Modification of Polypropylene with Maleic Anhydride: Ultrasonic Irradiation Effects

EDUARDO A. GONZALEZ DE LOS SANTOS, MARIA JOSEFINA LOZANO GONZALEZ, MARIA CONCEPCION GONZALEZ

Centro de Investigación en Quimica Aplicada, P.O. Box 379, Saltillo Coah., México 25000

ABSTRACT: The mechanochemical reaction of modificated of polypropylene (PP) with maleic anhydride (MAH) has been studied by ultrasonic irradiation as an energy source at 60°C. Through 2^3 factorial experimental design, three variables and their interactions were studied: the percentage of MAH, the percentage of benzoyl peroxide (BPO), and ultrasonic irradiation intensity (Watts). According to the results, an increase of wt % of MAH gave a negative effect in the grafting yield; in addition, this negative effect was observed in the interaction of MAH : BPO at a high range of wt %, this behavior is attributed to the homopolymerization of MAH at the experimental conditions employed. The higher positive effect onto the grafting yield was observed for the variable watts (ultrasonic irradiation intensity), even at low intensity. The better interaction of variables gave a MAH grafting degree of 4.65 wt % (93% yield). In addition, the effect of ultrasonic irradiation on the number-average molar mass (M_n), weight-average molar mass (M_w), and polydispersity index (M_w/M_n) was measured. It was observed that the M_w decreased 13.73% and the M_w/M_n also decreased by 11.98%. The observed effect was attributed to the degradation mechanism induced by the ultrasound, which consists in the generation of macroradicals and their recombination. The product PP-g-MAH was characterized by infrared spectroscopy, also was used to prepare polypropylene–nylon-6 blends. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 45–52, 1998

Key words: polypropylene; maleic anhydride; grafting of polypropylene; ultrasonic irradiation effects; mechanochemical reaction

INTRODUCTION

The chemical modification of synthetic and natural polymers open a wide scope of possibilities for different applications. In general, the chemical modification of polymers is made with the purpose to obtain reactive centers in order to increase the interfacial interaction between poly-mer–polymer blends or polymer–filler composites to maximize the physical properties. Among others, the modifier agents used onto polypropylene (PP) are acrylic acid,[1,2] maleic anhydride (MAH),[3,4] Ziegler–Natta catalyst,[5,6] and borane derivatives.[7]

The modifications can be done mainly by two different processes, molten and solution. A better interaction and reactivity between the polymer and other components in the system can be achieved in solution[8,9]; however, this process is expensive.

Specifically in polymers, the ultrasound has been used for many different processes,[10] that is,
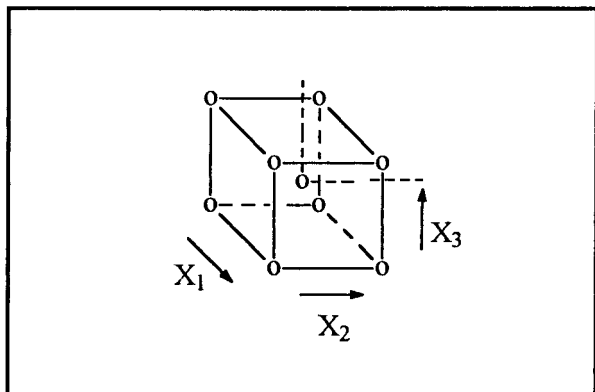
Figure 1 Geometry of the 2^3 factorial experimental design. Each cube dimension represents a variable (X_1 = MAH; X_2 = BPO; X_3 = Watts) in the experiment, and each point represents a set of experimental conditions.

polymerization of monomers, depolymerization, molecular weight control, and, recently, for the synthesis of grafted and block copolymers.[11] The particular interest in the ultrasonic process is because is an important technique for generating macroradicals almost at room temperature and with a homogeneous molecular weight.[12]

The present investigation was undertaken to study the ultrasonic irradiation effect in the mechanochemical grafting reaction of PP with maleic anhydride. In order to improve the grafting yield, a free radical generator (BPO) at rather low concentration was used; additionally, the interaction between the BPO, the MAH, and the ultrasonic irradiation intensity are discussed.

