

# Solid Phase Graft Copolymerization. I. Effect of Initiator and Catalyst

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## Synopsis

Polypropylene–maleic anhydride (PP–MA) graft copolymers were produced from isotactic homopolymer polypropylene (molecular weight > 150,000) utilizing the technique of solid phase graft copolymerization. A high degree of graft (about 8–10%) was achieved on 150 mesh (U.S. Standard Sieve) samples using this process. This free-radical-initiated, catalyst-aided grafting process was effective at low temperatures (100–120°C), atmospheric pressure, and low residence times (60 min). The powder was mixed in a low shear, fixed speed, continuous mixer where the ingredients were added in stages to effect the reaction. The interfacial agent was used to etch the polymer to provide sites for the reaction. The powder was removed from the reactor on completion of the reaction. This process can be further applied to graft other reactive monomers on polypropylene (PP).

## INTRODUCTION

The primary objective of this study was to develop a new, energy efficient, low temperature, low pressure, low cost process to produce grafted polymers, especially polypropylene maleic anhydride copolymers. The goal was also to develop a process which utilizes only small amounts of solvents and to avoid expensive solvent recovery. Therefore, it was necessary to design a reactor which would effectively produce PP–MA graft copolymers with high comonomer content at lowest possible residence time in the reactor.

The secondary objective was to evaluate the effects of types and amounts of catalyst, free radical initiator, temperature, and residence time on the degree of graft and the effectiveness of the process. The approach taken in this research is based on reaction engineering principles as well as polymeric reactions.

## BACKGROUND

Graft copolymers of polypropylene and maleic anhydride have been investigated by several investigators using various techniques. Some of the key techniques are listed below.

1. **Polymerization from the Monomers.** In this process the copolymer is synthesized directly from the monomer. The reaction is effected at high temperatures and pressures in the presence of a catalyst.<sup>1</sup>

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2. **Solution Process.** In this process PP is dissolved in a suitable solvent and reacted with maleic anhydride in the presence of a free radical initiator.<sup>2</sup> The reaction is performed in liquid phase and the formed copolymer is precipitated from the solution with the aid of another solvent.<sup>3</sup>
3. **Melt Process.** Polypropylene is melt processed in a mill with the aid of a free radical initiator. The degree of graft achieved varied depending on the temperature, residence time, and the amount of free radical initiator.<sup>4</sup>
4. **Irradiation Process.** High energy radiation is applied to the polymer to generate free radicals. The free radicals formed react with the monomer to form the graft copolymer. This process is expensive and is currently being used to etch the polyolefin film prior to printing.<sup>5</sup>
5. **High Temperature Thermal Grafting Process.** This process has been extensively used to effect high graft level in the copolymer. The reaction is performed at 325°C. The free radicals are generated at the high temperature which effect the reaction.<sup>6</sup>
6. **Vapor Phase Grafting Process.** Vapor phase grafting of oriented PP fibers have been investigated to improve the adhesion and dyeability of the fiber.<sup>7</sup>
7. **Solid Phase Graft Copolymerization Process.** This is the process under current investigation. Similar work has been performed by Fumio et al.<sup>3</sup> Their objective was to prepare PP-MA copolymers to be used for reactive alloying with polyamides and polystyrene. They achieved low levels of graft (1.4%), which was sufficient for their analysis. However, the process under consideration in this paper is unique due to the following reasons:
  - a. *Low Temperature Process:* The reaction is performed at low temperature (100–120°C) well below the melting point of the polymer, unlike thermal grafting which is done at high temperatures (325°C).
  - b. *Low Pressure Process:* The reaction is performed at atmospheric pressure.
  - c. *Solvent Recovery:* Since this process utilizes small amounts of solvents, it is adsorbed onto the polymer and need not be recovered.
  - d. *Equipment:* This process utilizes existing equipment with slight modification.
  - e. *Process Modification:* This process can be easily modified to prepare other reactive polymer systems.

### APPLICATIONS OF PP-MA COPOLYMER

Several applications have been found for the PP-MA copolymer, some of which are listed below.

1. PP-MA copolymer is extensively used as a coupling agent to bond the glass fiber to the PP matrix.
2. The copolymer is used as a polymeric adhesive to bond polymer substrates in coextrusion, lamination applications.
3. Incompatible polymer alloys like PP-polycarbonate and PP-polyamides can be made compatible using PP-MA copolymer. Without the compatibilizing agent the alloy would not possess strength and would delaminate.

