

Dioxazoline Coupling of Maleic Anhydride Modified Polyethylene

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ABSTRACT: Maleic anhydride modified polyethylene (PEgMA) coupling reactions were realized using a dioxazoline coupling agent, (1,3-phenylene)-bis(2-oxazoline), in an internal mixer. In preliminary studies and in model reactions, it was shown that anhydride/oxazoline reactions were very slow or nonexistent compared to acid/oxazoline reactions. The main observed coupling is due to acids resulting from anhydride hydration. In a second part, the coupling reactions were preceded by an anhydride hydration realized by direct injection of different water quantities. In these cases, the couplings were more efficient than when PEgMA

were directly used. At high temperature some of the formed succinic acids were dehydrated, leading to the initial succinic anhydrides. The study of the effect of the molar ratio of oxazoline/anhydride on the PEgMA coupling showed that the maximum apparent coupling was obtained when the ratio was 4. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 837–843, 2005

Key words: coupling; modification; oxazoline; polyethylene; rheology

INTRODUCTION

The addition of highly reactive coupling agents during the last steps of polymer synthesis by polycondensation leads to high-molar-mass polymers at relatively low temperature, a short reaction time, and no vacuum.^{1,2} The use of different types of coupling agents, e.g., diepoxides, diisocyanates, and carbodiimides, is reported in the literature.^{3–6} Dioxazoline was also used as a coupling agent of carboxyl-terminated polyesters³ and polyamides^{2,7} and in the condensation reaction of a dicarboxylic fatty acid.⁸ Anhydride/oxazoline reactions have been described in the literature. Frump⁹ reported a reaction of 2-methyl-4,4'-bis(acetoxymethyl)-2-oxazoline and maleic anhydride, leading to an ester amide. More recently, a mass reaction of succinic anhydride with a dioxazoline gave a highly cross-linked structure in 3 min.¹⁰ At relatively low temperature, the copolymerization of 2-methyl oxazoline and succinic anhydride gave a 50% conversion after a few days of reaction.

Carboxylic acid reaction on oxazoline is a relatively fast reaction, leading to ester amides when conducted in mass at high temperature.^{7,8,11–13} Secondary reactions were also described. The amide obtained by the

acid/oxazoline reaction can react on an other oxazoline function¹⁴, and ester amide function degradations were also observed at high temperature.^{15,16}

From the literature analysis, the choice of a dioxazoline as coupling agent of maleic anhydride modified PE seems to be coherent, and the aim of this study is to evaluate the coupling efficiency of (1,3-phenylene)-bis(2-oxazoline), PBO, on these polymers. One expected application of such coupling is modification of the rheological properties of polyolefin through molar mass and structure evolution control of these polyolefins. A second application is for the synthesis of polyethylene–polypropylene copolymer using maleic anhydride modified PE and PP by statistical coupling using dioxazoline. These copolymers, acting as an in situ prepared emulsifier for PP/PE blends, may compatibilize the two phases.

This study is divided into two parts according to the nature of the functions on which the bisoxazoline reacts: succinic anhydride or succinic acid.

EXPERIMENTAL

Materials

The maleic anhydride grafted polyethylenes (PEgMA) used in this study were PE XA254 and PE XA255, supplied by Solvay. PE XA254 and PE XA255 contain, respectively, 0.16 and 0.18 wt % of grafted succinic

