

Synthesis and Characterization of Poly(methyl methacrylate-*co*-maleic anhydride) Copolymers and Its Potential as a Compatibilizer for Amorphous Polyamide Blends

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ABSTRACT: Poly(methyl methacrylate-*co*-maleic anhydride) copolymers (MMA-MA) have been synthesized by solution method, using toluene as solvent and benzoyl peroxide as initiator. The MMA-MA copolymers were characterized by size exclusion chromatography, Fourier transforms infrared spectroscopy (FTIR), and titration. It was found that the modified polymerization procedure used in this work was more effective in controlling the molecular weight when adding different amounts of maleic anhydride (MA) than procedures previously used. In spite of the significant difference in reactivity ratios between MMA and MA, up to 50% of the MA added to the reactor was incorporated into the copolymer. The evidences for reactions of the MA groups of the MMA-MA copolymer with

the amine end groups of the amorphous polyamide (aPA) during melt blending was obtained by rheological measurements. In this work, the molecular weight and the content of MA reactive functional groups in the MMA-MA copolymer were varied independently and its effects on the interaction with aPA were studied. It was observed that a compromise between molecular weight and the level of reactive functional group of the compatibilizer should be sought to improve the compatibilization of the polymer systems. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3248–3252, 2007

Key words: synthesis; MMA-MA acrylic copolymers; amorphous polyamide

INTRODUCTION

Without compatibilization highly immiscible polymer blends generally exhibit poor mechanical properties and unstable phase morphology.¹ The technique of adding a reactive compatibilizer in immiscible polymer blends was investigated extensively^{2,3} and is effective for controlling the morphology development and improving the mechanical properties in a variety of polymer blends. Appropriate functionalized block and graft copolymers can be used as reactive compatibilizers for immiscible polymer systems, for it is capable of interacting with both phases of the system. Usually, one segment of the copolymer molecules interact with the disperse phase of the system while the other segment with a functional groups react with the functional groups of the matrix of the polymer blend.^{2,4} The resulting copolymer molecules formed *in situ* at the interface between the disperse phase and the matrix of the polymer blend usually affects the morphology

evolution of the blend and leads to a finely disperse phase morphology.¹

Maleic anhydride (MA) modified polymers are often used as compatibilizers in blends with polyamide (PA) because of the high probability of chemical reaction between MA functional unities and the amine end-groups of PA during melt blending.^{5–8} This reaction is expected to occur fast and results in imide linkage formation, as shown in Figure 1. This same behavior is observed in blends with amorphous polyamide (aPA).^{9,10} Methyl methacrylate based copolymers are miscible with acrylonitrile-styrene copolymer (SAN) for a wide range of acrylonitrile (AN) content, and therefore, the poly(methyl methacrylate-*co*-maleic anhydride) (MMA-MA) copolymers are very promising in compatibilizing PA and SAN based polymers blends.¹¹

The main focus of this work is on the investigation of the synthesis of MMA-MA through solution polymerization by varying independently molecular weight and MA level in the copolymer. The copolymers synthesized were characterized by size exclusion chromatography (SEC), titration, and Fourier transforms infrared spectroscopy (FTIR). The evidences for reactivity between MMA-MA copolymers and the aPA were also studied using rheological measurements.

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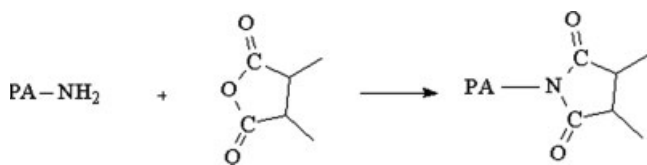


Figure 1 Scheme of interface grafting by reaction between a carboxyl group of MA and a PA amino end group.

EXPERIMENTAL

Materials

The amorphous polyamide (aPA) used in this study was supplied by Dupont under the tradename SELAR PA 3426, chemical structure is illustrated in Figure 2 and the characteristics of this material are shown in Table I. The MMA-MA copolymers were synthesized in our laboratory by solution polymerization.

Copolymer synthesis

The MMA-MA used in this study was synthesized by a modified solution polymerization of the monomers methyl methacrylate, MA, and ethyl acrylate (EA). The EA comonomer increases the thermal stability of the copolymer against depolymerization.¹² These monomers were supplied by Metacril, Merck, and Aldrich, respectively. The MMA and EA monomers were distilled twice under reduced pressure at 35°C prior to use.

