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Grafting of fluorinated oligomers on to high-density polyethylene (HDPE) in the molten state

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Abstract

The grafting reaction of fluorinated maleamic acid and maleimide oligomers on to high-density polyethylene (HDPE) in the molten state is described. Temperature and roller speed play an important role since the greater these are, the greater the grafting rate. The same compounds have also been grafted using an initiator under the same conditions. It has been shown that the maleimide forms are more reactive than maleamic acid. This can be explained by steric hindrance which decreases the grafting rate. The use of an initiator favours grafting.

Keywords: Grafting molten state; Maleimide; Maleamic acid; Free-radical initiators; Fluorinated oligomers

1. Introduction

The functionalization of polyolefins through the graft copolymerization of unsaturated monomers or through the condensation reactions of α-hydroxy or α-amino oligomers on to modified polyolefins such as polyethylene (g) maleic anhydride has been studied extensively. The last example has been successfully used in the formation of polyamide 6 (polyamino caprolactam)/EPR (ethylene–propylene rubber) blends to improve the impact resistance of PA 6 [1,2]. The synthesis of functionalized EPR possessing tertiary amino groups on the chain has been studied by Martuscelli et al. [3]. The reaction between *N*,*N*-dimethylethylenediamine and EPR (g) maleic anhydride leads to functionalized EPR.

Another method for introducing chemical groups along a polymer backbone involves graft copolymerization of unsaturated monomers or oligomers such as the dibutyl maleate or diethyl fumarate [4] using free-radical initiation. The functionalization of polyethylene diene terpolymer (EPDM) in the bulk through dicumyl peroxide-initiated grafting of dibutyl maleate (DBM) has been studied in the 140–200 °C range [5]. The best results obtained in grafting conversion were ca. 50% with 10% w/w of DBM.

Our interest in the synthesis of graft copolymers involves both kinds of processes. The condensation of aliphatic and aromatic amines with a polyethylene (g) maleic anhydride was first investigated [6]. The present work describes the second process, i.e. the free-radical grafting of fluorinated unsaturated oligomers on to high-density polyethylene (HDPE).

2. Results and discussion

2.1. Synthesis of fluorinated maleamic acid and maleimide oligomers [7,8]

The initial fluorinated amine was synthesized as described previously [6]. It was then reacted with maleic anhydride at −10 °C in chloroform in order to obtain the maleamic acid form **I**. The maleimide form was obtained by dehydration of **I** in the presence of acetic anhydride. Both compounds **I** and **II** were characterized by ^{1}H NMR spectroscopy, FT-IR spectrometry and GC-MS.

2.2. Grafting of fluorinated maleamic acid and maleimide oligomers on to high density polyethylene (HDPE)

The grafting reaction was carried out in a Brabender batch mixer employing 5 g of fluorinated oligomer to

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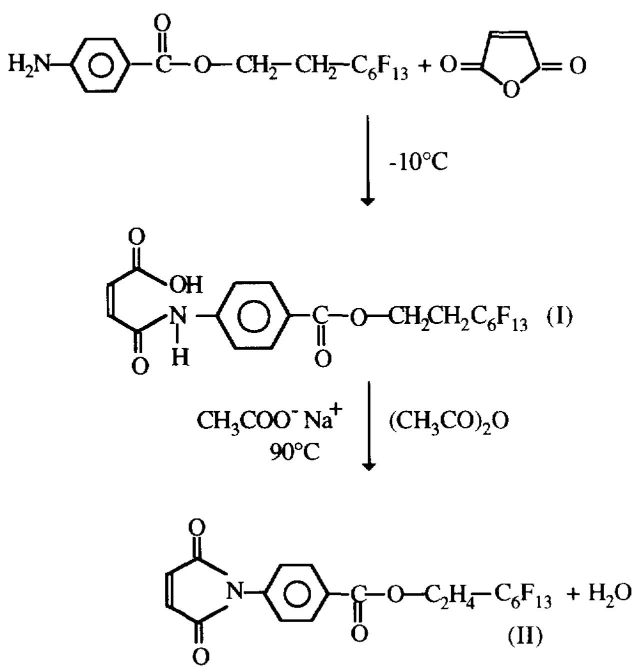