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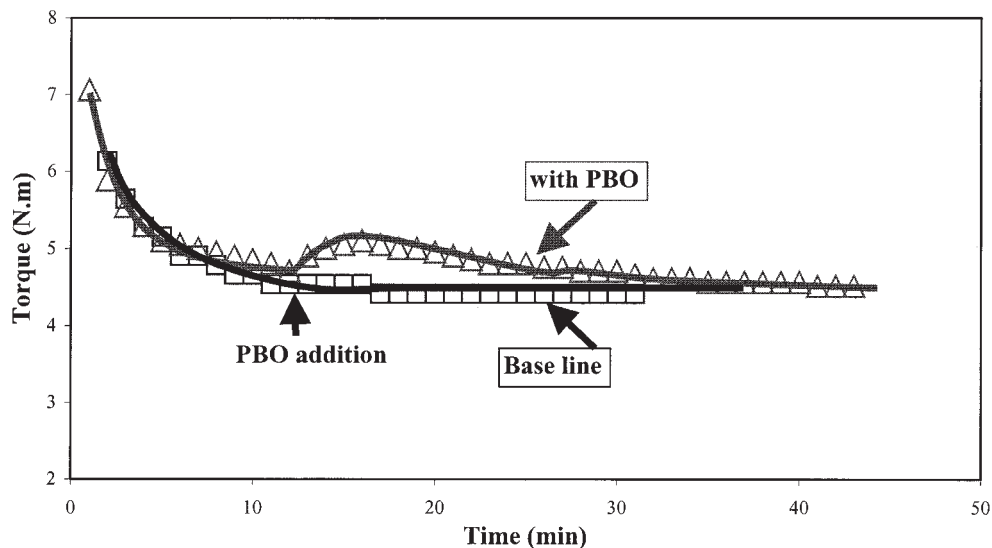


Figure 1 Evolution of the torque recorded during the reaction of the PBO on PEGMA at 150°C in an internal mixer (PEGMA = XA254, $x = 1$).

anhydride. The dioxazoline (PBO) was 2,2'-(1,3-phenylene)-bis(2-oxazoline) from Mikuni Chemical. The 2-phenyl-2-oxazoline and the succinic anhydride were purchased from Aldrich. All reactants were used as received without further purification.

Condensation reactions

Reactions on polymers were conducted using a Haake Rheomix 600 internal mixer. Typically, 40 g of polymer was first introduced into the internal mixer at the desired temperature and rotation rate until melting was complete. The other reactants were then introduced. For sampling, rotation was interrupted for less than 15 s and samples were taken off rapidly.

For model reactions, a 500-mL three-neck flask was equipped with a mechanical stirrer, nitrogen inlet, condenser, and addition funnel. The reactor was heated in an oil bath at 80°C. The device was dried in an oven at 120°C for 2 h before use to avoid anhydride hydration by residual water. The toluene used as solvent was first purified by distillation. A total of 200 mL of toluene was introduced into the reactor. When the temperature stabilized, the reactants were added (0.1 mol oxazoline and 0.1 mol anhydride).

Characterization

A Waters size exclusion chromatograph (SEC) instrument equipped with differential refractometer (R401) and UV absorbance detector (Model No. 440) was used for the model reaction analysis. The solvent was tetrahydrofuran at a 1.0 mL/min flow rate and at room temperature. Styragel HR1, HR3, and HR4 columns were used.

Oscillatory shear flow was used to obtain both the dynamic viscosity and the modulus of the polymers in the molten or liquid state above the glass transition of the components. Measurements were carried out in a Rheometric Scientific RDA2 system equipped with a plate-plate geometry (diameter 40 mm, gap 2mm) during frequency sweeps (0.05 to 100 rad/s) at 170°C within the linear viscoelastic domain.

Fourier transform infrared spectroscopy was performed using a Nicolet Magna-IR 550 spectrometer. An Ever-Glo source was used along with a KBr beam splitter and a DTGS-KBR detector. Films (100 μm) were used for polymer analysis. They were prepared as follows.

A total of 150 mg was placed between two silicone papers in a press at 160°C and pressed progressively up to 60-bar pressure. The press was then opened and the film taken off for analysis. The polymers were pressed for less than 1 min to limit structural modification.

RESULTS AND DISCUSSION

Reactivity of the PBO on the succinic anhydride functions

PBO and PEGMA melt reaction

The torque evolution during the PBO reaction on molten maleic anhydride grafted polyethylene, for a stoichiometric ratio $X = 1$, is shown in Figure 1. In this case, the oxazoline functions should react on the maleic anhydride grafted functions. Since the polymer was not dried before use, it is possible that some anhydride functions were hydrated, leading to acids. Their rate is not evaluated. (The stoichiometric ratio,

