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Monitoring the chemical crosslinking of propylene polymers through rheology

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Abstract

The chemical crosslinking of propylene polymers is described; the reaction has been performed under dynamic conditions, using a peroxide and a furan or bis-maleimide-based coagent as crosslinking promoter; the reaction mechanisms have been investigated through FT-IR spectrometry. Crosslinking experiments have been carried out while keeping constant the amount and the nature of peroxide and increasing the coagent concentration; four different coagents have been used. The samples have been studied, in the molten state, by measuring the melt flow rates (MFR) and the values of G' (storage modulus), G'' (loss modulus), Tg(δ) (ratio G''/G'), and η^* (complex viscosity), in the frequency range 10^{-2}–10^{2} rad s^{-1}. Another set of measurements has been performed on the same materials, collecting for each sample the values of η^0 (zero shear viscosity) and J_e^0 (steady state creep compliance) by creep–creep recovery experiments. The effects of crosslinking degree estimated by gel content and through rheological measurements allows one to evaluate the efficiency of the coagent both in terms of prevention of β-scission and promotion of the crosslinking reactions. These results are discussed with reference to the selection of proper conditions of the crosslinking process in order to achieve a material having desired MFR, rheological behavior and melt elasticity for selected application.

Keywords: Polypropylene; Crosslinking; Rheology

1. Introduction

Fractions of branched or crosslinked polymer are able to confer to the material some interesting and useful properties; in particular, it is possible to increase its melt strength, making possible the production of foams. Moreover, crosslinking and branching can improve some processing characteristics allowing the production of highly processable materials for fibers and blow molding applications. From a morphological point of view, it is possible to classify four kinds of 'chain extended' materials (Fig. 1): long chains can be attached to the linear polymer creating a branched polymer which is characterized by high values of melt elasticity and melt strength. If the number of bonds between the chains increases, fractions of insoluble, crosslinked polymer can be formed [1]. With polymers having a high degree of crosslinking but low values of the average molecular weight, high melt flow rates (MFR) but high values of melt elasticity named 'hyperbranched' are sometimes obtained.

Each of these morphological characteristics can be evidenced by a proper rheological analysis, performed on the molten material, but it is anyway important to say that the materials, produced through crosslinking reactions, are composed by two or more of these model polymers. Crosslinking of polyolefins is usually carried out by inducing the formation of a non-terminal macroradical, which can give interchain bonds through recombination. The macroradicals can be produced by extraction of hydrogen atoms from the polymeric chains by radical initiators created thermochemically or photochemically. Macroradicals can be created through direct scission of the chemical bonds present in the chain structure as well; this happens when the material is treated with high energy radiations (γ-rays, electron beams) and terminal macroradicals are also created [2–7]. Polyethylene, if treated with radical initiators, crosslinks easily, but isotactic polypropylene, especially if treated with peroxyalcohols, degrades through a β-scission mechanism; crosslinking [7,8] can be partially observed

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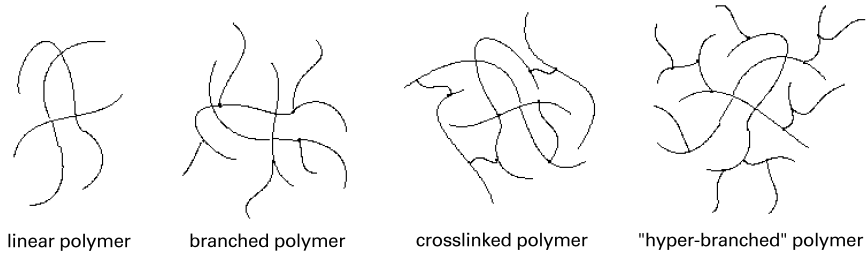


Fig. 1. Molecular structure of different chain extended polymers.

by using high amounts of peroxide or employing peroxides derived from aromatic acyl-peroxides [9]. These initiators create, through decomposition, aromatic radicals which extract preferably hydrogen atoms from methyl or methylene groups in the polypropylene chain, and do not give β-scission thus originating crosslinking points through recombination. By addition of a coagent, which is able to give rapid addition to the macroradical, it is possible to prevent the chain degradation, especially if the new macroradical is not able to give hydrogen extraction from the tertiary carbons present in the macromolecular chains of PP (stabilized macroradical) [10–14]. The macroradical so formed leads to intermolecular bonding through coupling with another stabilized as well as with non-terminal macroradical (Fig. 2).

Furan derivatives having a ring conjugated double bond substituted with an electron attracting group, provide these two requirements; an imine group can also be used, in these derivative the electron attracting effect is due to the nitrogen atom [11,12]. Bis-maleimide derivatives are able to promote crosslinking but unable to stabilize the macroradical (Fig. 3), since they react with it in the same way as maleic anhydride. The strongly reactive radical created by the addition of the macroradical to the double bond gives quickly hydrogen extraction from the backbone, recreating tertiary macroradicals which undergo β-scission [14,15].

Independent of the used coagent, if the crosslinking reaction is carried out in a mixer onto the molten polymer during mixing, 'dynamical' conditions of reaction are said to be used; as a consequence, the crosslinked fractions tend to be dispersed in a non-crosslinked matrix in the shape of small grains. This morphological property is fundamental in order to have an easily processable material [13]. Crosslinking and branching have dramatic effects on the rheological properties of the material in the molten state [16,17]. In order to measure these effects, two kinds of rheological experiments have been performed mainly: frequency sweep tests on parallel plate rheometer under controlled strain conditions, and experiments of creep–creep recovery using a cone-plate controlled stress rheometer. In the dynamic frequency sweep tests, the increase in melt elasticity causes an increase in the values of the storage modulus (G') and, consequently, a decrease in the loss tangent (Tg(δ)), which is mostly evident at lower frequencies; as a consequence, it is possible to observe a change of the slope in the rheological curves, this evidence allowing one to evaluate the transition from a branched polymer to a crosslinked one. In crosslinked polymers in fact, unlike in linear ones, the curve of the complex viscosity does not show a plateau value (η^0), at lower frequencies, but grows more relevantly the crosslinking degree being more. Branched polymers present a plateau value in the curve of η^*, but at lower frequencies, it grows still and this increment starts at higher frequencies when the branching degree is more; moving up to crosslinked materials as described earlier, the plateau value is not visible any more (rubber-like behavior) [18,19]. Melt elasticity can be quantitatively estimated through experiments of creep–creep recovery, performed onto the molten polymer [20,21]: two or more

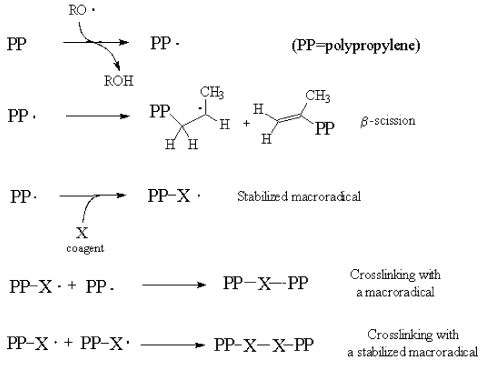


Fig. 2. Reactions of the polypropylene macroradicals with a coagent.

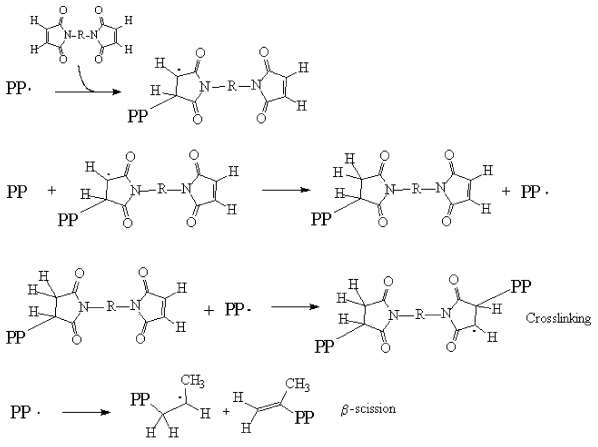


Fig. 3. Reactions of the polypropylene macroradicals with bis-maleimide.

controlled stress creep steps are applied on the material through rotation of the mobile upper cone, acquiring the behavior of the shear viscosity; at a given point, the applied stress is suddenly removed and the behavior of the modulus, as a function of time ($G(t)$), is acquired. The more relevant the viscous behavior of the material, the more sensible is the decay of $G(t)$ during the recovery step; usually, the inverse of the modulus is acquired at this step: the 'recoverable compliance' ($J_r(t) = 1/G(t)$) is a time-growing quantity which tends to an asymptotic value, named 'zero shear recoverable compliance' (J_r^0). J_r^0 represents a numerical estimation of the melt elasticity, which is higher, the chains of the polymeric material being more entangled, and mostly depends, in growing relevance order, on average molecular weight, molecular weight distribution and degree of branching [21,22]. The aim of this work is to study the peroxide-based chemical systems for the crosslinking reactions carried on isotactic polypropylene. Since the main reason of this study is the identification, for an applicative purpose, of a valid system branching and/or crosslinking reactions, primary attention has been focused on the investigation of the final characteristics of the modified materials. Chemical and rheological analysis have been performed, trying to extrapolate from this data the differences between the different coagents and the use of their different amounts.

2. Experimental

2.1. Reagents and instrumentation

2.1.1. Reagents

Bis furfurylaldazine (VP3) (Sigma-Aldrich) bis *p*-phenylen maleimide (Sigma-Aldrich), dicyclohexil carbodiimide (Sigma-Aldrich), dimethyl-amine-pyridine 2,6 (Sigma-Aldrich) di *tert*-butyl *p*-cresole (BHT), (Sigma-Aldrich), malonic acid (Sigma-Aldrich) and 2,5-dimethyl-2,5-di-*tert*-butylperoxy hexane (Akzo-Nobel) have been used as provided without further purification. Furanal and diethyl malonate (Sigma-Aldrich) have been purified by distillation under reduced pressure. Pyridine and piperidine, (Carlo Erba) have been purified by distillation on KOH pellets. Solvents have been purified by standard procedures.