4. PP is extensively used in sterilizable packaging. Fillers improve the structural integrity of the packaging. PP-MA copolymer improves the adhesion between the filler and PP, thereby improving the dimensional stability and heat resistance of the part at elevated temperatures.
5. PP-MA copolymer is extensively used to coat metal substrates to prevent corrosion and to improve chemical resistance. Without PP-MA copolymer, PP does not bond to the metal.
6. PP-MA copolymer is also used in the solidification of radioactive waste.
7. Maleic anhydride improves microbial resistance of the copolymer.
8. Maleic anhydride improves the dyeability of PP fiber.
9. PP-MA copolymer with reinforcing agents is used in laminated paper substitutes.

## EXPERIMENTAL

### Reactor Modification

A twin blade low shear multiport mixer was used to perform the solid state grafting process. A glass window was provided at the top of the reactor to monitor the color shift during the reaction. An opening was provided at the top to add the ingredients into the reactor. Inlet and outlet were provided for the inert gas on the top of the reactor.

A thermocouple was introduced from the bottom of the reactor and was placed close to the mixing zone. A temperature controller was connected to the thermocouple to monitor and control the reactant temperature. The exhaust gases were bubbled through water and vented to the atmosphere.

### Ingredients Used in the Formulation

**Polymer.** Solid phase grafting was performed on homopolymer isotactic polypropylene (molecular weight > 150,000). The PP flake was further ground cryogenically to a powder to pass through a 150-mesh screen.

**Comonomer.** Maleic anhydride was obtained in a briquette form. It was ground in a ball mill to a powder.

**Free Radical Initiator.** Wet benzoyl peroxide (99% pure) was used as an initiator in our analysis. It was obtained in a powder form.

**Catalyst.** Two types of catalyst were investigated in the current investigation. Catalyst "A" was used for initial analysis.

**Interfacial Agent.** Benzene and toluene were used as interfacial agents in our analysis.

### Mixing Procedure

The formulations were added to the reactor in the following sequence.

1. Polypropylene was added to the reactor and the mixing rotors were turned on. Total batch size was predetermined to be 200 g.
2. Maleic anhydride, free radical initiator, catalyst, and the interfacial agent were divided into four equal parts by weight. They were added into the reactor in 15-min intervals, after PP attained the reaction temperature.

3. The interfacial agent was mixed with the catalyst and then was added into the reactor.
4. Nitrogen was purged into the reactor initially as the PP attained the set temperature. It was turned off just prior to the first addition of the ingredients.
5. Once the PP attained the reaction temperature, maleic anhydride, benzoyl peroxide, and the catalyst (in the interfacial agent) were added into the reactor in that order. The timer was started. Subsequent additions were made into the reactor at 15-min intervals. The reaction was terminated after 60 min by emptying the contents of the reactor into a sample container.
6. Exactly 20 g of the reaction product was taken in a 500-mL round-bottomed flask. It was extracted with 400 mL of distilled water for 24 h. The extracted solution was stored for further analysis. The extracted polymer was washed with distilled water and dried in a hot air oven for 4 h.
7. Quantitative determination of maleic anhydride was performed using wet chemical methods. The procedure used for wet chemical analysis is based on dissolution of the polymer followed by titration.
8. Qualitative determination of maleic anhydride was performed by Fourier transform infrared spectroscopy (FTIR).

## RESULTS AND DISCUSSION

### Effect of Free Radical Initiator and Catalyst Concentration

The interdependence of the percentage of grafting and initiator concentration is given in Figures 1 and 2.