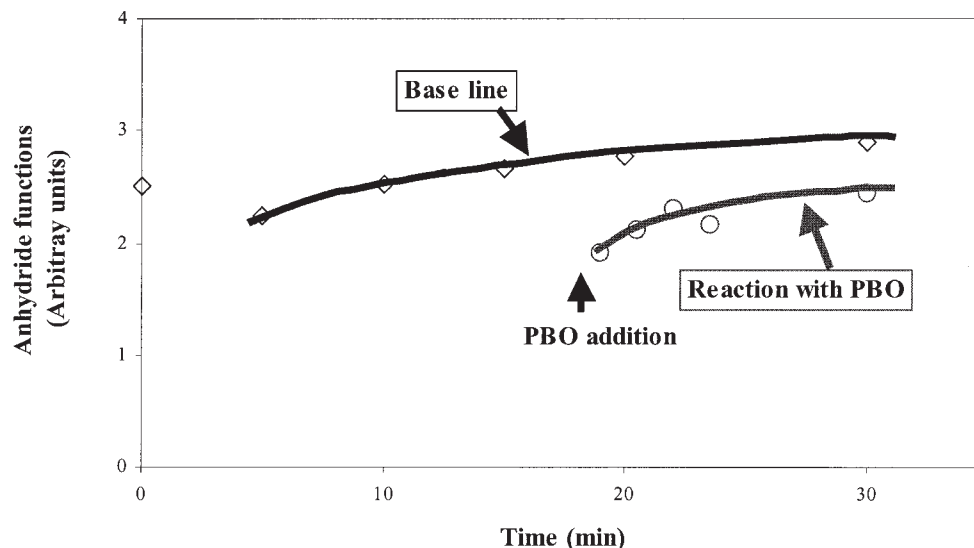


Figure 2 Evolution of the maleic anhydride functions rate, determined by FTIR (PEgMA = XA254, reaction temperature = 150°C).

denoted X , is defined as the number of oxazoline functions to the succinic anhydride grafted function. $X = 1$ corresponds to one oxazoline function for one anhydride function and one oxazoline function for two acid functions.)

The torque increase successive to the PBO addition is connected with the reaction between the dioxazoline and the maleic anhydride grafted polyethylene. This reaction increases the molar mass by coupling of the polymer chains and thus increases the viscosity of the reaction medium, leading to an increase of the internal mixer torque. In this case, the torque increase is relatively low and goes through a maximum after 5-min reaction. The coupling reaction thus does not seem to lead to high-molar-mass polymers. The IR spectra of specimens taken during reaction of maleic anhydride grafted polyethylene confirm coupling (Fig. 2). The baseline represents the anhydride band for the pure PEgMA in the mixer. The rate of the anhydride formation in the medium increases with time. This is due to diacid dehydration into anhydride. For the reactive system, at the addition of dioxazoline, the anhydride rate decreased rapidly and then increased slowly between 20 and 30 min reaction time. This can be explained by taking into account the different reactions involved in this system. In addition to the expected oxazoline/anhydride condensation reaction, a part of the anhydride was first hydrated, leading to dicarboxylic acids. The dicarboxylic acid can either react with dioxazoline or be dehydrated, leading to anhydride. This dehydration increases the anhydride concentration even in the reactive system. This demonstrates that the apparent dehydration rate, just after the dioxazoline important reaction observed at the moment it was introduced, is higher than the acid and anhydride condensation with dioxazoline. Comparing

the maleic anhydride functions rate evolution in the reactive and nonreactive system, it can be concluded that the maleic anhydride consumption is approximately 30%.

This relatively low conversion can only partly be attributed to the fact that the anhydride/oxazoline reaction was studied in the melt and that the reactants were not miscible. In such a case, even with good mixing, the reactant conversion is limited. This low conversion can also be due to the reactivity of the functions used, with the condensation being due to anhydride/oxazoline or acid/oxazoline reaction. To explain the preceding results, the oxazoline/anhydride reactivity was suspected to be low. For this reason, the anhydride reactivity with oxazoline needed to be verified.

Phenyl oxazoline and succinic anhydride model reaction

A reaction was conducted in anhydrous medium in toluene at 90°C between PBO and succinic anhydride and another between phenyl oxazoline and succinic anhydride. In both cases, no reaction was observed by SEC or FTIR even after 8 h. These experiments prove the very low reactivity or nonreactivity of anhydride on oxazoline. From this it can be concluded that the condensation observed in the preceding part is principally due to acid/oxazoline reactions. The high temperature required for melt reactions causes progressive dehydration of diacids and reformation of the cyclic anhydride, and due to the low reactivity of anhydride with dioxazoline the overall observed conversion is limited.