2.1.2. Instrumentation

PP samples have been prepared using an internal Brabender Plastograph PL2100 mixer, torque and temperature data have been acquired by Brabender Mixing software WinMix ver. 1.0. MFR have been measured with a CEAST grader, rheological measurements have been performed using a controlled stress rheometer Rheometrics SR-5000 and elaborated with software packet Rheometrics Orchestrator ver. 6.3.3.

FT-IR spectra were performed with a Fourier Transform Spectrometer 'Perkin–Elmer FT-IR 1750'. Spectra of chemicals have been made on films produced by the evaporation of $CHCl_3$ solutions on KBr windows. PP samples spectra have been acquired on films made by compression molding by deposition between two KBr windows; the samples used for IR characterization have been washed for 16 h with warm acetone, with the exception of the PPBFA samples which have been washed for 36 h.

Proton magnetic resonance spectra were performed with a spectrometer 'Varian Gemini 200 MHz'; all the spectra were made in solution of deutero-chloroform, chemical shifts were assigned in ppm using tetramethylsilane (TMS) as internal standard.

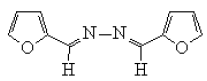
2.2. Synthesis of butyl 3-(2-furanyl) propenoate (BFA)

2.2.1. Synthesis of 3-(2-furanyl)-2-propenoic acid

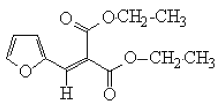
Anhydrous pyridine (150 ml), malonic acid (25 g, 0.24 mol) and anhydrous piperidine (0.012 mol) were introduced, in nitrogen atmosphere, in the order into a three-necked 100 ml flask, equipped with a charge funnel, refrigerant and mechanical agitator. After cooling the solution to 0 °C by means of a bath of ice, furfuraldehyde (23 g) was added. Afterwards, the temperature was raised to room temperature. The solution was maintained at reflux of the solvent for 3 h. The pyridine was distilled off at reduced pressure. The brown solid was dissolved in ethyl ether. Then, the remainders of pyridine and piperidine were extracted with three 50 ml portions of 1% HCl solution. After evaporating the ethyl ether, the reaction product was purified by precipitation with HCl from an alkaline aqueous solution. The yield of 3-(2-furanyl)-2-propenoic acid was 29.01 g (87 wt%).

2.2.2. Synthesis of butyl 3-(2-furanyl) propenoate

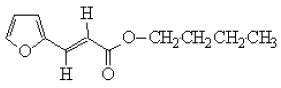
As described in Section 2.2.1, a solution in CH_2Cl_2 (150 ml) of 20 g 2-furanyl-propenoic acid (0.145 mol), 10.73 g of butanol (0.145 mol), and 0.4 g of dimethyl-amine-pyridine (0.035 mol) were charged into the same apparatus. Then, 30.1 g dicyclohexil carbodiimide dissolved in 50 ml CH_2Cl_2 was added at room temperature. The mixture was stirred continuously for 90 h. The white solid precipitate (dicyclohexyl urea) thus produced was separated by filtration on diatomaceous earth (Celite®) and washed on the filter with two portions of CH_2Cl_2. Afterwards, the filtrated solution was washed firstly with three 100 ml portions of a 1% HCl solution, then with two portions of an aqueous solution saturated with K_2CO_3 and at last with distilled water. Most of the solvent of the solution thus washed was distilled off at reduced pressure. Then, the concentrated solution was kept in refrigerator for 24 h. The precipitate (dicyclohexyl urea) thus obtained was separated by filtration as explained earlier. After evaporating the solvent completely, the reminder was distilled at reduced pressure. The butyl 3-(2-furanyl) propenoate (a colorless viscous oil, $b.p. = 138$ °C at 10^{-1} mmHg) has been obtained with the yield of 75 wt% (21.11 g).



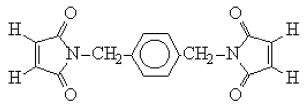
bis-(2-furanyl) aldazine (VP3)



ethyl 2-carboxyethyl 3-(2-furanyl) propenoate (CEFA)



butyl 3-(2-furanyl) propenoate (BFA)



N,N dimethylen p-phenylen bis maleimide (BMI)

Fig. 4. Coagents employed in the peroxide-activated crosslinking reactions on PP

IR main peaks: 3015–3005, $\nu_{(H-C=)}$ 2997–2970, $\nu_{(H-C-)}$ 1715, $\nu_{(C=O)}$ 1640, $\nu_{(C=C)}$ 1158, $\nu_{(C-C(=O)-O)}$

^{1}H NMR assignments: 0.9 ppm, 3 protons, triplet (CH_3 butyl); 1.3 ppm, 2 protons, multiplet; 1.6 ppm, 2 protons, multiplet, (CH_2–CH_2 butyl); 4.2 ppm triplet 2 protons (O–CH_2 butyl); 6.2–6.3 ppm doublet 1 proton, (olefin position 2); 6.4 ppm double doublet, 1 proton, (furane ring position 4); 6.6 ppm doublet 1 proton, (furane ring position 3); 7.4–7.5 doublet, 1 proton, (olefin position 3); 7.5 doublet, 1 proton, (furane ring position 5).

2.3. Synthesis of ethyl 2-carboxyethyl 3-(2-furanyl) propenoate (CEFA)

Anhydrous pyridine (150 ml), diethyl malonate (35 g, 0.22 mol) and anhydrous piperidine (0.94 g, 0.011 mol) were introduced, in nitrogen atmosphere, in the order, into a three-necked 100 ml flask, equipped with a charge funnel, refrigerant and mechanical agitator. After cooling the solution to 0 °C by means of a bath of ice, furfuraldehyde (21.12 g, 0.022 mol) was added. Afterwards, the temperature was raised to room temperature. The solution was maintained at reflux of the solvent for 2 h. The pyridine was distilled off at reduced pressure. Then, the remainder has been dissolved in ethyl ether and washed with 50 ml with two 50 ml portions of a 0.5% HCl aqueous solution. The ether was evaporated and the resulting brown oil was separated in the components through flash chromatography using silica as stationary phase and a solution ethyl acetate–eptane (3:1 vol) as eluent. The ethyl 2-carboxyethyl 3-(2-furanyl) propenoate (a colorless solid having a melting point of 49.1 °C) was recovered through crystallization from a solution of ethyl acetate–eptane (1:1 vol) with the yield of 37.17 g (71 wt%).

IR main peaks: 3015–3005, $\nu_{(H-C=)}$ 2997–2970, $\nu_{(H-C-)}$ 1720–1175 (double peak), $\nu_{(C=O)}$ 1643, $\nu_{(C=C),}$ 1166 (broad), $\nu_{(C-C(=O)-O).}$

^{1}H NMR assignments: 1.2–1.3 ppm, 6 protons, 2 near triplets (CH_3 ethyl groups); 4.2–4.35, 4 protons, 2 near quartets, (O–CH_2 ethyl); 6.4 ppm double doublet, 1 proton (furane ring position 4); 6.7 ppm doublet, 1 proton, (furane ring position 3); 7.4 doublet, 1 proton (olefin position 3); 7.5 doublet 1 proton (furane ring position 5).

2.4. Preparation of the modified samples of isotactic PP

Twenty grams of a crystalline propylene homopolymer (MFR of 10 g/10′ for Moplen X30G and of 1 g/10 for Moplen Q30P) was introduced into an internal Brabender Plastograph PL2100 mixer at the temperature of 180 °C. After 4 min at the said temperature, the cross-linking co-agent was added to the polymer; the mixing of the said components was carried out at 180 °C at a speed of 80 rpm. After 2 min from the addition of the cross-linking co-agent, 2,5-dimethyl-2,5-di-tert-butylperoxy hexane was added while continuing stirring. After 14 min from the introduction of the polymer 0.2 g of stabilizer (BHT) have been added. The total mixing time was 15 min. All the samples were prepared following the procedure described earlier; the relative amounts of the reagents are reported, as parts by weight relative to 100 parts by weight of the polymer, in the tables.

2.5. Determination of the gel content

All the samples have been extracted using the same procedure.

A weighted amount of the sample (2 g) has been suspended in 200 ml of dried xylene at room temperature, the suspension has been warmed under continuous stirring until the boiling temperature of the solvent (135 °C), and the solution has been kept under reflux for 1 h.

The warm solution has been then filtered to remove the soluble fraction, and the residue washed with 50 ml of boiling xylene until the filtrate did not present polymer precipitation any more.

The residue was then washed with cold acetone and dried until constant weight.

2.6. Rheological measurements

2.6.1. Sample preparation

A 2.3 mm, thick compression moulded plaque of about 10 g of polypropylene sample was prepared using a laminating press, the temperature of the plates was of 200 °C and the whole time of permanence in temperature of the material was about 5 min. Disks having a diameter of 2 cm were cut

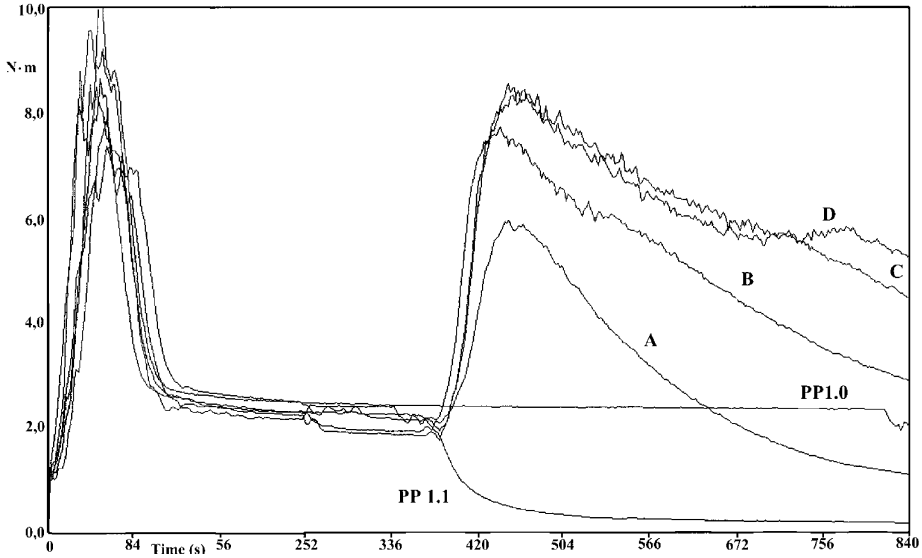


Fig. 5. Behavior of the mixing torque for the samples modified with VP3: (A) PPVP3 1.2; (B) PPVP3 1.3; (C) PPVP3 1.4; (D) PPVP3 1.5.

off the layer, these disks have been employed for frequency sweep experiments performed with the parallel plates rheometer. For samples having values of the melt flow rate over 100 g/10′, disks were used, having a diameter of 4 cm, prepared following the same procedure described from a layer having a thickness of 1.1 mm; these last disks were also used for the creep–creep recovery experiments performed with the cone-plate rheometer.