The polymerization reaction was carried out in a reactor under intensive mixing and nitrogen atmosphere at 80°C for 8 h. The copolymers were synthesized with 1, 5, and 10 wt % of MA, using toluene as solvent. To obtain copolymers of different molecular weights, it was used benzoyl peroxide (BzP) as initiator at different concentration: 1% of peroxide for high molecular weight (HMW); 2% of peroxide for medium molecular weight (MMW); and 5% of peroxide for low molecular weight (LMW) copolymers. Appropriate volume of the solvent was added to maintain the monomers concentration at 2 mol/L. Table II presents the composition used in the polymerization of the MMA-MA copolymers. The copolymers obtained in the polymerization were fractionated by precipitation in excess of methanol

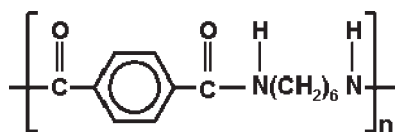


Figure 2 Chemical structure of aPA.

10:1 to remove all toluene and non-reacted MA. The synthesis procedure used in this work is a modified version of similar methodologies used in the literature.^{13–15}

Size exclusion chromatography analysis

The molecular weight of MMA-MA was determined by SEC calibrated with polystyrene standards using equipment Waters 410 with refraction index detector. Samples were diluted tetrahydrofuran (THF) in a concentration of 2 mg/mL and the solutions were filtered before the measurements were done.

Determination of MA content

A modified procedure of the titration method described by Li et al¹⁶ was used in this work to determine the content of MA in the MMA-MA copolymers. This method consists in reacting water with anhydride groups in appropriate organic solvent.

The following steps describe the modified method used in this work:

1. A sample containing 1 g of copolymer was dissolved in 200 mL of chloroform at the boiling temperature;
2. About 0.5 mL of water was added to hydrolyzed the MA and convert it to carboxylic acid;
3. The solution was maintained at the above mentioned condition for 8 h; and
4. The sample solution was titrated using a standardized solution of 0.1M potassium hydroxide (KOH) in methanol, using phenolphthalein as acid-base indicator. The numbers of moles of anhydride groups containing in the original sample are equal the half of the numbers of moles neutralized by the KOH.

Fourier transforms infrared spectroscopy

The infrared analyses were performed in a Perkin-Elmer spectrophotometer model Spectrum 1000 with 32 scans and 1 cm⁻¹ resolution.

TABLE I
Characteristics of the Used Materials

Material	MFI (g/10 min)	Composition	Molecular weight (g/mol)	T _g (°C)
aPA	4.9 ± 0.2	End group content: [NH ₂] 37 μeq g ⁻¹	$\bar{M}_n = 12,000$ $\bar{M}_w = 47,000$	127

TABLE II
Composition Used in the Synthesis of
MMA-MA Copolymers

MMA-MA	MMA (mL)	MA (g)	EA (mL)	BzP (g)	Toluene (mL)
MMA-MA0 HMW	93	0	1.8	1	420
MMA-MA1 HMW	90	3	1.8	1	413
MMA-MA5 HMW	79	15	1.8	1	426
MMA-MA10 HMW	74	20	1.8	1	431
MMA-MA1 MMW	90	3	1.8	2	412
MMA-MA5 MMW	79	15	1.8	2	428
MMA-MA10 MMW	74	20	1.8	2	433
MMA-MA1 LMW	90	3	1.8	5	415
MMA-MA5 LMW	79	15	1.8	5	433
MMA-MA10 LMW	74	20	1.8	5	439

Rheological measurements

Rheological measurements were performed in a Haake torque rheometer with a 50 cm³ mixing chamber and standard rotors, operating at 260°C and 60 rpm for 10 min. The composition of the aPA/MMA-MA blend studied was 94/6 wt/wt.

RESULTS AND DISCUSSION

Synthesis and characterization of the MMA-MA copolymers

The molecular weights of the MMA-MA copolymers synthesized are shown in Table III. The values of the molecular weight are similar within each series of HMW, MMW, and LMW for different MA concentration. The molecular weight of the copolymer increases with the reduction in the concentration of benzoyl peroxide added. In previous works in our laboratories,^{17,18} using dimethyl sulfoxide (DMSO) as solvent and 2,2'-Azobis(2-methylpropanonitrile) (AIBN) as initiator, it was obtained and studied MMA-MA copolymers with a wide and not controlled variation of molecular weight when added different MA amounts. The synthesis procedure used in this work