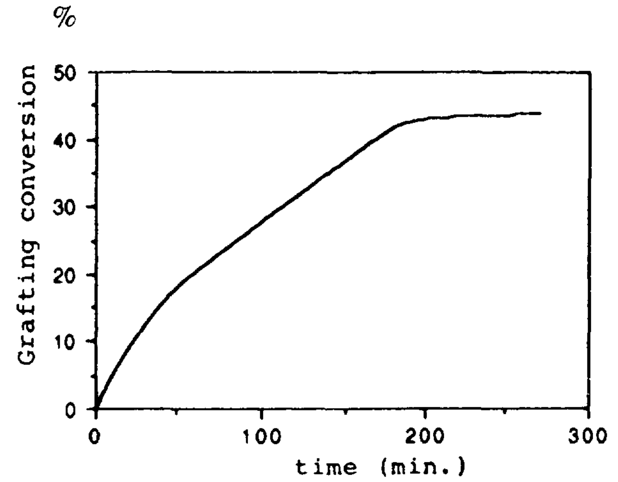

Fig. 1. Grafting rate of maleamic acid versus time (experimental conditions: 200 °C, 100 rpm, 10% w/w).

50 g of HDPE. The temperature was fixed at 200 °C and the roller speed at 100 rpm. Samples of the batch mix were removed at different times and after purification the copolymers obtained were characterized by FT-IR analysis. The grafting rate was determined by fluorine elemental analysis. The copolymers were purified by dissolving in refluxing toluene, precipitation with acetone and filtration. Unreacted monomer which was soluble in acetone was eliminated by this treatment. A plot of the grafting rate versus time is reported for maleamic acid in Fig. 1 and for maleimide in Fig. 2.

It is interesting to determine whether the maleamic acid did or did not transform into maleimide during the grafting reaction. FT-IR analysis provided only a partial answer. Thus, FT-IR analysis of polyethylene (g) maleamic acid ($t = 100$ min) in the 3000–4000 cm^{-1} region showed that cyclisation did not occur since a signal corresponding to an N–H vibration was observed at 3330 cm^{-1}. This signal was not observed in the FT-IR spectrum of the maleimide–HDPE graft copolymer. However, it is not possible to conclude that none of the maleamic acid molecules were converted into the maleamide form before or after the grafting reaction. It is possible that some of the molecules (depending on the reaction kinetics involved) transformed into maleimide during the process. Morever, it is difficult to determine if the conversion of maleamic acid into maleimide occurs before or after grafting (i.e. grafting of maleamic acid on to the HDPE occurs first and then cyclisation occurs). Further studies are required to resolve this issue.

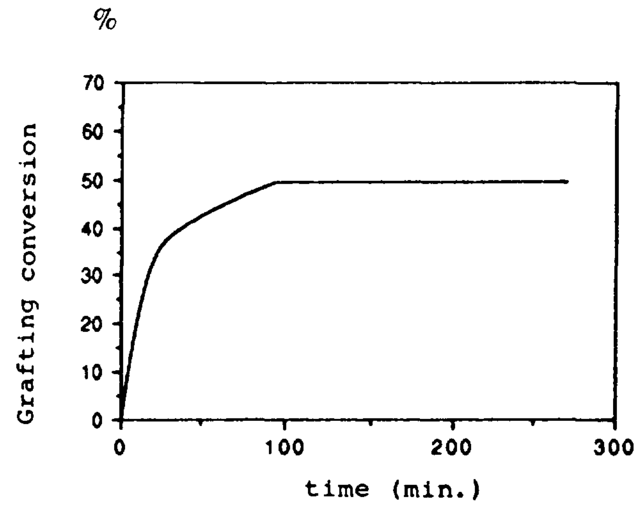

Fig. 2. Grafting rate of malemide versus time (experimental conditions: 200 °C, 100 rpm, 10% w/w).

2.3. *Influence of reaction parameters on the grafting rate of fluorinated maleimide (without initiator)*

Variation in the reaction parameters, i.e. the temperature and roller speed, was studied. A comparison between kinetics observed is reported below.

2.3.1. *Influence of temperature*

Studies of the rate of grafting were conducted at 200 °C and 250 °C, respectively, and the results are reported in Fig. 3. It should be noted that the higher the temperature, the higher the grafting rate.

2.3.2. *Influence of roller speed*

Two grafting studies were undertaken at shear rates of 100 rpm and 150 rpm, respectively (Fig. 4). In this case, the results show that the higher the shear rate, the greater the grafting conversion.