2.6.2. Frequency sweep experiments

The frequency sweep experiments have been performed in the range 0.01–100 rad s^{-1}. The sweep has been carried out under conditions of controlled applied stress. The value of the stress has been fixed with the aim of keeping the values of the strain between 0.5 and 150%, conditions in which the instrument is able to keep the control over the measurements.

All the experiments have been performed at the temperature of 200 °C, in nitrogen atmosphere, the measurement gap between the plates was 2 mm and the diameter of the plates 2 mm, for all the samples, with the exception of the ones having an MFR over 100 g/10′, the gap used in this case was 1 mm and plates having diameter of 4 mm were used.

2.6.3. Creep–creep recovery experiments

All the experiments of creep–creep recovery have been carried on at the temperature of 200 °C in nitrogen atmosphere using a measurement gap between the point of the upper cone and the lower plate of 0.043 mm. The diameter of the fixtures was 4 cm. The applied stresses varied, depending on the MFR values of the samples, between 2 and 30 Pa, and two creep steps of 10 min with growing values of the applied stress have been performed. Each test has been repeated thrice using different stresses in order to have repeated values of J^0. The average standard deviation on this value in the whole series of the experiments was about 15%.

Table 1
Polypropylenes modified with peroxide and bis furfuril aldazine (VP3)

Sample	Peroxide (wt%)	Coagent (wt%)	Gel content (wt%)	MFR (g/10′)
PP1.0	0	0	–	
PP1.1	1	0	–	
PPVP3 1.2	2	0.4	6.10	
PPVP3 1.3	2	0.6	38.4	
PPVP3 1.4	2	0.8	56.5	
PPVP3 1.5	2	1	56.4	
PP2.0	0	0	–	1.00
PP2.1	0.8	0	–	171
PPVP3 2.1	0.8	0.4	–	28.8
PPVP3 2.2	0.8	0.6	0.71	13.8
PPVP3 2.3	0.8	0.8	2.00	6.96
PPVP3 2.4	0.8	1.0	16.6	6.15

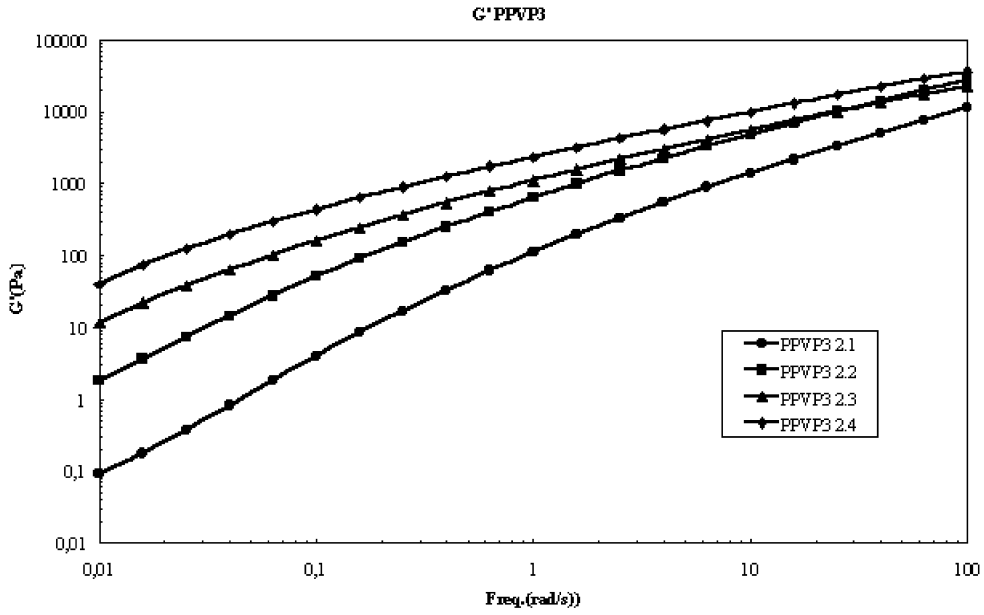


Fig. 6. G' (storage modulus) of the samples modified with VP3.

3. Results and discussion

Each coagent has been used to prepare two sets of samples starting from two different commercially available polypropylenes, Moplen X30G and Moplen Q30P, by Basell Polyolefins; the two materials have different melt flow rates: 10 and 1 g/10′, respectively. In the former set, the samples have been prepared using a higher amount of peroxide and FT-IR spectra and the curves mixing torque vs. time as well as the obtained gel content have been determined. The rheological experiments have been performed on the latter set of samples, in which lower amounts of peroxide has been used in order to have low gel content and low grade of chain scission (visbreaking). These 'low modified' materials have allowed us to perform rheological experiments giving more reproducible results; also, the curves of the rheograms are much less perturbed.

Samples of the former set have been prepared starting from Moplen X30G and are labeled with PPxxx 1.x, the latter, prepared starting from Moplen Q30P, with PPxxx 2.x, where 'xxx' represents the short name of the coagent. All samples have been prepared using the same peroxide: 2,5 dimethyl 2,5-ditertbutyl peroxy-hexane. The four different coagents employed in this work are reported in Fig. 4, with their short name.

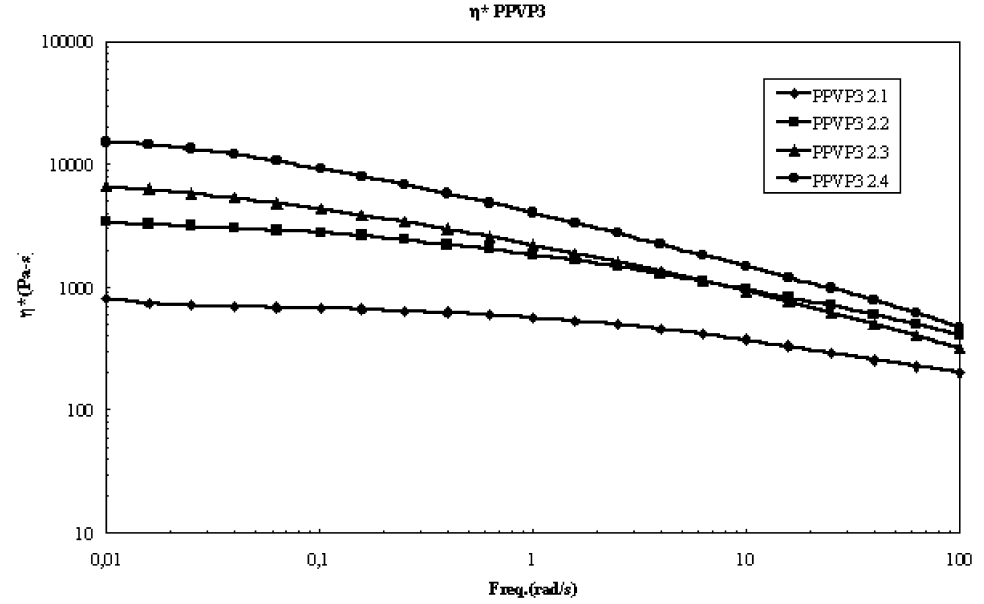


Fig. 7. η^* (complex viscosity) of the samples modified with VP3.

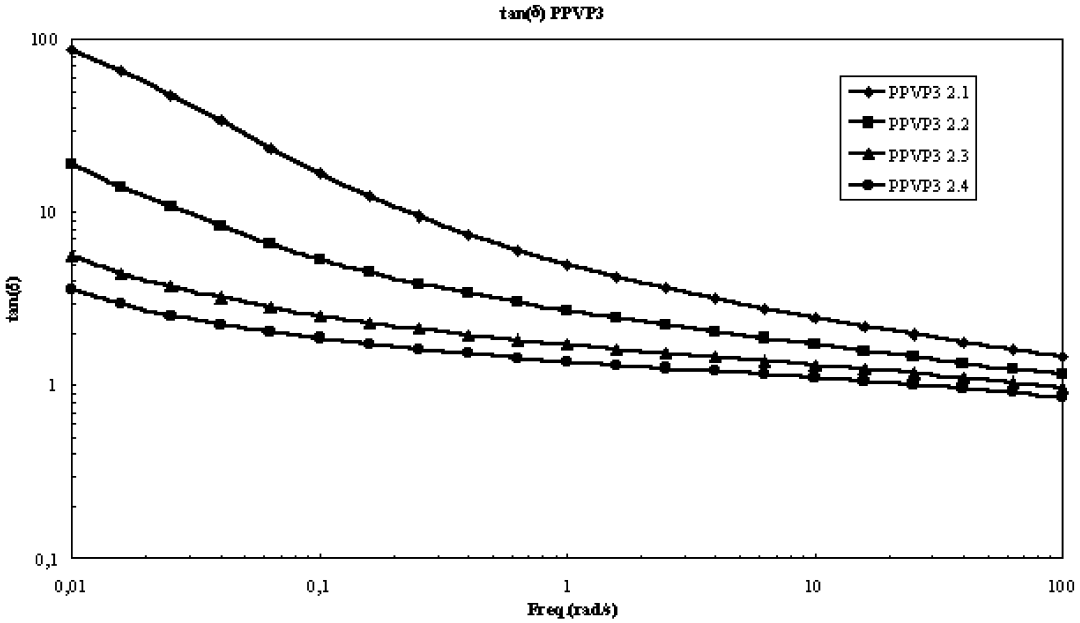


Fig. 8. tan(δ) (loss tangent) of the samples modified with VP3.