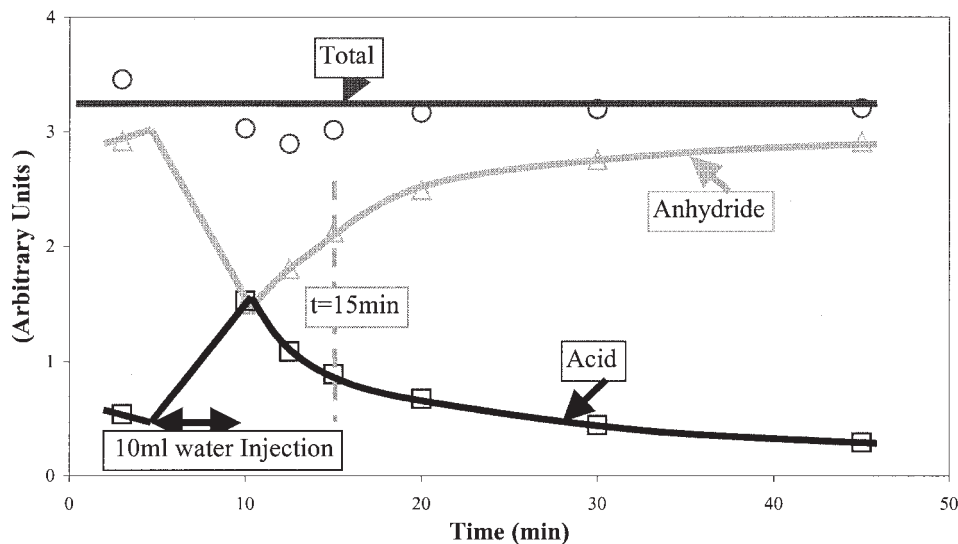


Figure 3 Anhydride and acid function rate evolution with time for PEGMA at 150°C (a) without water addition (PEGMA = XA254) and (b) with 10-mL water injection.

Dioxazoline reaction on partially hydrated maleic anhydride grafted polyethylene

From the preceding part, it appears that in order to enhance the system reactivity and the dioxazoline coupling of the functionalized polyethylene, anhydride hydration should be favored. A hydration/dehydration study was performed by the addition of water during mixing in the internal mixer of a maleic anhydride grafted polyethylene using experimental conditions equivalent to those used for coupling reactions. Water was continuously injected into the internal mixer between 5 and 10 min. The reaction evolution was monitored by FTIR.

Results are given in Figure 3. As expected, the acid concentration continuously increased during the water injection while the anhydride concentration decreased. However, as soon as the water injection was stopped, the acid concentration decreased while the anhydrides were reconstituted.

From this it appeared that in order to favor the acid/oxazoline reaction, water should first be introduced to hydrate the anhydride functions and maximize the acid concentration, and then oxazoline should be injected.

Reactions were realized under these conditions. The torque curves obtained during the reaction of the PBO on PEGMA that was partially hydrated with various quantities of water (10 and 20 cc) are presented in Figure 4. The initial reaction rate and the torque maximum are higher than those obtained with non-hydrated PEGMA, confirming that the PBO reactivity with the carboxylic acid functions (diacids coming from anhydride hydration) is larger than the direct reaction of the PBO on the maleic anhydride functions. The hydration rate also seems to have an effect on the reaction extent.

The FTIR spectra of the reactive system (10 mL water, 150°C, $x = 2$) before dioxazoline injection and at the end of the reaction shows that no residual acid was obtained at the end of the reaction and also shows the presence of the characteristic peaks of ester and amide formed functions (Fig. 5).

Because the reaction of the hydrated system was higher than the reactivity of the nonhydrated one, the rest of this study was carried out on hydrated PEGMA.

In Figure 6 the evolution of the PEGMA viscoelastic properties with the reaction with water and PBO are presented. The important increase in the conservation and loss moduli, as well as the higher values of the complex viscosity of the modified PEGMA, shows clearly the effectiveness of coupling reactions leading to an increase of the molar mass.