EXPERIMENTAL

Materials

Polypropylene (powder) from Rexene Resins, Houston, TX [melting flowing index (MFI) = 14.2 g/10 min at 230°C] was used as received, MAH was crystallized from CCl_4 and dried under vacuum at 25 mm Hg/2 h, and BPO was dissolved in acetone and precipitated by adding two volumes of water then dried under vacuum at room temperature for 24 h. Xylene was distilled from CaH_2, and acetone was distilled from Drierite ($CaSO_4$) before use. All chemicals were supplied by Aldrich Chem. Co., Milwaukee, WI.

Equipment

For the mechanochemical reaction, a sonicator reactor Branson Sonifer Model 250 with nominal

frequency of 25 kHz was used. For the infrared (IR) study, a Nicolet FTIR-710 spectrophotometer was used. The gel permeation chromatograph used was a Watters Model 150-C, using 1,2,4-trichlorobenzene ($k = 0.000232$, $\alpha = 0.658$) at 140°C and polystyrene as standard.

Software

The experimental set according to a 2^3 factorial design, eight points, three central repetitions, and the response (wt % of MAH grafted) were fed to a statistical analysis program, REGRESSION-I from Statistical Programs, Houston, TX (1985). The same results can be obtained using the statistical tools from EXCEL V5.0a from Microsoft OFFICE V4.2 (1985–1994). The graphical representations were achieved on MATLAB V4.2 software, from The Math Works Inc., Natick, MA (1993).

General Procedure

According to a 2^3 factorial experimental design,[13,14] three factors (variables) and two levels (high and low), eight points, and three central repetitions were run, with each point representing a set of experimental conditions (Fig. 1) in which each factor has its low and high level, which represent the maximum and minimum range previously established from the three variables used. The cube in Figure 1 and its interior represents

Table I   Experimental Conditions and Results Obtained for the Modification Reaction Under Study, According to a 2^3 Factorial Design

Entry No.	MAH	BPO	Watts	Grafted MAH	Yield
1	5	0.5	58	2.93	58.60
2	30	0.5	58	0.61	2.03
3	5	3.0	58	4.3	86.0
4	30	3.0	58	0.9	3.0
5	5	0.5	62	4.65	93
6	30	0.5	62	2.18	7.26
7	5	3.0	62	4.19	83.80
8	30	3.0	62	2.52	8.40
9	17.5	1.75	60	1.0	5.71
10	17.5	1.75	60	1.1	6.28
11	17.5	1.75	60	1.5	6.57