3.1. Polypropylenes modified with bis furfuryl aldazine (VP3)

Bis furfuryl aldazine (VP3) is well known as a crosslinking coagent, and is presumed that the addition of the macroradical takes place at the level of the nitrogen atom. The IR spectra of the pure coagent presents the sharp absorption peak at 1520 cm^{-1}, which is weakly present, in the modified polypropylene, after washing with acetone, then very few unreacted functional group seems to be present, in spite of the bifunctional nature of the coagent. The mixing torque grows rapidly after the addition of the peroxide (Fig. 5) showing that the chain extension takes place. The growth of the torque value is caused by the increment of the viscosity, then of the average molecular weight; due to the formation of bonds between the chains. From a certain moment on, the value of the torque begins to decrease, because of the dispersion of the crosslinked fractions in the not crosslinked matrix. The values of MFR and gel content (Table 1) indicate the crosslinking: the gel content is high and grows with increasing coagent relative amount, but the high values of the MFR evidence a lowering of M_w due to the β-scission reaction. The values of MFR are higher than for the starting material and the reference (PP) sample PP 2.0, anyway, they decrease evidently in the set with increasing coagent amount.

3.1.1. Melt rheology of the samples modified with VP3

The shapes of the curves of the storage modulus (G') and viscosity (η) (Figs. 6 and 7) confirm the results of the gel content determination: the rheological behavior changes from the first two samples, branched, no gel content (PPVP3 2.1 and 2.2) to the last two, crosslinked, gel content present (PPVP3 2.3 and 2.4). In the crosslinked materials, the values of G' and η are higher at lower frequencies, the result being a change of the slope (rubber-like behavior). The decrease in the tan(δ), with increasing coagent content, (Fig. 8) is more relevant at lower frequencies, confirming that these samples present the typical properties of highly entangled materials [18].

The creep steps confirm the change of the rheological behavior, which has been observed in the parallel plates experiments, indeed the shear viscosity (Fig. 9), grows in the set and shows the transition from branched to crosslinked material. The steady state, in crosslinked materials (constant value of viscosity), is reached slowly

Table 2
Polypropylenes modified with VP3: creep–creep recovery data

Sample	MFR (g/10′)	Coagent (wt%)	J_r^0 (Pa^{-1})	η Step 1 (Pa s)	η Step 2 (Pa s)
Moplen Q30P	1	–	1.949×10^{-3}	47,780	49,900
Moplen X30G	10	–	1.680×10^{-3}	2665	2652
PPVP3 2.1	28.80	0.4	1.414×10^{-3}	1258	1251
PPVP3 2.2	13.80	0.6	2.532×10^{-3}	3233	3186
PPVP3 2.3	6.96	0.8	7.001×10^{-3}	13,770	13,340
PPVP3 2.4	6.15	1	9.400×10^{-3}	15,160	13,850

Table 3
Polypropylenes modified ethyl 2-carboxyethyl 3-(2-furanyl) propenoate (CEFA)

Sample	Peroxide (wt%)	Coagent (wt%)	Gel content (wt%)	MFR (g/10′)
PP1.0	0	0	–	
PP1.1	1	0	–	
PPCEFA 1.2	2	0.590	–	
PPCEFA 1.3	2	0.885	–	
PPCEFA 1.4	2	1.181	–	
PPCEFA 1.5	2	1.476	Traces	
PP2.0	0	0	–	1.0
PP2.1	0.8	0	–	171
PPCEFA 2.1	0.8	0.590	–	161
PPCEFA 2.2	0.8	0.885	–	118
PPCEFA 2.3	0.8	1.181	–	57.1
PPCEFA 2.4	0.8	1.476	–	33.8

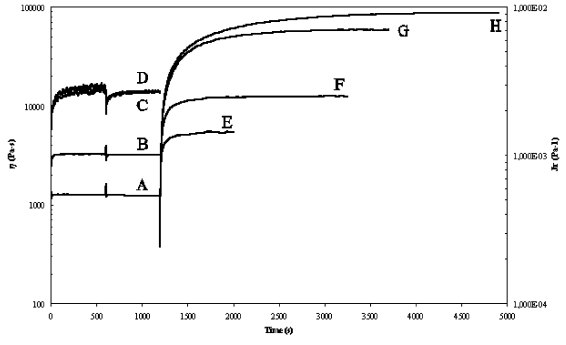


Fig. 9. Creep–creep recovery experiments on the samples modified with VP3: (A) η PPVP3 2.1; (B) η PPVP3 2.2; (C) η PPVP3 2.3; (D) η PPVP3 2.4; (E) J_r^0 PPVP3 2.1; (F) J_r^0 PPVP3 2.2; (G) J_r^0 PPVP3 2.3; (H) J_r^0 PPVP3 2.4.

and no transient peak of viscosity at the change of the stress can be observed. The recoverable compliance grows with the increasing amounts of coagent and its high values (Table 2) reveal a dramatic increment in the melt elasticity. It can be noticed that samples having quite high values of MFR present high compliance also. This does not happen in linear polymers reasonably due to the presence of branched and/or crosslinked fractions.

3.2. Polypropylenes modified with ethyl 2-carboxyethyl 3-(2-furanyl) propenoate (CEFA)

If 2-carboxyethyl 3-(2-furanyl) propenoate is used, the crosslinking reaction proceeds through the coupling of the radicals. The plastograms (Fig. 10) show a behavior of the mixing torque similar to polypropylenes modified with VP3. It increases in the first few minutes after the addition of the peroxide because of the extent of the crosslinking reactions, and after 2 min, it begins to decrease. Anyway, gel content is absent in all the samples (Table 3) and the values of the MFR, even if they decrease by increasing the concentration of the coagent, are evidently higher than for the previous samples prepared with VP3.

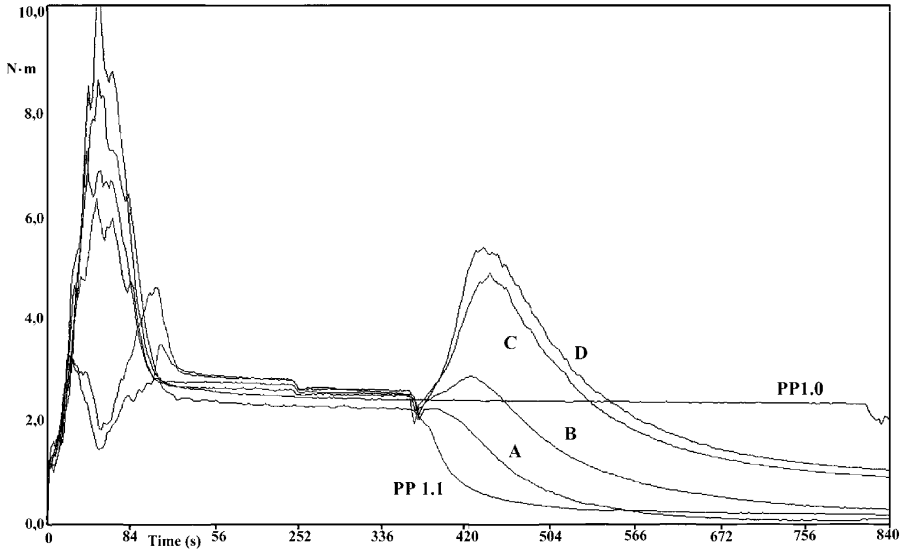


Fig. 10. Behavior of the mixing torque for the samples modified with CEFA: (A) PPCEFA 1.2; (B) PPCEFA 1.3; (C) PPCEFA 1.4; (D) PPCEFA 1.5.

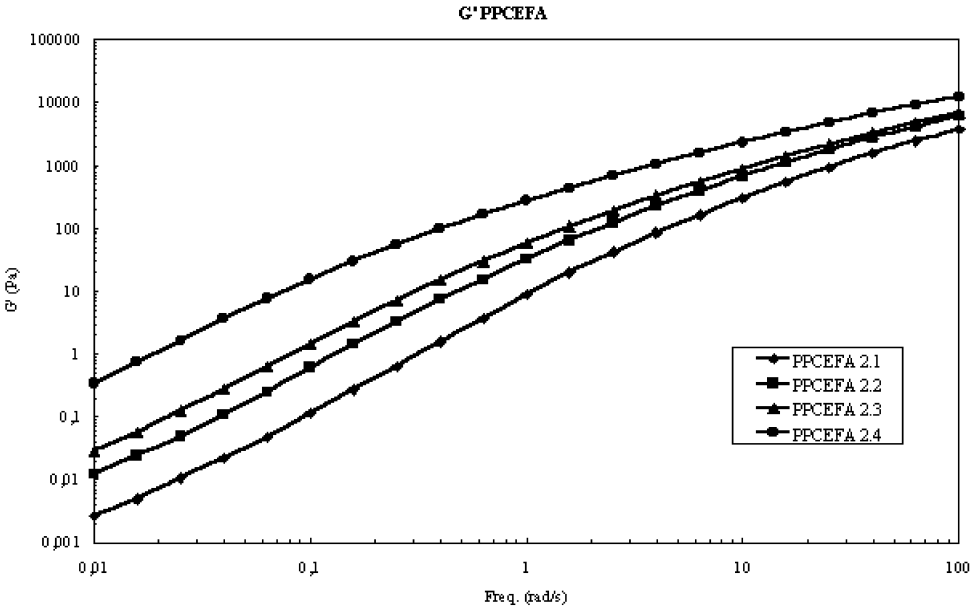


Fig. 11. G' (storage modulus) of the samples modified with CEFA.