Effect of the PBO stoichiometry on the oxazoline/acid reaction

Because the reactions realized in the melt used reactants that were not perfectly miscible, an experimental study that varies the stoichiometry was necessary to optimize reaction conditions.

Experiments were made using different stoichiometric ratios. The effect of the oxazoline/anhydride on the torque evolution with reaction time is illustrated in Figure 7. An increase of the stoichiometric ratio from 1 to 4 results in an increase of the reaction initial rate evaluated from the torque initial slope and the reaction conversion evaluated from the torque curve maximum. For values of the stoichiometric ratio higher than 4, the reaction rate seems unchanged, but the torque curve maximum decreases.

The expected reaction is the acid/oxazoline reaction. For a homogeneous system, and if no secondary

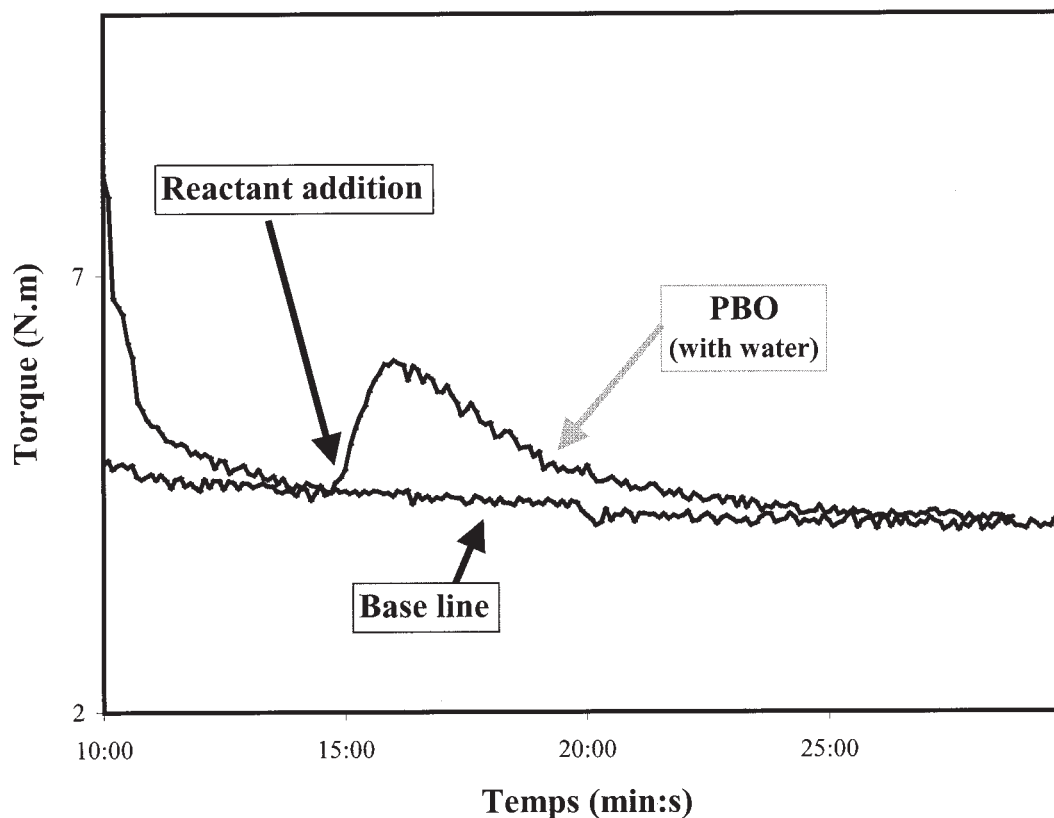


Figure 4 Torque evolution during PBO reaction on PEGMA hydrated by 10 or 20 mL water at 150°C (PEGMA = XA255, $x = 2$).