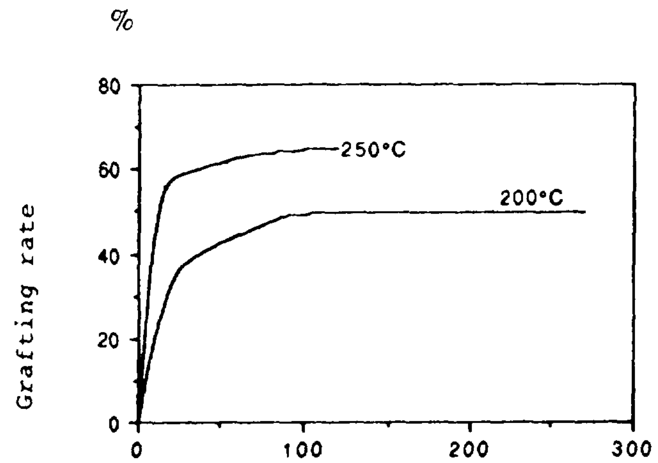

Fig. 3. Influence of temperature on the grafting rate.

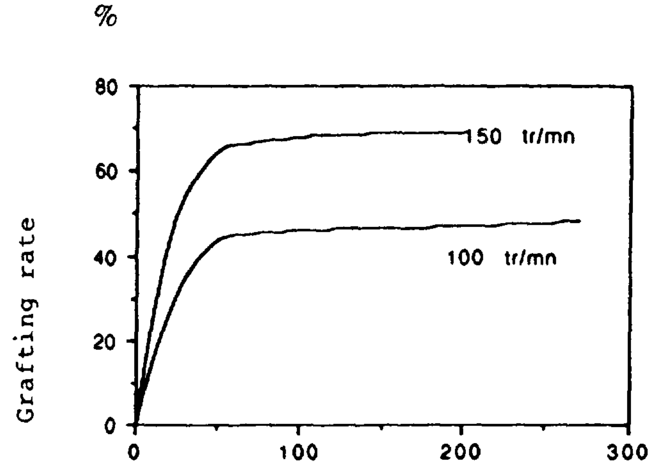

Fig. 4. Influence of roller speed on the grafting rate at 200 °C.

2.4. *Grafting of maleamic acid and maleimide compounds on to HDPE using a free-radical initiator*

In order to increase the free-radical concentration in the mixture, the free-radical initiator TRIGONOX 145 (2,5-dimethyl-2,5-bis(t-butylperoxy)-3-hexyne) was used. Its half lifetime at 180 °C is ca. 3.5 min. This initiator was used by Seadan [9] in his study of the interfacial grafting of maleic anhydride on to HDPE.

We first investigated whether the free-radical initiator induced any crosslinking with HDPE. Experiments were performed using 50 g of HDPE with initiator concentrations varying between 0 to 0.3 wt.%. All other experimental conditions were maintained as previously (200 °C, 100 rpm). The reaction time was fixed at 10 min. The recorded evolution of torque with the rollers showed that an increase in viscosity occurred in all the cases but all the samples were soluble in refluxing toluene. Hence, it may be concluded that although coupling occurred, the product was not crosslinked.

In order to increase the diffusion of the peroxide into the polymer during the reaction, dimethylformamide (DMF) was used as a solvent at 0.3% w/w concentration. Fig. 5 shows the difference in torque evolution in the presence and absence of DMF. The presence of DMF increases the coupling reaction for the same initiator concentration and it may be deduced that DMF increases the diffusion of the free-radical initiator. The resulting HDPE was however still soluble in refluxing toluene, indicating that it was not totally crosslinked.

In a second experiment, we used the same conditions for grafting maleamic acid (**I**) and the maleimide form **II** on to HDPE. The same concentrations were used as before (10% w/w of fluorinated compounds). Comparisons of the grafting conversion obtained for $t = 10$ min are reported in Table 1.

The results reported in this table show that the grafting conversion is determined by experimental conditions and more particularly by the free-radical concentration in the mixture during thermo-mechanical treatment. Increasing temperature and an increase in the roller speed considerably increase the grafting conversion of the fluorinated oligomers employed. It should