BPO, MAH, and grafted MAH were based on 2 g of PP and are expressed in weight percent and yield is expressed in percent.
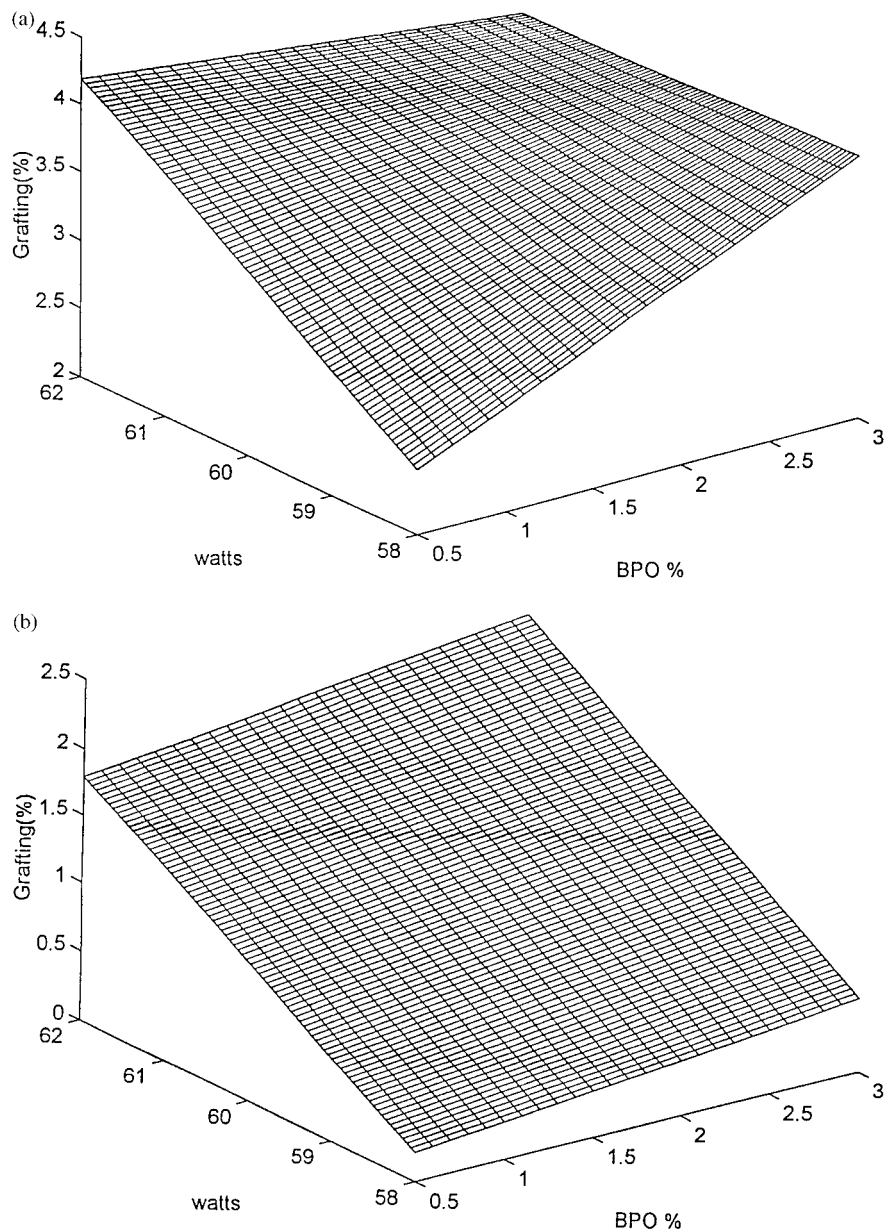
Figure 2   (a) Graphical representation of surface response for eq. (1) along the range of BPO and Watts at a low level of MAH (5 wt %). (b) Graphical representation of the surface response for eq. (1) along the range of BPO and Watts at a high level of MAH (30 wt %).

the available factor space in which the experiment can be run. The experimental conditions shown in Table I were based on 2 g of PP. The specific amounts of MAH and BPO were placed with 60 mL of xylene in a sonicator reactor flask under inert (N_2) atmosphere. The ultrasonic horn (10 mm o.d.) was immersed (2.5 cm) into the reaction mixture, and a fixed acoustic intensity according to Table I was applied during 25 min at 60°C using

a temperature-controlled water bath. After that, 120 mL of acetone was added to the reaction, the product was filtered off, washed several times with acetone, and dried overnight under 85°C/40 mm Hg conditions.