3.2.1. Melt rheology of the samples modified with CEFA

The dynamical frequency sweep experiments, performed on the samples of PP modified with CEFA, confirms the formation of branched materials only; in the rheological experiments, no change of the slope, with increasing coagent amounts, and no rubber-like behavior are observed (Figs. 11–13).

The experiments of creep–creep recovery give values of compliance growing with the amount of the coagent, but low (Table 4) and even lower than the starting material until the third sample. We can assume that the CEFA coagent, considering the low values of viscosity also, is unable to prevent the β-scission reaction. Also, the shear viscosity curves are typical of linear or branched polymers (Fig. 14), as observed for the first two samples in the set of the VP3-modified polypropylenes.

The CEFA coagent shows lower efficiency, as a crosslinking promoter, than VP3, probably due to its monofunctional nature, which allows the formation of a crosslinking point, only after the recombination of the radicals. Also, the

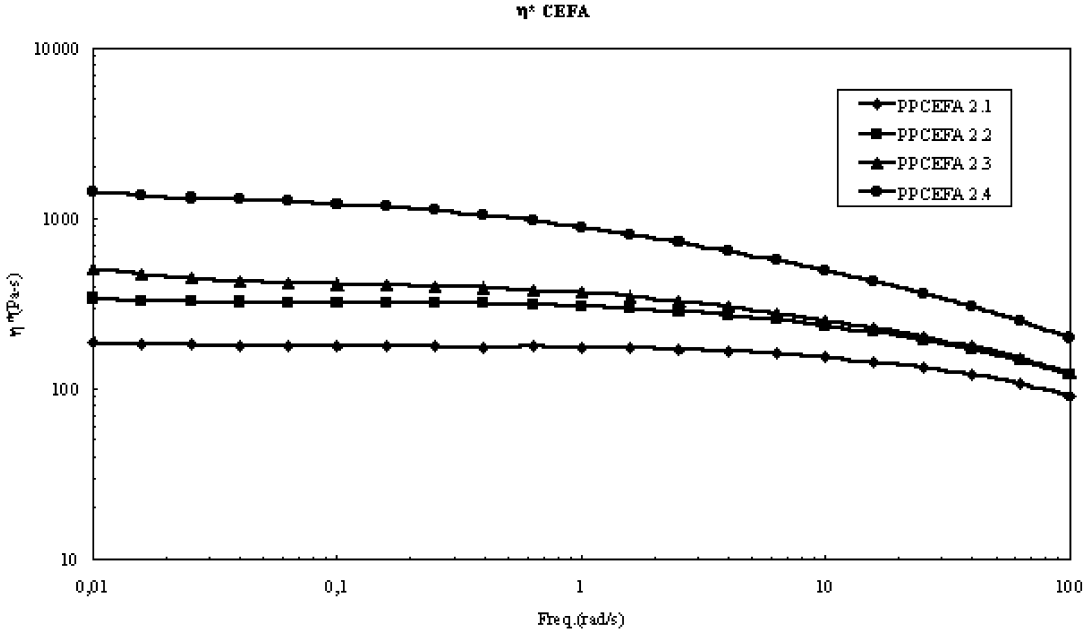


Fig. 12. η^* (complex viscosity) of the samples modified with CEFA.

Table 4
Polypropylenes modified with CEFA: creep–creep recovery data

Sample	MFR (g/10′)	Coagent (wt%)	J_r^0 (Pa^{-1})	η Step 1 (Pa s)	η Step 2 (Pa s)
Moplen Q30P	1	–	1.949×10^{-3}	47,780	49,900
Moplen X30G	10	–	1.680×10^{-3}	2665	2652
PPCEFA 2.1	161.00	0.59	7.250×10^{-4}	172.23	170.27
PPCEFA 2.2	118.00	0.885	8.540×10^{-4}	317.97	310.11
PPCEFA 2.3	57.10	1.181	1.350×10^{-3}	672.77	660.17
PPCEFA 2.4	33.80	1.476	3.690×10^{-3}	2093.5	2031.2

Table 5
Polypropylenes modified with peroxide and butyl 3-(2-furanyl) propenoate (BFA)

Sample	Peroxide (wt%)	Coagent (wt%)	Gel content (wt%)	MFR (g/10′)
PP1.0	0	0	–	
PP1.1	1	0	–	
PPBFA 1.1	2	0.412	–	
PPBFA 1.2	2	0.618	–	
PPBFA 1.3	2	0.824	Traces	
PPBFA 1.4	2	1.030	5.22%	
PP2.0	0	0	–	1.0
PP2.1	0.8	0	–	171
PP–BFA 2.1	0.8	0.412	–	130
PP-BFA 2.2	0.8	0.618	–	35
PP–BFA 2.3	0.8	0.824	–	2.8
PP-BFA 2.4	0.8	1.030	Traces	0.7

sterical hindrance of the two carboxyethyl groups can negatively affect the efficiency of the coagent as a crosslinking promoter.

3.3. Polypropylenes modified with butyl 3-(2-furanyl) propenoate (BFA)

The substitution of a carboxyethyl group in position 2 with a hydrogen atom can be obtained synthesizing an alkyl ester of the 3-(2-furanyl) propenoic acid. The butyl ester of the 3-(2-furanyl) propenoic acid (BFA) gives the polypropylene crosslinking and chain extension. The formation of crosslinking points is shown by the mixing torque growth after the addition of the peroxide (Fig. 15). The mixing torque grows more slowly and reaches the maximum value later than using VP3 or CEFA. Zero or low gel content

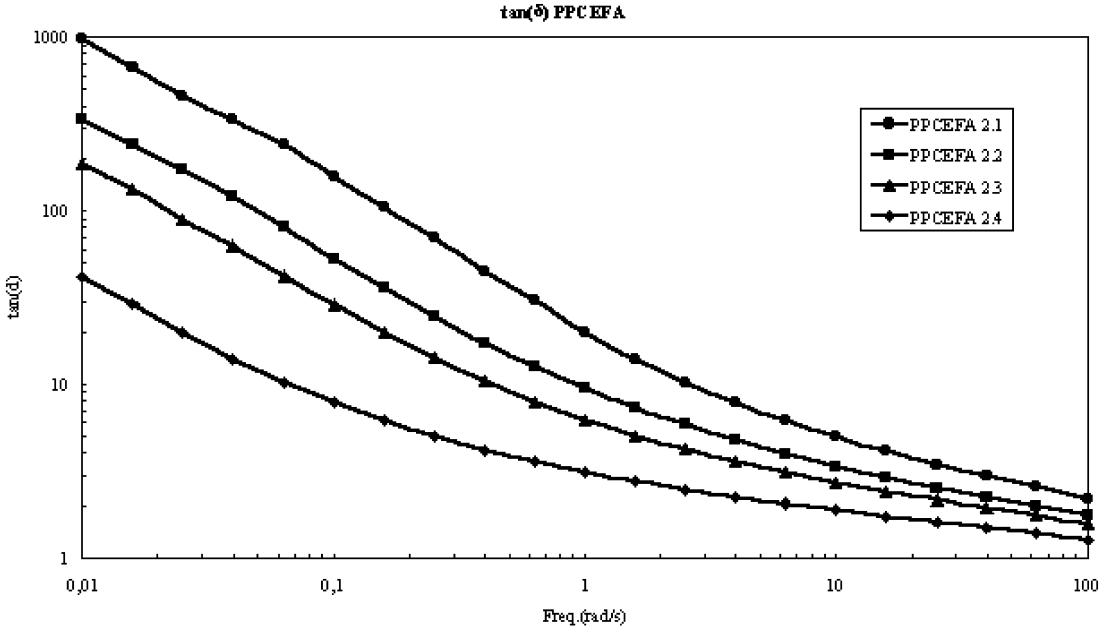


Fig. 13. tan(δ) (loss tangent) of the samples modified with CEFA.

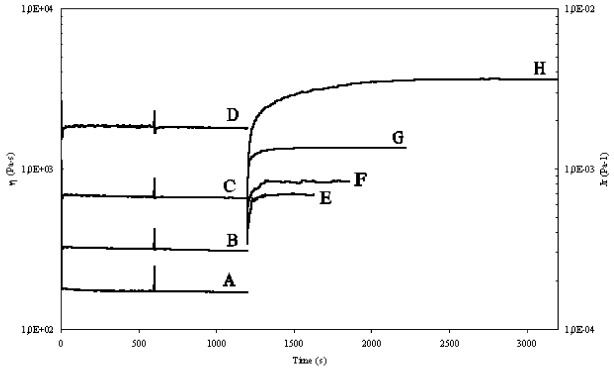


Fig. 14. Creep–creep recovery experiments on the samples modified with CEFA: (A) η PPCEFA 2.1; (B) η PPCEFA 2.2; (C) η PPCEFA 2.3; (D) η PPCEFA 2.4; (E) J^0 PPCEFA 2.1; (F) J^0 PPCEFA 2.2; (G) J^0 PPCEFA 2.3; (H) J^0 PPCEFA 2.4.

has been obtained and the values of MFR are very low, even lower (in the sample PPBFA 2.4) than that of the starting material (Table 5).

The FT-IR analysis (Fig. 16) reveals, in the modified materials, the presence of a peak at 1646 cm^{-1}, which is assignable to a C=C stretching. This peak is not present, at this wavelength, in the spectrum of the neat BFA coagent (the C=C stretching is at 1638 cm^{-1}), and in the spectra acquired on the samples modified with CEFA. Considering the fact that all the samples have been carefully washed with warm acetone before the analysis to remove the unreacted coagent, we can then conclude that there is a new organic radical, having a different double bond, chemically grafted to the polymer.