TABLE III
SEC Results for the MMA-MA Copolymers Synthesized

Copolymer	M_n (g/mol)	M_w (g/mol)	M_w/M_n
MMA-MA0 HMW	31,386	55,924	1.78
MMA-MA1 HMW	30,729	52,386	1.61
MMA-MA5 HMW	29,398	57,474	1.95
MMA-MA10 HMW	23,408	60,365	2.57
MMA-MA1 MMW	19,779	34,217	1.73
MMA-MA5 MMW	19,253	33,782	1.75
MMA-MA10 MMW	15,636	42,839	2.73
MMA-MA1 LMW	12,364	22,895	1.85
MMA-MA5 LMW	9262	25,185	2.71
MMA-MA10 LMW	8081	22,643	2.80

and their results suggest that the use of a solvent containing benzene ring in its structure, which acts as chain transfer in radical reaction,¹⁹ allow an easier and more accurate control of the molecular weight and of the MA level during the copolymerization of the copolymer MMA-MA. Our speculation is also based on the knowledge that azonitriles are generally considered as chemicals with no tendency toward chain transfer whereas peroxides initiators have very significant chain transfer constants¹⁹; it is known also that chain transfer agents are used to control the molecular weight of polymers obtained by free-radical polymerization.^{20,21}

Table IV presents the results of the titration analysis of the MA groups in the MMA-MA copolymers. The results of titration give the composition of the MMA-MA copolymers obtained. The incorporation of MA into MMA-MA copolymer during polymerization is less than the amount added in the solution and this fact is related to the differences between reactivity ratios of the monomers used. For the case where the two monomer reactivity ratios are different, $r_1 > 1$ and $r_2 < 1$, the copolymer will contain a larger amount of the more reactive monomer in random placement in the chain.²⁰ For the comonomer pair MMA-MA, the MMA reactivity ratio is 3.10 and MA reactivity ratio is 0.01.²² Therefore, in the polymerization of the MMA-MA copolymer less MA is incorporated compared to the amount available in the solution.

The incorporation of MA in the MMA-MA copolymer was also confirmed using FTIR spectroscopy. Figure 3 shows the FTIR spectra for the series of MMA-MA copolymers with HMW. The transmittance peaks at 1820 cm⁻¹ (peak 1) and 1770 cm⁻¹ (peak 2) can be assigned to asymmetric and symmetric C=O stretching vibration of the MA, respectively. It is important to notice that when the MA amount is increased, the intensity of the transmittance peaks is also increased. These results corroborate

TABLE IV
Titration Results for the MMA-MA Copolymers Synthesized

Copolymer	Maleic anhydride incorporated in the copolymer (%)
MMA-MA1 HMW	1.08 ± 0.02
MMA-MA5 HMW	5.00 ± 0.08
MMA-MA10 HMW	9.80 ± 0.40
MMA-MA1 MMW	0.83 ± 0.06
MMA-MA5 MMW	5.14 ± 0.10
MMA-MA10 MMW	8.97 ± 0.21
MMA-MA1 LMW	0.74 ± 0.03
MMA-MA5 LMW	5.97 ± 0.17
MMA-MA10 LMW	8.27 ± 0.37

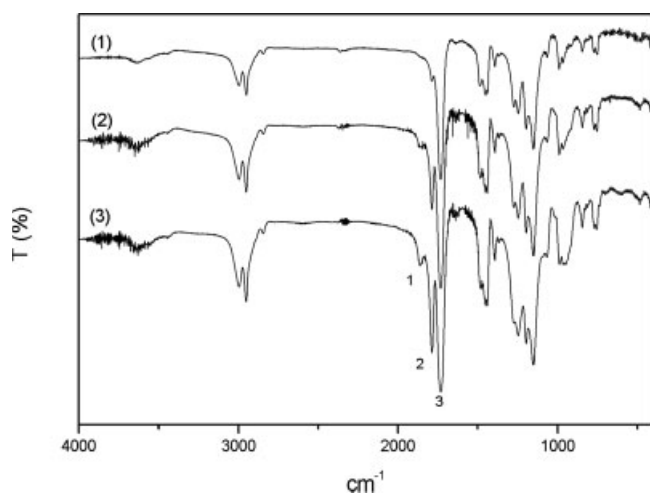


Figure 3 FTIR spectra of the copolymer studied: (1) MMA-MA1HMW, (2) MMA-MA5HMW, and (3) MMA-MA10HMW.

rate qualitatively with the titration results. The absorption band at 1735 cm^{-1} (peak 3) can be assigned to MMA groups in the copolymer.