The quantitative determination of grafted MAH onto PP was determined using the titration technique reported by Gaylord.[15] In addition, the grafted MAH was determined by the IR method
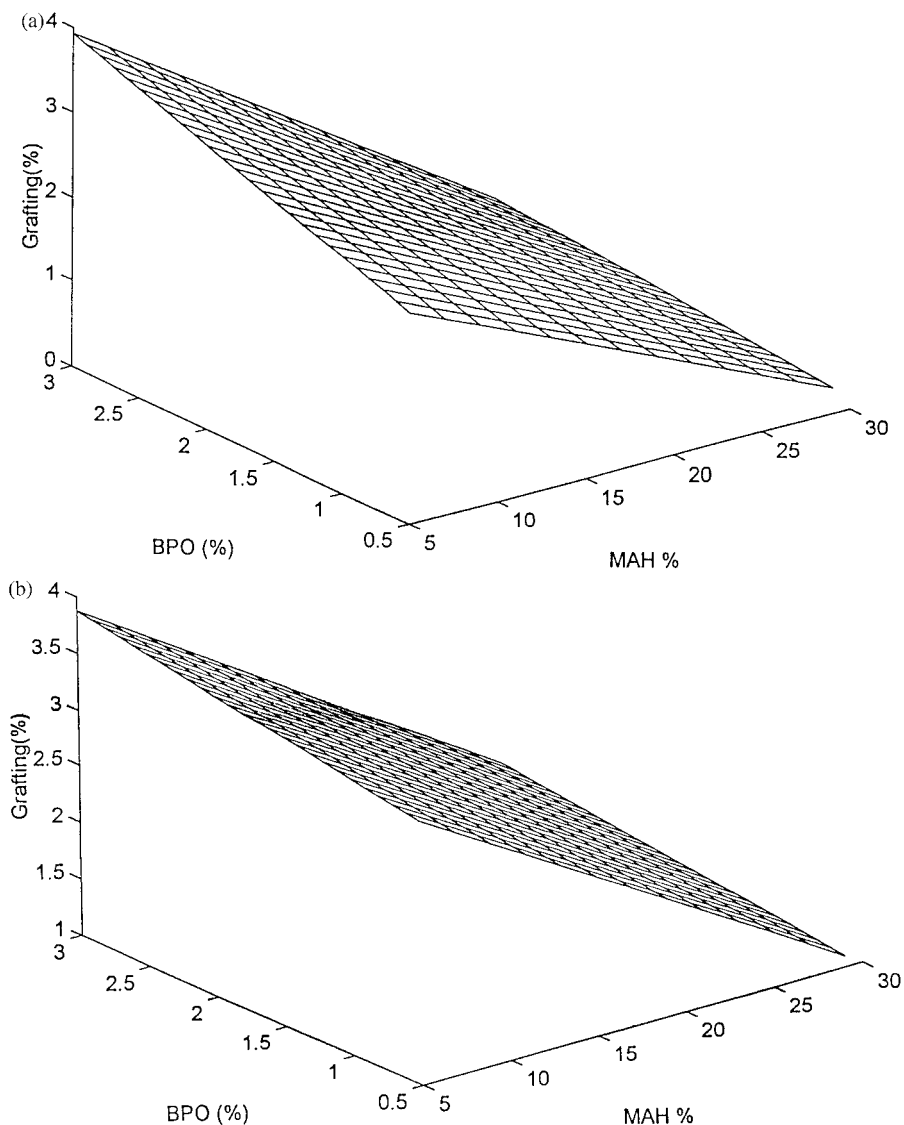
Figure 3   (a) Graphical representation of surface response for eq. (1) along the range of BPO and MAH at low level of ultrasonic intensity (58 watts). (b) Graphical representation of surface response for eq. (1) along the range of BPO and MAH at a high level of ultrasonic intensity (60 watts).

reported by Achmad,[16] using a calibration curve and the intensity of the band at 1785 cm^{-1}, attributed to the carbonilic groups of MAH. As both techniques gave similar results, only the Achmand method was used for the whole samples. The MAH content grafted onto the PP was expressed as the weight percentage of MAH (wt % MAH) in the product.

RESULTS AND DISCUSSIONS

A 2^3 factorial design was used to determine the effects of the percentages of MAH and BPO and the ultrasound intensity on the mechanochemical modification reaction of PP by MAH. Table I shows the results of the weight percent of MAH grafted in the PP and the experimental conditions used in the factorial design. The equation obtained after the computational analysis based on data from Table I is shown below:

$$Y = 2.35 - 1.23X_1 + 0.192X_2 + 0.6X_3$$
$$- 0.035X_1X_2 + 0.197X_1X_3$$
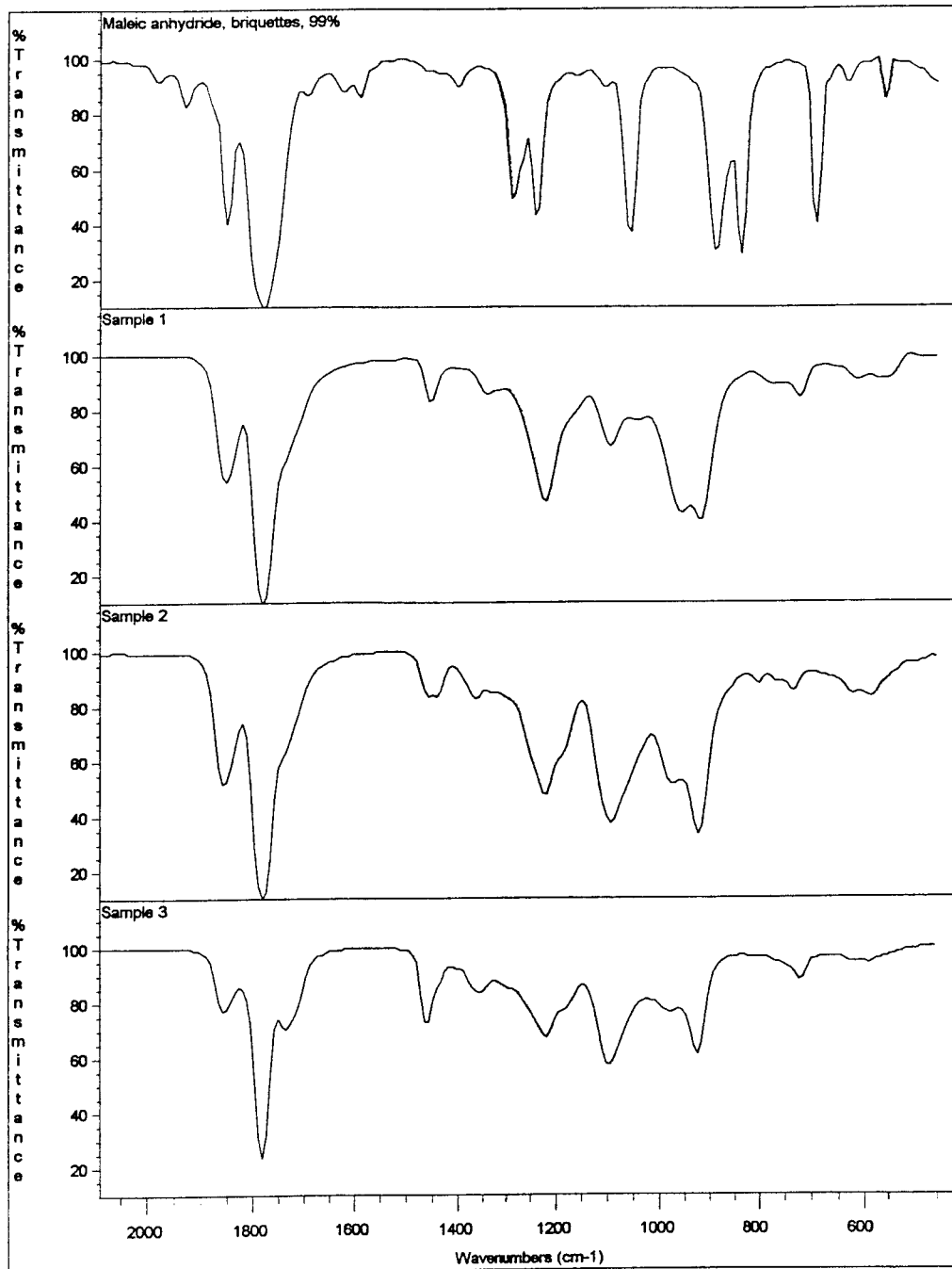$$- 0.222X_2X_3 + 0.235X_1X_2X_3 \quad (1)$$

Figure 4 FTIR spectrums of MAH and MAH polymerized under mechanochemical reaction conditions.

where Y is the percentage of MAH grafted, X_1 is MAH, X_2 is BPO, and X_3 is Watts.

It can be observed from this equation and from Table I that several negative effects on yield are manifested as follows: variable X_1, interaction $X_1 : X_2$, and interaction $X_2 : X_3$. Actually, increasing X_1(MAH %), the higher negative effect is observed. On the other side, X_2, X_3, interaction $X_1 : X_3$, and interaction $X_1 : X_2 : X_3$ have a positive effect on yield (Y).