This can be explained considering that this monofunctional, furane-based, coagent is also able to give, together with the

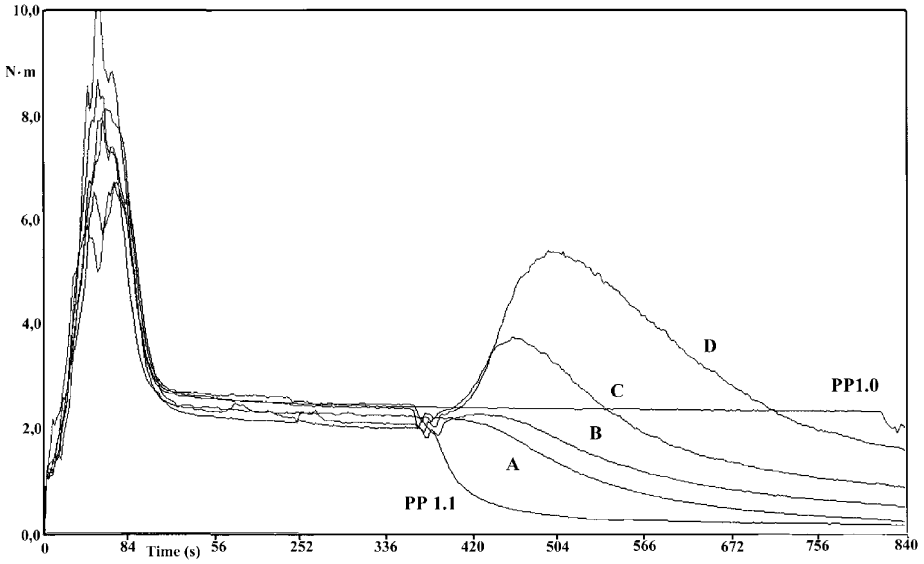


Fig. 15. Behavior of the mixing torque for the samples modified with BFA: (A) PPBFA 1.1; (B) PPBFA 1.2; (C) PPBFA 1.3; (D) PPBFA 1.4.

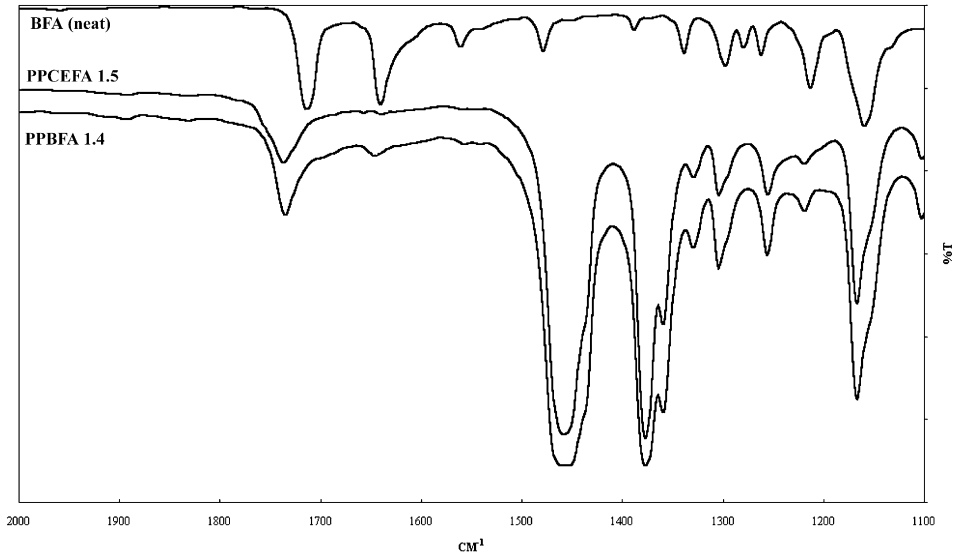


Fig. 16. FT-IR spectra of the CEFA and BFA modified polypropylenesand of the neat BFA coagent.

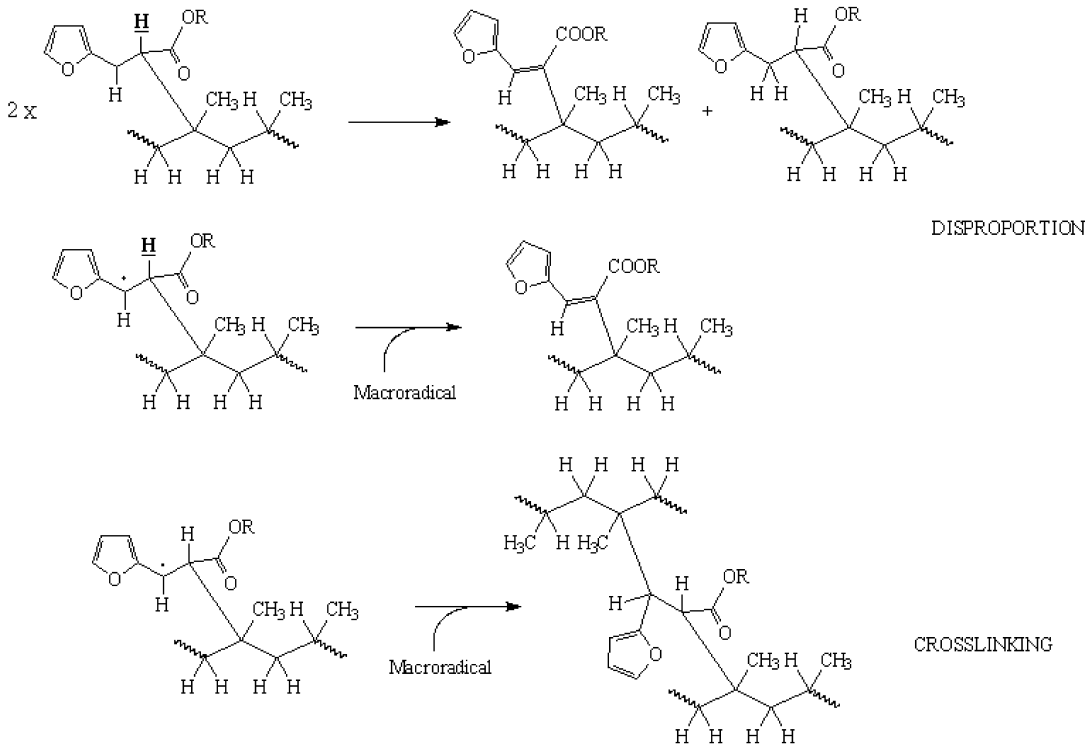


Fig. 17. Reactions of the grafted furane radical having an extractable hydrogen.

crosslinking reactions, the extraction of a hydrogen (underlined one in Fig. 17) from the stabilized radical. This reaction recreates the double bond and acts as a termination reaction without leading to crosslinking.

3.3.1. Melt rheology of the samples modified with BFA

The experiments performed using the plate–plate rheometer do not show the shape of the curves typical of branched polymers, and the last sample (PPBFA 2.4), does

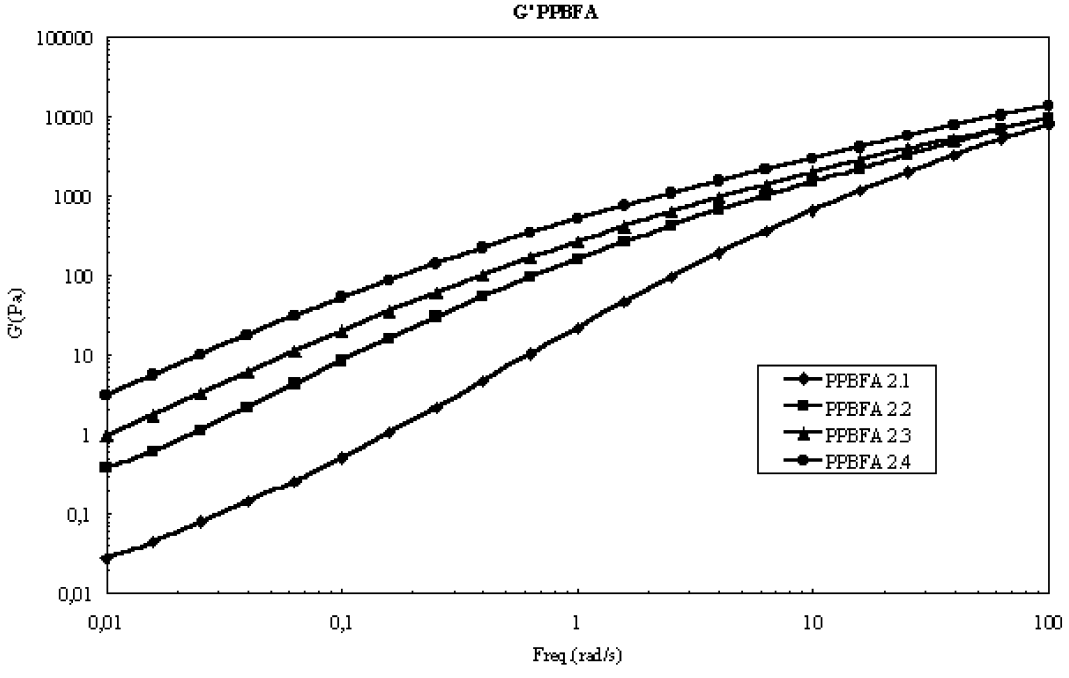


Fig. 18. G' (storage modulus) of the samples modified with BFA.