reaction occurs, optimum coupling should be obtained for an oxazoline/anhydride stoichiometric ratio of 2. The PBO is not totally miscible in the reaction medium. The reaction thus proceeds in a heterogeneous medium so it is necessary to operate with an excess of dioxazoline to make available the quantity

necessary for the coupling reaction with diacids. When the stoichiometric ratio is 4, only half of the used dioxazoline reacts. The other part remains in the system and acts as a plasticizer. For an important dioxazoline excess (stoichiometric ratio higher than 4), in addition to chain coupling, the dioxazoline can

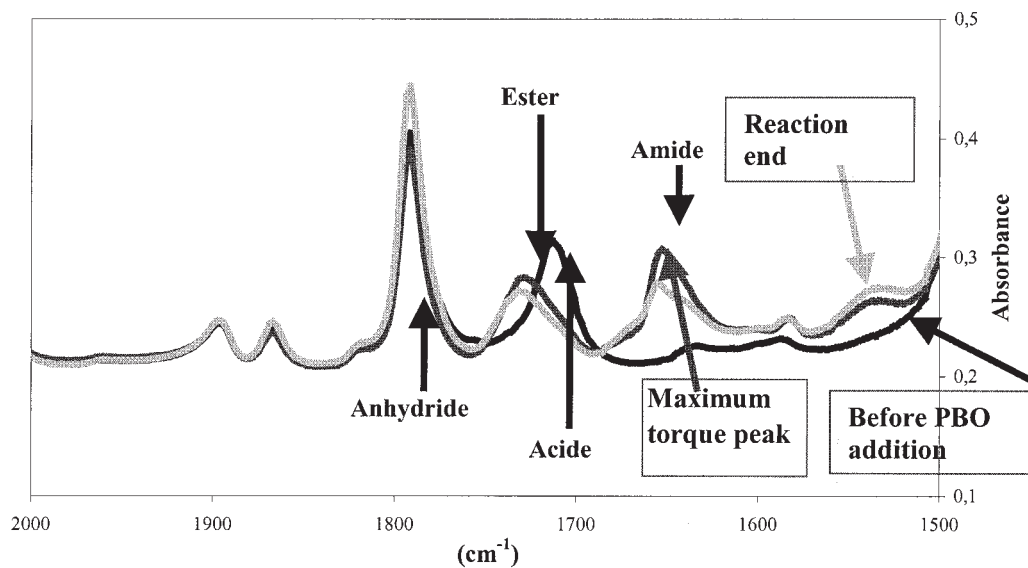


Figure 5 Evolution of the IR characteristic peaks of the functions consumed and produced during the reaction of the PBO on hydrated PEGMA at 150°C (PEGMA = XA255, 10 mL water, $x = 2$).