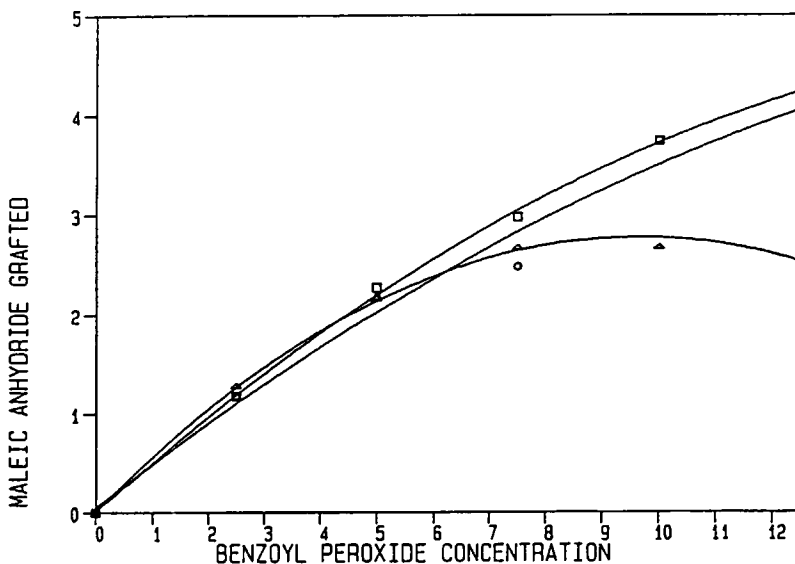


Fig. 1. Effect of initiator concentration on graft level at 100°C using 10% by weight of solvent: (Δ) no catalyst; (○) 2% catalyst A; (□) 5% catalyst A.

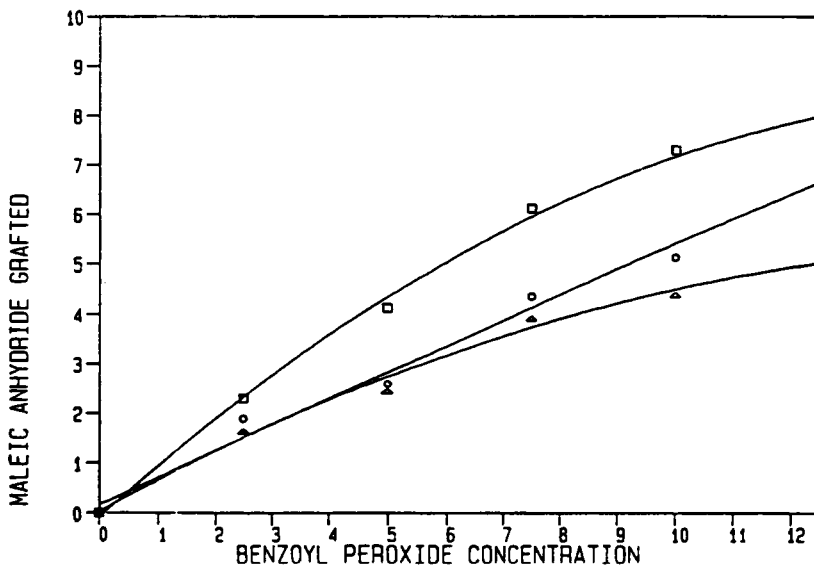


Fig. 2. Effect of initiator concentration on graft level at 120°C using 10% by weight of solvent: (Δ) no catalyst; (○) 2% catalyst A; (□) 5% catalyst A.

#### At 100°C

**0% Catalyst.** Using benzene as the interfacial agent, in the absence of catalyst, the degree of grafting increased with the initiator concentration and leveled off beyond 7.5% by weight of initiator. The maximum attainable graft level was about 2.6%.

**2% Catalyst.** In the presence of 2% catalyst the degree of graft did not increase at low levels of initiator (at 7.5% level). But at high levels of initiator (12.5%) the degree of graft increased by about 85%. A minimum was observed in the graft level at 7.5% initiator concentration. This could be due to the decreasing molecular weight of the side chains caused by the free radical initiator and the increased tendency of the maleic anhydride towards homopolymerization. This phenomenon was observed by the increase in the degree of pigmentation in the reaction product.

**5% Catalyst.** At 5% catalyst concentration, the degree of graft increased significantly to 4.0% graft level as the amount of initiator increased.

#### At 120°C

**0% Catalyst.** Figure 2 illustrated the effect of the amount of initiator and catalyst on the graft level in the copolymer. It can be seen that, at 0% catalyst, the graft level steadily increased to 5% at 12.5% initiator concentration. The curve appeared to level off beyond 12.5% initiator concentration.

**2% Catalyst.** At 2% catalyst concentration, the effect of catalyst was observed only over 7.5% initiator concentration. The overall graft increased from 5.0 to 6.8% at 12.5% initiator concentration.

**5% Catalyst.** Significant increase in comonomer content was observed at 5% catalyst concentration. The graft level increased from 5.0 to 8.0% level at 12.5% initiator concentration.