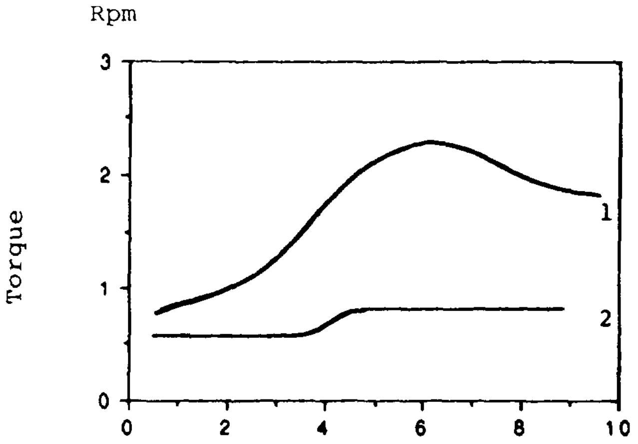

Fig. 5. Evolution of torque for HDPE + 0.3 wt.% TRIGONOX 145 (1) with and (2) without 0.3% DMF (experimental conditions: 200 °C, 100 rpm, 10 min).

Table 1
Grafting conversion for $t = 10$ min in relation to the reaction conditions employed

Fluorinated oligomer	Initiator	Temperature (°C)	Roller speed (rpm)	Grafting yield (%)
Maleamic acid	without	200	100	2
Maleamic acid	with	200	100	35
Maleimide	without	200	100	22
Maleimide	without	200	150	35
Maleimide	without	250	100	41
Maleimide	with	200	100	80

be noted that the maleimide form appears to be more reactive than the maleamic acid form. This may be explained by the conformation of the double bond relative to the maleate forms, which are known to be less reactive than fumarate because of steric hinderance. The use of a free-radical initiator increases the grafting conversion and good results are obtained within short reaction times (80% conversion for $t = 10$ min).

3. Experimental details

FT-IR spectra were recorded using a Nicolet 510 P spectrophotometer while ^{1}H NMR spectra were recorded using a Bruker 200 instrument. GC-MS analyses were undertaken using a Hewlett Packard 5890 A chromatograph equipped with a 25 m × 0.23 mm column of silica grafted with polydimethylsiloxane. Mass spectra were recorded using a 5970 A detector at 70 eV for electron impact.

3.1. Synthesis of maleamic acid ()

A solution consisting of 0.1 mol of maleic anhydride in 200 ml of chloroform was added to 0.1 mol of 4-(2′F-hexyethyl)amino benzoate in 200 ml of chloroform at −20 °C. Maleamic acid (**I**) precipitated from the solution was filtered. The yield was 70%. ^{1}H NMR δ: 10.7 (s, 1H); 8.2 (d, 2H); 7.9 (d, 2H); 6.75 (d, 1H); 6.4 (d, 1H); 4.7 (t, 2H); 4.5–3.0 (m, 1H); 2.85 (tt, 2H) ppm. MS *m/z* (rel. int.%): 483 (20); 137 (10); 120 (100); 69 (10). IR (cm^{-1}): 3340; 1720; 1635; 1539; 1286; 1143; 1124; 852, 767; 700.

*3.2. Synthesis of maleimide form **II***

Compound **I** (9×10^{-3} mol), 0.09 mol of acetic anhydride and 0.065 mol of sodium acetate were reacted for 2 h at 90 °C. The resulting mixture was precipitated with cold water and maleimide **II** isolated by filtration in 70% yield. ^{1}H NMR δ: 8.15 (d, 2H); 7.6 (d, 2H); 7.05 (s, 2H); 4.7 (t, 2H); 2.85 (tt, 2H) ppm. MS *m/z* (rel. int.%): 563 (18); 200 (100); 172 (10); 119 (5); 69 (5). IR (cm^{-1}): 1728; 1711; 1606; 1518; 1392; 1182; 862; 815; 771; 734; 702.

3.3. Grafting reactions

(a) Without initiator

HDPE (50 g) and 5 g of fluorinated oligomers were introduced into the batch mixture and heated at the desired temperature. The roller speed was then fixed and samples were removed at different times. The copolymer obtained was purified by dissolving it in refluxing toluene, precipitating with acetone and filtration. Grafting conversion was determined by fluorine elemental analysis.

(b) With initiator

The above procedure was undertaken with the variation that, after 30 s, 0.3 wt.% of TRIGONOX 145 in 0.3% of DMF was added. The copolymer obtained was purified and analyzed as described previously.

4. Conclusions

The work described demonstrates a new approach to the introduction of specific fluorinated groups on to polyolefins in one macromolecular step. Optimization of the experimental conditions gave graft copolymers with a good grafting conversion. The maleimide form seems to be more reactive than maleamic acid. Continuation of this work will involve conducting the method on industrial equipment such as an extruder.

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