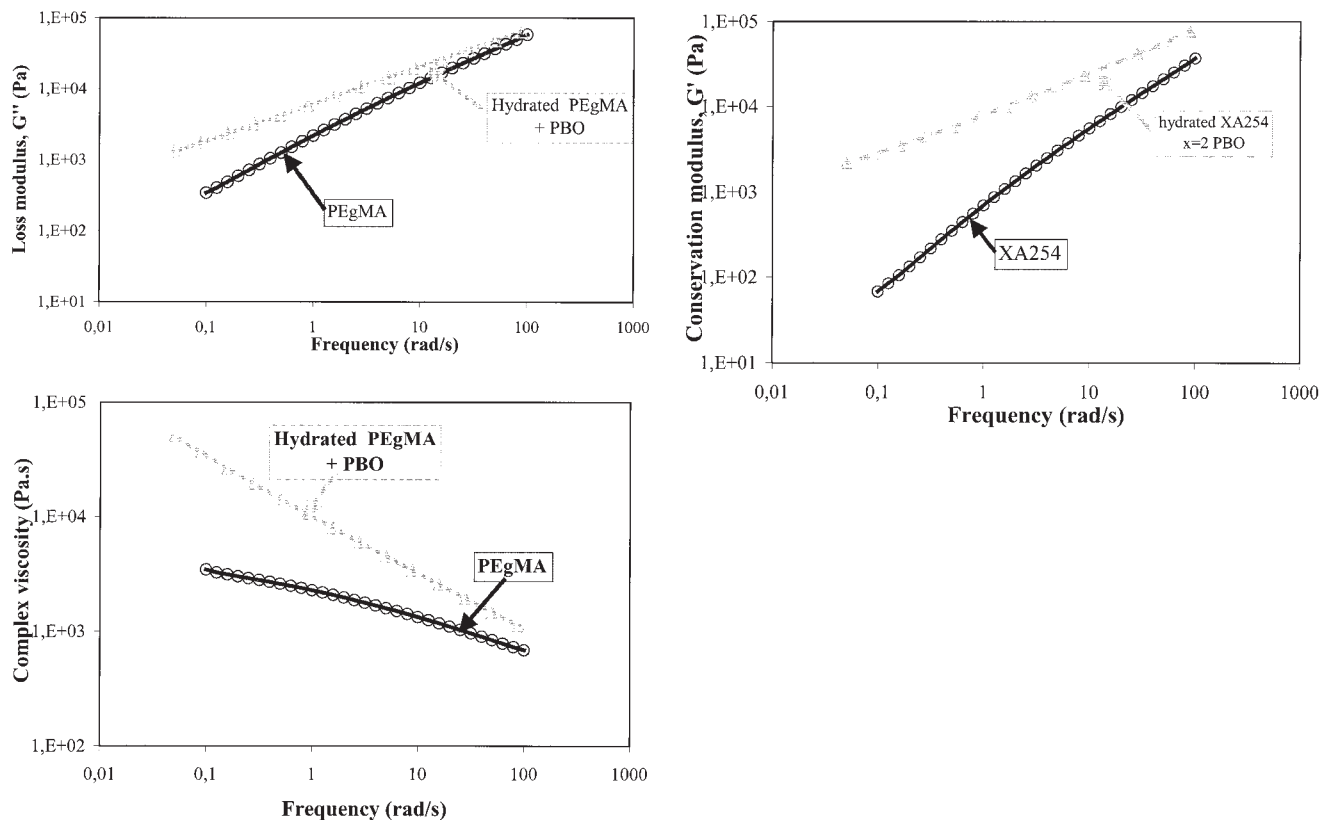


Figure 6 Evolution of rheological properties with the reaction of the PBO on hydrated PEGMA at 150°C (PEGMA = XA255, 10 mL water, $x = 2$).

either react with only one polymer chain (only one of the two oxazoline functions of PBO reacts) or remain in the reactive system and act as a plasticizer. In both cases, the viscosity increase is lower than that obtained with the stoichiometric ratio of 4.

The analysis of the IR spectra of these products shows that, whatever stoichiometric ratio was used, the reaction was never total. The peak characteristic of the maleic anhydride functions never disappeared completely.

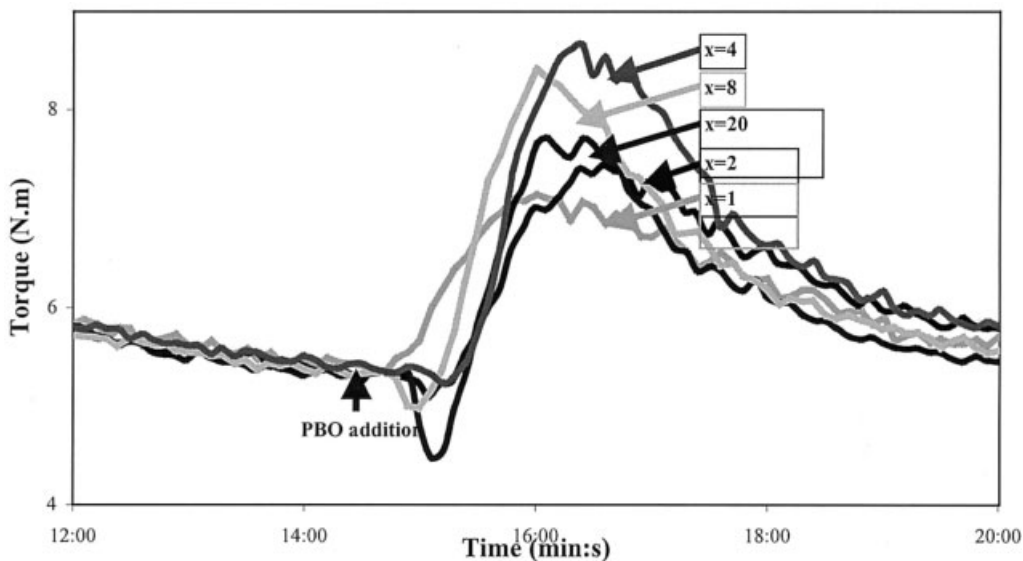


Figure 7 Evolution of the internal mixer torque with time during the reaction of the PBO on PEGMA hydrated by 10 mL water at 150°C with variable x values (PEGMA = XA254).