Reactivity of MMA-MA copolymers with aPA

An illustration of the variation of torque registered in the internal mixer during the preparation of the mixtures of aPA and MMA-MA copolymer with high M_w and different MA concentration are shown in Figure 4. It is observed a very low torque level for the neat MMA-MA copolymer. The torque level for the neat aPA is higher than for the neat MMA-MA copolymer, but still can be considered low. For the mixtures we can observe that when MMA-MA0 is added to the aPA the torque level is reduced compared to the torque value obtained for mixing neat aPA. When MMA-MA copolymers with increasing values of MA concentration are added to the aPA, a corresponding increase in the torque level is observed for the mixtures. The torque values are correspondent to the viscosity of the mixtures and this increase in viscosity observed for the systems studied in this work is consistent with the speculation of the formation of graft copolymers during the melt mixing process, probably because of the graft reactions of end groups of aPA with MA.^{2,5}

The torque level values after 2 min of mixing for the blends aPA/MMA-MA with different MA content in the copolymer and with different molecular weight are shown in Figure 5. It is observed an increase in the level of torque for mixing with the increase in MA content in the copolymer independently of the copolymer's molecular weight. At low level of MA (1% MA), variation in molecular weight of the copolymer does not lead to a change in the

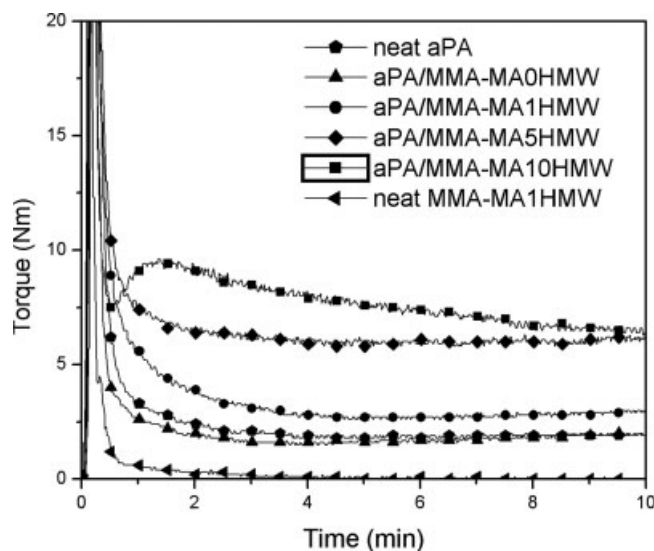


Figure 4 Torque versus time for aPA/MMA-MA mixtures at 260°C .

torque level for the mixture. However, for higher MA level (5 and 10% MA) in the MMA-MA copolymer a more viscous response is observed. It can be observed also that the copolymer MMA-MA with the MMW ($M_w \sim 35,000$) leads to the highest torque values for the compatibilized aPA/MMA-MA systems. These observations indicate that these compositions (5 and 10% MA) have higher viscosity, which is believed to be due to a higher level of reaction occurring in these systems. It is important to notice that these results are observed for very similar mass temperature during mixing.

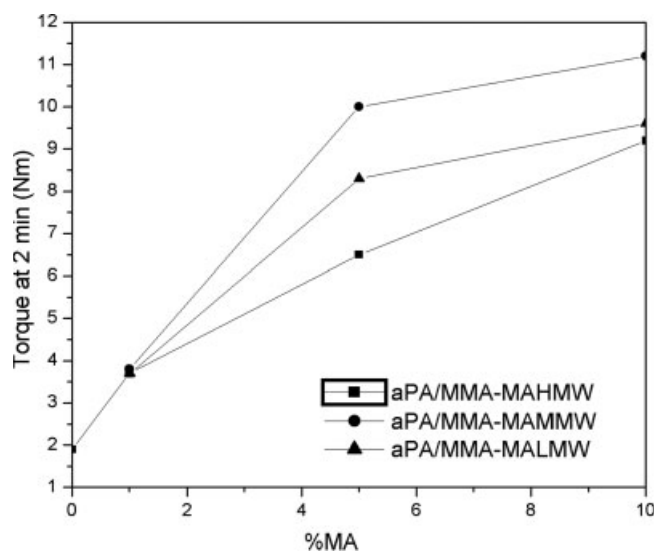


Figure 5 Torque at 2 min of mixture versus % of MA ($x = \%AM$).

CONCLUSIONS

The synthesis and characterization of MMA-MA copolymer has been investigated. Through the modified synthesis procedure used in this work, it was possible to obtain MMA-MA copolymers with good control of both molecular weight and concentration of reactive functional groups of the compatibilizer during the synthesis independently. The results obtained by SEC analysis indicate that the use of solvents such as toluene, containing benzene rings, and initiator such as peroxide that shows chain transfer characteristic enhances the molecular weight control during solution polymerization of the MMA-MA copolymer. As a result of the reactivity ratios difference, the amount of MA incorporated in the molecules of the MMA-MA copolymer was lower than the MA added to the reactor.

It was also investigated the copolymer reactivity with aPA. The copolymers having the MMW with high MA quantities (5 and 10% MA) leads to higher torque values during mixing as evidenced by torque rheometry. This indicates that a compromise between molecular weight and the level of reactive functional group of the compatibilizer should be sought to improve the compatibilization of polymer systems.

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