The higher positive effect on the yield is observed for the variable X_3 (Watts). This factor is
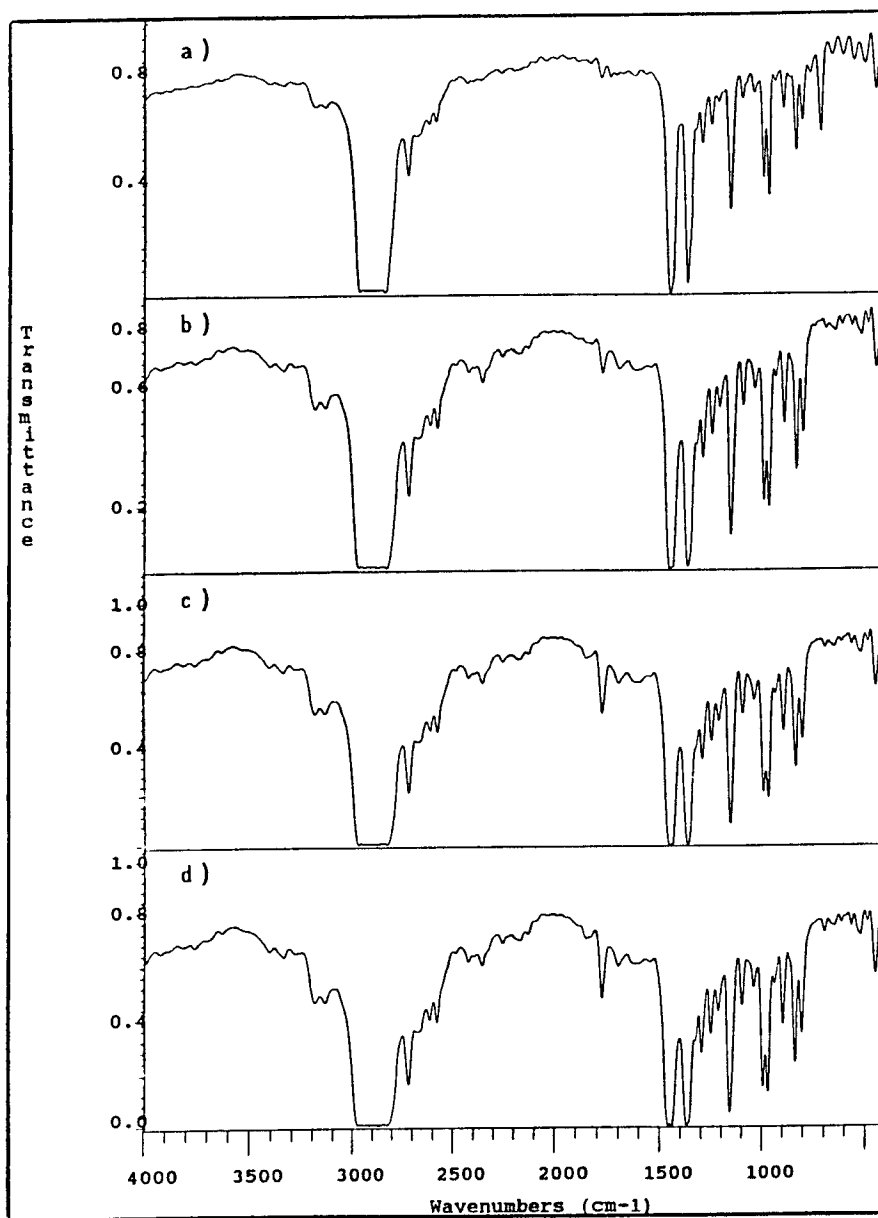
Figure 5 FTIR spectrums of (a) unmodified PP, (b) PP-*g*-MAH, entry 9, (c) entry 6, and (d) entry 5.

the energy that activates the BPO, which in turn initiates the grafting reaction. The higher grafting value of 4.65% (93% of yield, entry 5 in Table I) was obtained when the lower range of MAH and BPO were used at the higher level of Watts. The lowest grafting value of 0.61% (entry 2) was obtained when the higher level of MAH and the lower level of BPO and watts were employed.

The graphical representation of yield (surface response) for eq. (1) is shown in Figure 2(a,b).

In general, when the MAH goes from the lower (5 wt %) to the higher (30 wt %) level, the surface response decreased in 2.5 units. In the same way, at a low and high level of Watts, the reduction of grafting yield is minimum along the range of BPO [Fig. 3(a,b)]. However, along the range of MAH, a drastic reduction is observed. The last tendency is magnified at the higher level of Watts [see Fig. 3(b)].

The low grafting yield observed when the MAH

Table II   Average Values of M_w, M_n, and M_w/M_n of Polypropylene and Irradiated Polypropylene

Value	Polypropylene	Irradiated PP[a]	Irradiated PP + BPO[b]
M_w	231643	224044	199856
M_n	95101	92182	89579
M_w/M_n	2.5348	2.4303	2.2310

The experimental conditions were similar to the general procedure, but the MAH was excluded.