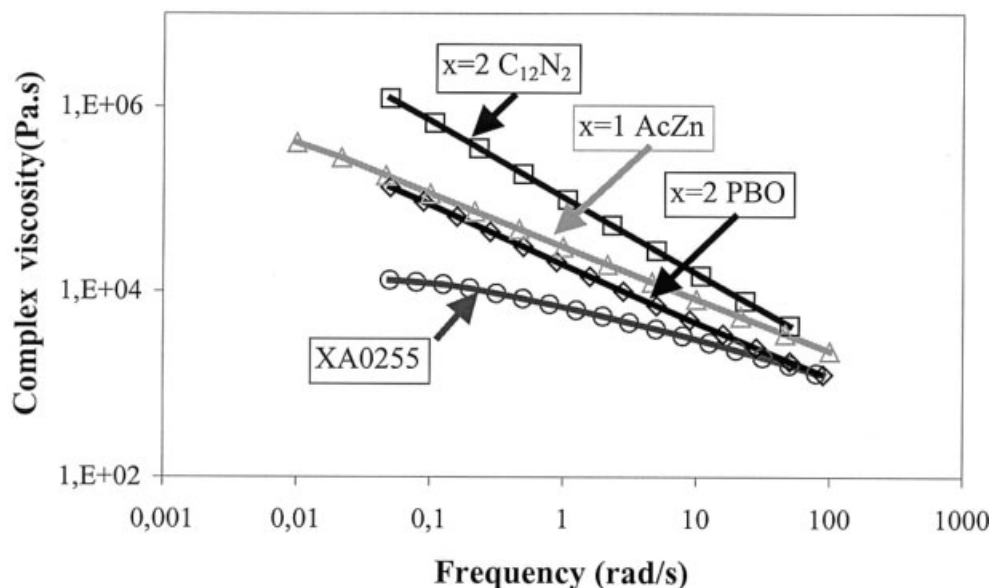


Figure 8 Complex viscosity evolution with frequency at 175°C of the products obtained by PBO, $C_{12}N_2$, and AcZn coupling of PEGMA (10 mL water addition for PBO coupling and 2 mL water addition for AcZn).

PBO compared to other coupling agents

As shown in the preceding parts and for different reasons, PBO can only lead to correct coupling of anhydride-grafted polyolefins under certain constraining conditions. Other coupling agents can also be used.

A metallic salt, zinc acetate (AcZn), acts as an ionic coupling agent and 1,12-diaminododecane ($C_{12}N_2$) acts as covalent coupling agent.

Reactions were performed under equivalent conditions using PBO, zinc acetate, and 1,12-diaminododecane. Specimens were collected at the end of the reaction and analyzed. The complex viscosity evolution with shear rate of these products is compared in Figure 8.

Under the conditions used, when zinc acetate and 1,12-diaminododecane were used, the viscosity of the obtained products was higher than when PBO was used. It can be deduced from this that zinc acetate and 1,12-diaminododecane coupling was more efficient than PBO coupling.

CONCLUSIONS

Maleic anhydride modified polyethylene coupling using (1,3-phenylene)-bis(2-oxazoline) was investigated. The coupling reaction with succinic acid, produced by preliminary hydration by water, was shown to give faster and more efficient coupling than when PEGMA was used without hydration. The reaction proceeded

in a few minutes at 150°C. Maximum coupling was obtained for an oxazoline to anhydride molar (stoichiometric) ratio of 4. However, under the conditions used in this study, complete anhydride conversion was never obtained. This was attributed to succinic acid dehydration at the temperature used and to partial immiscibility of the reactants used. The use of zinc acetate or 1,12-diaminododecane gave more efficient coupling reactions.

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