Samples

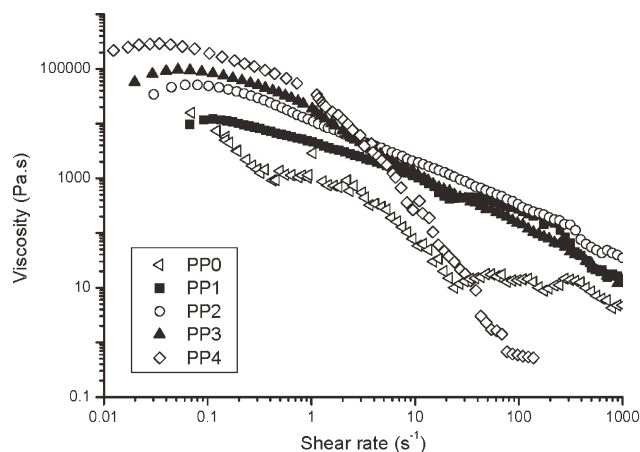| Sample code	Gel content w/w (%)
PP1	17.36
PP2	41.03
PP3	74.44
PP4	75.1

See Table I for sample composition.

Figure 7 Variation of the viscosity as a function of the shear rate for the different samples at $T = 200°C$. See Table I for composition.

$$\eta_0 = A e^{(-E_a/RT)}$$

where A = constant; E_a = activation energy, in kJ mol^{-1}; T = temperature, in K; R = gas constant, equal to 8.314 J K^{-1} mol^{-1}. Table IV lists these E_a values for the different compositions. Here again, sample PP2 is the one that behaves in a particular way, showing the highest E_a value. It is observed that for a given proportion of crosslinking agent the viscosity increases with temperature. This unusual behavior could be explained by the fact that crosslinking is favored by an increase of temperature, thus overcoming the effect of temperature on the sample viscosity. On the other hand, the sample PP4 presents a negative value of the activation energy, due to the fact that the viscosity of this sample decreases as the temperature increases, in agreement with the usual behavior. This may be attributed to the partial destruction of the highly crosslinked structure of this sample which shows the highest gel content.

Figure 8 shows the effect of temperature on the viscosity-shear rate behavior. In this case, the material prepared with the highest crosslinking agent content (sample PP4)) is analyzed: a phase transition is observed first at the intermediate shear rates; this transition is less pronounced at higher processing temperatures, and also, the range of shear rate in which this transition appears is shorter. Thus, we can conclude that, in this case, the viscosity evolution is very sensitive to the temperature. Let us compare, for

TABLE IV
Activation Energies for the Different Samples

Sample code	E_a (kcal mol^{-1})
PP1	4.332
PP2	37.135
PP3	13.397
PP4	−17.01

For sample composition, see Table I.

instance, the two extreme curves corresponding to $T = 180$ and $220°C$ in Figure 8. In the former case, the crosslinking reaction predominates, but, in the latter, there is a continuous equilibrium between the crosslinking reaction (formation of the long-chain bridges), and their opening. The two other curves represent intermediate states. This finding is of importance, and shows that the crosslinked material undergoes an opening of the crosslinked part at high temperatures and intermediate shear rates (laminar flow). This phenomenon is more apparent for higher crosslinking degrees. This is due to the fact that the links between the different bridges are covalent bonds. Covalent bonds are known to be very strong at low temperatures in the solid state, as well as at low shear rates in the molten state. However, these bonds become weaker at high temperatures at intermediate and high shear rates, i.e., in the molten state (220°C in our case, see Fig. 8). This behavior is, in a certain way, similar to the one characteristic for the Diels–Alder reaction[20,21] that occurs in a "Sol–Gel" system. It has been noticed that, even for high crosslinking degrees (i.e., for high crosslinking agent contents), the viscosity values obtained at high shear rates are very low for all compositions, and quite similar to those of virgin iPP (see Fig. 7).

We consider such a result to be extremely interesting from the processing point of view. In fact, this crosslinking method could be used as a new chemical tool to obtain a new iPP type with good and controllable melt strength characteristics.[15,16]

CONCLUSIONS

1. From the various rheological studies performed, we conclude that the crosslinking reaction follows an exponential law. This is correlated by the Monsanto technique and, as

TABLE III
Newtonian Viscosity at Different Temperatures for the Different Samples

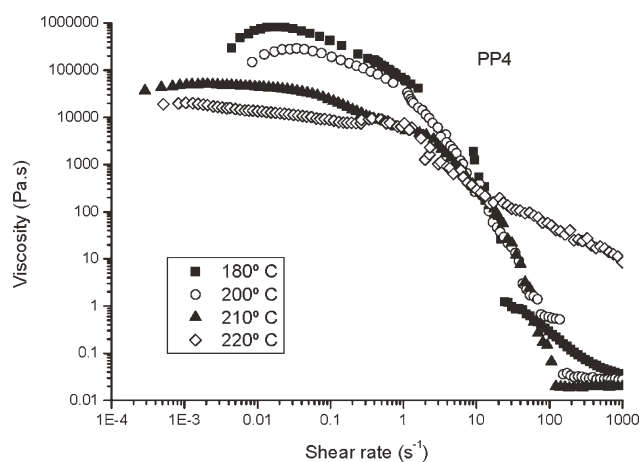| Sample code	PP1		PP2		PP3		PP4	
Temperature (°C)	180	200	180	200	180	200	180	200
η_0 (Pa s)	9790	12,000	7960	48,900	43,800	82,200	427,000	19,2000

See Table I for sample composition.

Figure 8 Variation of the viscosity as a function of the shear rate for sample PP4 (see Table I) measured at various temperatures ranging from 180 to 220°C.

expected, the crosslinking degree is strongly dependent on the crosslinking agent content.

2. The crosslinking time t_B is mainly influenced by the temperature. However, this dependence is nonlinear.

3. The crosslinked sample PP2 presents a particular behavior: its decreasing T_B dependence with the temperature (DRA study) is different with respect to the T_B increasing one shown by the other compositions. In addition, from the steady-state study, it is found that this material shows a higher energy of activation.

4. The steady-state rheological analysis shows that the effects of temperature and shear rate are closely interrelated: the rheological behavior, as well as the reverse crosslinking reaction that takes place, are detected through a sharp decrease of the viscosity at intermediate shearings. All the viscosity values are similar at high shear rates, and not very different from that of pristine iPP.

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