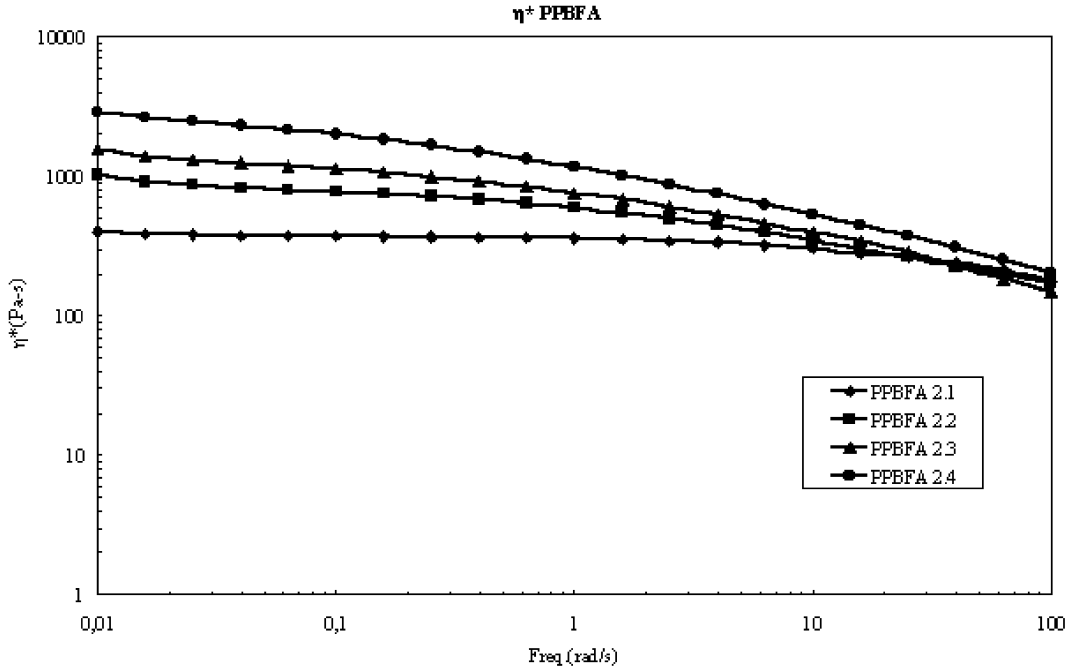


Fig. 19. η^* (complex viscosity) of the samples modified with BFA.

not, however, provide evidence of rubber-like behavior (Figs. 18–20).

Even if the samples present low values of the melt flow rate, recovery experiments give lower compliances than expected for branched polypropylenes (Table 6), thus confirming that BFA is not very efficient in the promotion of crosslinking reactions. The sample PPBFA 2.4 presents, in the behavior of the shear viscosity, the same change of rheological behavior, observed for a crosslinked polymer (Fig. 21). The change is especially evident while comparing the second and fourth sample.

3.4. Polypropylenes modified with N,N p-phenylen bis maleimide (BMI)

If a bis maleimide coagent is used, the resulting materials are not crosslinked, but present no gel content and all the values of MFR are very high (Table 7). Chain extension

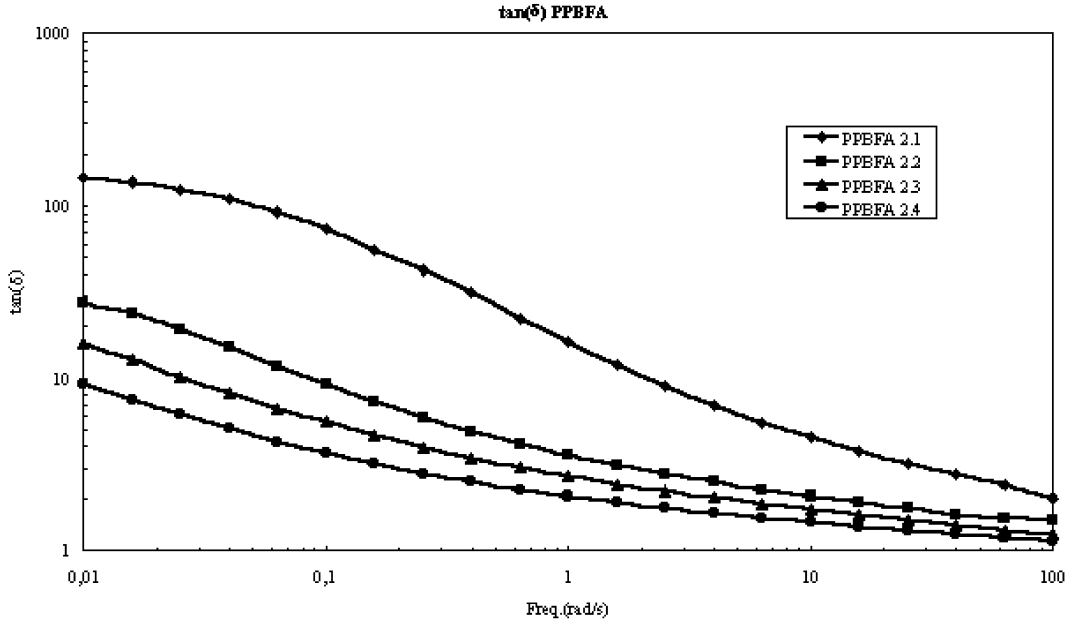


Fig. 20. tan(δ) (loss tangent) of the samples modified with BFA.

Table 6
Polypropylenes modified with BFA: creep–creep recovery data

Sample	MFR (g/10′)	Coagent (wt%)	J_r^0 (Pa^{-1})	η Step 1 (Pa s)	η Step 2 (Pa s)
Moplen Q30P	1	–	1.949×10^{-3}	47,780	49,900
Moplen X30G	10	–	1.680×10^{-3}	2665	2652
PPBFA 2.1	130	0.412	1.865×10^{-3}	197.7	193.4
PPBFA 2.2	35	0.618	3.384×10^{-3}	1059.2	1018.3
PPBFA 2.3	2.8	0.824	5.000×10^{-3}	2844.9	2786.7
PPBFA 2.4	0.7	1.030	5.310×10^{-3}	5943.5	5824.9

Table 7
Polypropylenes modified with *N,N p*-phenylen bis maleimide (BMI)

Sample	Peroxide (wt%)	Coagent (wt%)	Gel content (wt%)	MFR (g/10′)
PP1.0	0	0	–	
PP1.1	1	0	–	
PPBMI 1.1	2	0.46	–	
PPBMI 1.2	2	0.92	–	
PPBMI 1.3	2	1.38	–	
PPBMI 1.4	2	1.84	–	
PPBMI 1.5	1	2.30	–	
PP2.0	0	0	–	1.0
PP2.1	0.8	0	–	171
PPBMI 2.1	0.8	0.92	–	136
PPBMI 2.2	0.8	1.38	–	175
PPBMI 2.3	0.8	1.84	–	164
PPBMI 2.4	0.8	2.30	–	89

reactions can proceed through addition to both the maleimide rings only. No stabilization of the macroradical is provided by this coagent and hydrogen extraction from the macromolecular chain remains effective, and the tertiary on-chain macroradicals evolve easily to β-scission products. Indeed, the mixing torque (Fig. 22) grows rapidly after the addition of the peroxide, but it decreases quickly few seconds later when the consumption of the coagent makes the chain degradation the only proceeding reaction. Consequently, high values of MFR are obtained and increasing the coagent relative amount does not have a relevant effect; in order to have acceptable values of MFR, it is necessary to use less peroxide as in the sample PPBMI 1.5.

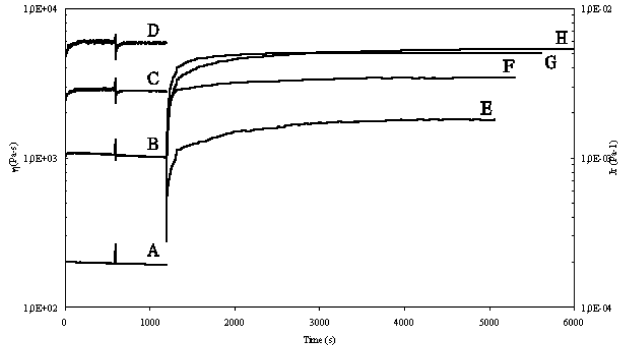


Fig. 21. Creep–creep recovery experiments on the samples modified with BFA: (A) η PPBFA 2.1; (B) η PPBFA 2.2; (C) η PPBFA 2.3; (D) η PPBFA 2.4; (E) J^0 PPBFA 2.1; (F) J^0 PPBFA 2.2; (G) J^0 PPBFA 2.3; (H) J^0 PPBFA 2.4.

3.4.1. Melt rheology of the samples modified with BMI

The dynamical frequency sweep rheological analysis of the samples treated with BMI gives perturbed curves of G' and η^* (Figs. 23 and 24) due to high MFR and presence of branched fractions.

The results of the creep–creep recovery tests (Table 8, Fig. 25) show that the measurement of the recoverable compliance even if the MFR values are very high reveals the typical rheological behavior of the hyperbranched polymers.