[a] Two grams of polypropylene irradiated with ultrasonic intensity of 62 Watts for 25 min at 60°C.

[b] As per sample 1, with 0.5 wt % BPO.

level was increased, can be explained assuming that the MAH undergo homopolymerization instead of grafting under the mechanochemical reaction condition (high irradiation intensity and a high percentage of MAH). It is possible that the MAH homopolymerize itself. It has been shown that MAH can be homopolymerized[17] with gamma and ultraviolet (UV) radiation in the presence of radical initiators, anionically with various bases, electrochemically, and under shock waves. MAH homopolymerize spontaneously[18,19] when heated at 170°C under pressures above 20,000 atm. The cavitation process, which is generated by ultrasonic irradiation,[10] can generate temperatures up to 10,000°C and pressures above 1000 atm, being enough energy to homopolymerize the MAH.

From the washed extracts, it was possible to identify the homopolymer of MAH by Fourier transform infrared (FTIR). Figure 4 shows evidence of the MAH polymerized. Samples 1–3 show the absence of the sharp C—H bands of MAH at 640 and 1057 cm^{-1} and the C=C bands at 867 and 892 cm^{-1}. In addition, the appearance of a broad absorption between 1150 and 1270 cm^{-1} can be observed. Similar results have been reported by other authors[20,21] and by liquid-phase polymerization experiments of MAH initiated by benzoyl peroxide.[22–24]

Figure 5 shows the FTIR spectra of PP and PP-*g*-MAH obtained from experimental samples. The modification of the region between 2000 to 1500 cm^{-1} was observed, specifically, the band at 1758 cm^{-1}, which is assigned to the carbonilic groups from the maleic anhydride. Notice how such a band becomes important in increasing the grafted MAH percentage.

Table II shows the results from GPC analyses of PP samples irradiated with ultrasound energy.

There was a decrease of 3.28% in the weight-average molar mass (M_w) for PP after irradiation with ultrasound and 13.78% for PP samples with 0.5 wt % of BPO. The number-average molar mass (M_n) was also modified in a 3.07% for PP and 5.81% for PP with 0.5 wt % of BPO. Moreover, the polydispersity index (M_w/M_n) was modified in 4.12% and 11.98% for PP and PP with 0.5 wt %, respectively (according to Table II). The dramatic reduction of the above polydispersity index can be explained by the ultrasonic degradation mechanism,[12,25,26] in which the generation of macroradicals induce the breakage of polymer bonds, then a recombination will follow, ending by the usual termination process.

CONCLUSION

It has been shown that PP-*g*-MAH can be prepared easily using ultrasound as an energy source. Such energy activates the BPO, which, in turn, will initiate the grafting reaction. In general, the mechanochemical reaction analysis shows a decrease in the grafting yield at a high concentration (30 wt %) of MAH. Additionally, it was found that the interactions MAH : BPO and BPO : Watts had a negative effect on the grafting yield. This behavior was attributed to the homopolymerization of MAH under the drastic reaction conditions of ultrasonic irradiation, and the to high concentration of MAH. From the experimental results and within the studied range of variables, it was observed that the best grafting conditions were as follows: a low level of BPO (0.5 wt %), a low level of MAH (5 wt %), and a high level of ultrasonic irradiation intensity (62 watts). If the MAH concentration goes higher than 10 wt %, the grafting yield decreases due to the homopolymerization of MAH. Furthermore, the ultrasonic irradiation intensity (58 to 62 Watts) employed in the present work and the benzoyl peroxide concentration (0.5 to 30%) had a remarkable effect on the M_w, M_n, and M_w/M_n of the polymer studied. The effect was attributed to the degradation mechanism induced by the ultrasound, which consists of the breakage of the polymer backbond with the subsequent generation of macroradicals, allowing easy chemical modifications on polymers with a few reactive centers (that is, PP and PE). This method offers a new route to obtain not only the PP-*g*-MAH but other materials also, such as photochromatic compounds[27] and polyphospho-

nates synthesised in solid phase,[28] which have been studied by our group using ultrasonic irradiation as an alternative energy source.

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