4. Conclusions

- Isotactic polypropylene can be crosslinked using peroxides as radical initiators and coagents able to react properly with the macroradicals, produced by the primary radicals, thus spacing them from the backbone and promoting chain extension and/or preventing the β-scission reaction.
- The capability to promote chain extension and to prevent the β-scission, are different depending on the molecular structure of the coagent, and the two actions are not necessarily related.
- Bis-furfuryl aldazine (VP3) promotes the crosslinking as

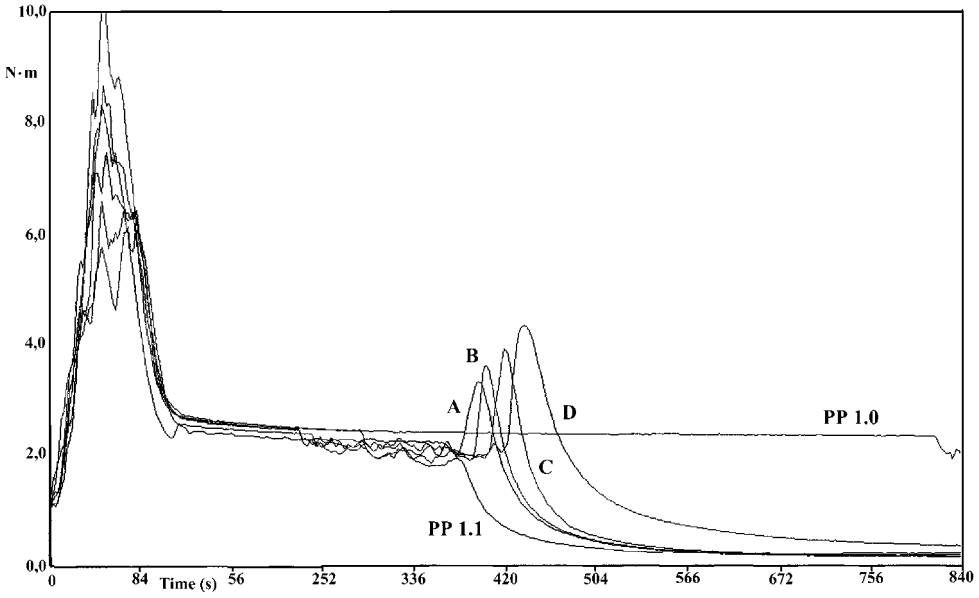


Fig. 22. Behavior of the mixing torque for the samples modified with BMI: (A) PPBMI 1.2; (B) PPBMI 1.3; (C) PPBMI 1.4; (D) PPBMI 1.5.

evident from the rheological properties of the modified samples easily: the values of recoverable compliance (melt elasticity) are high and the rheograms reveal the crosslinked nature of the materials. However, the high values MFR, indicate that VP3 is unable to prevent the β-scission reaction efficiently.

- The monofunctional coagent ethyl 2-carboxyethyl 3-(2 furfuril) propenoate (CEFA) gives chain extension, but the materials have high values of MFR and low values of recoverable compliance. These evidences show that CEFA is unable both to prevent the β-scission and to promote the crosslinking to a significant extent.
- If butyl 3-(2 furfuril) propenoate (BFA) is used, the melt elasticity is not so high, even if the reactions of chain extension happen and the values of MFR are much lower than the samples modified with VP3 and even lower than the starting polypropylene. It is then possible to conclude that this coagent, unlike the previous one, is capable of preventing the β-scission

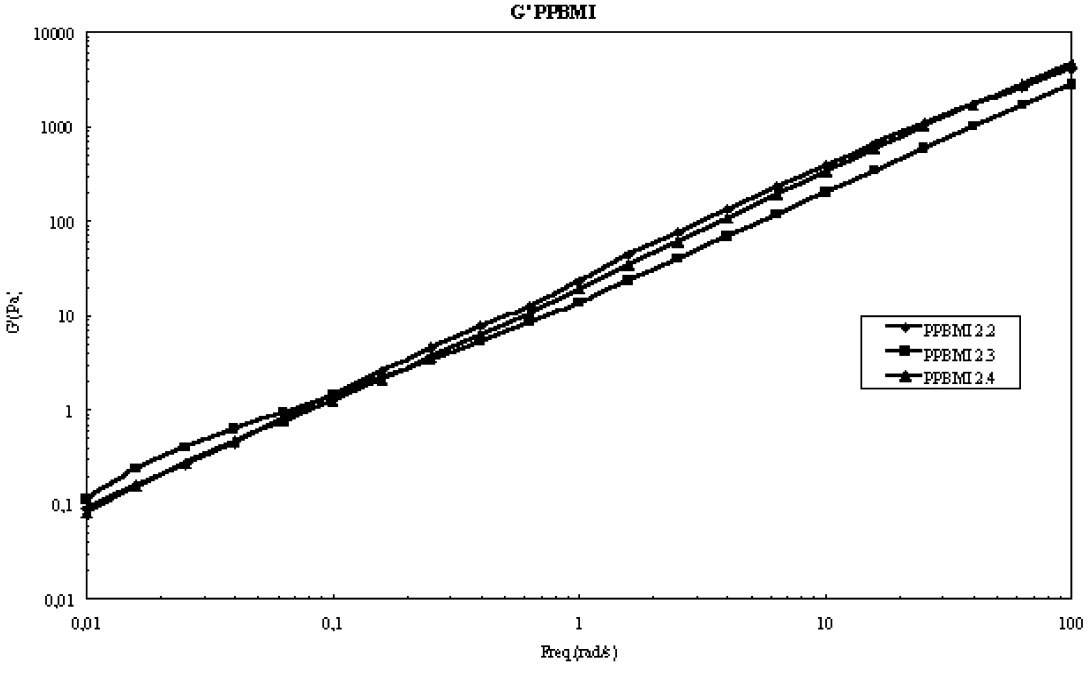


Fig. 23. G' (storage modulus) of the samples modified with BMI.

Table 8
Polypropylenes modified with BMI: creep–creep recovery data

Sample	MFR (g/10′)	Coagent (wt%)	J_r^0 (Pa^{-1})	η Step 1 (Pa s)	η Step 2 (Pa s)
Moplen Q30P	1	–	1.949×10^{-3}	47,780	49,900
Moplen X30G	10	–	1.680×10^{-3}	2665	2652
PPBMI 2.2	175	1.38	1.804×10^{-3}	127.33	125.78
PPBMI 2.3	164	1.84	2.242×10^{-3}	131.58	129.51
PPBMI 2.4	89	2.30	4.016×10^{-3}	251.28	248.35

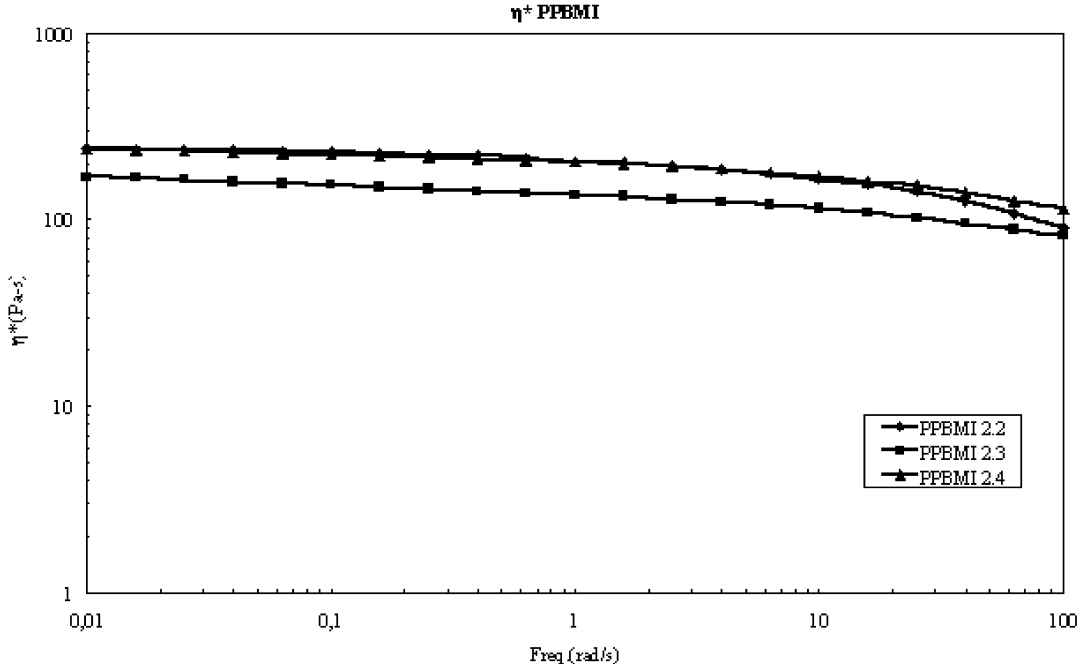


Fig. 24. η^* (complex viscosity) of the samples modified with BMI.

process efficiently, but does not promote the crosslinking reactions efficiently.

- FT-IR evidences, supported by the rheological experiments, allow one to propose a different scheme of reaction of BFA with respect to CEFA. In this scheme, a further reaction is present based on the hydrogen extraction, from the stabilized macroradical. This termination reaction does not lead to the formation of a crosslinking bond.
- *N,N para*-phenylen bis maleimide (BMI) promotes the crosslinking quickly, but is unable to prevent the β-scission at all; modified polypropylene having good values of recoverable compliance but very high MFR is then obtained. The rheological evidences show the typical behavior of highly branched material having low average molecular weight (hyperbranched polymer).
- In general, bifunctional coagents with two points of addition for the macroradical are more efficient in promoting the crosslinking than the monofunctional ones, in which the formation of a crosslink occurs through radical coupling only.
- Melt rheology experiments revealed themselves as powerful instruments to investigate the molecular characteristics modification. Some physical property of the material, as the shear behavior changing the crosslinking and branching degree, then by frequency sweep experiments can be more easily evidenced by creep–creep recovery tests, especially if materials having high MFR, are studied.

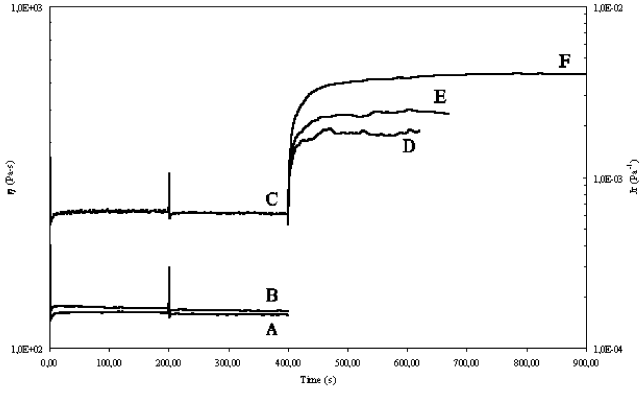


Fig. 25. Creep–creep recovery experiments on the samples modified with BMI: (A) η PPBMI 2.1; (B) η PPBMI 2.2; (C) η PPBMI 2.3; (D) J^0 PPBMI 2.1; (E) J^0 PPBMI 2.2; (F) J^0 PPBMI 2.3.

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