### FTIR Analysis

Fourier transform infrared spectroscopy analysis was performed on all samples. A sample FTIR spectrum of trial 068 is given in Figure 3. Two distinct peaks were observed in the FTIR spectra, which clearly identified the presence of maleic anhydride in the copolymer. The peaks occurring at 1790 and at  $1865\text{ cm}^{-1}$  confirmed the presence of carbonyl groups of the maleic anhydride in the grafted polymer. Similar identification technique was used by Minoura et al.<sup>2</sup> It is clear that the maleic anhydride peaks as identified in the infrared spectrum are from the copolymer and not from the free maleic anhydride. It is ensured that the free unreacted maleic anhydride was removed by extraction with water.

### Effect of the Type of Interfacial Agent

Benzene and toluene were used as interfacial agents in our study. It can be found from Figure 4 that, at a concentration of 10%, very little change was observed between benzene and toluene at 12.5% initiator and 10% maleic anhydride. For the initial analysis, therefore, it was assumed that the type of interfacial agent does not play a significant role in the graft level.

It was anticipated that the solubility of polypropylene, maleic anhydride, benzoyl peroxide, and the catalyst in the interfacial agent might play a role in the degree of graft level in the copolymer.

### Effect of Temperature and Catalyst Concentration

The effect of temperature and catalyst concentration on the graft level is given in Figures 5, 6, and 7. It was found that the graft efficiency increased from 2.6 to 5.0%, with the increase in temperature from 100 to 120°C in the absence of catalyst (Fig. 5).

A similar increase was observed at 2% catalyst level. There was a 70% increase in graft level at 2% catalyst concentration from 4.0% graft level to 6.8% graft level (Fig. 6).

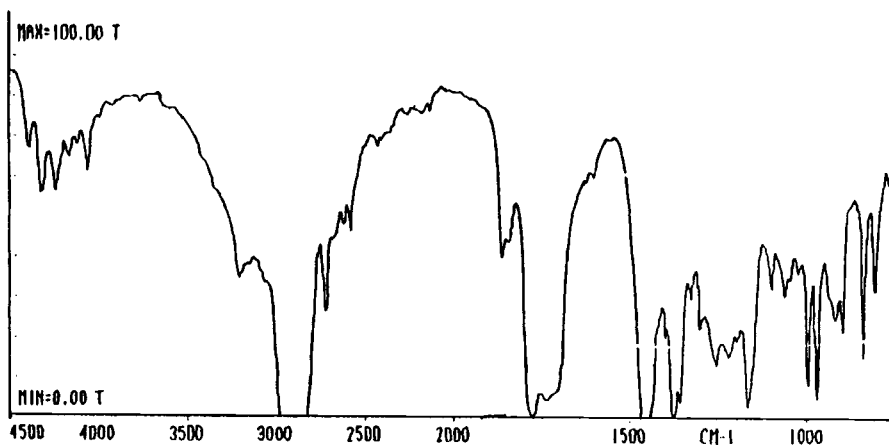


Fig. 3. Fourier transform infrared spectrum on polypropylene-maleic anhydride copolymer.

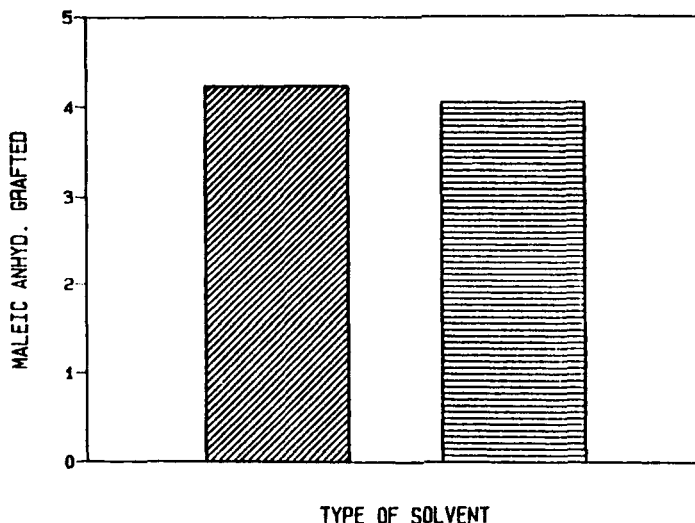


Fig. 4. Effect of solvent type on graft level: (▨) benzene (4.2% grafted); (▤) toluene (4.0% grafted).

The increase in graft level using 5% catalyst was much more dramatic at 120°C. The graft level increased from 4.236 to 8.0%. More than 60% increase in graft level was observed (Fig. 7).

The results clearly indicated that catalyst A functioned effectively as catalyst in the copolymerization of polypropylene and maleic anhydride in solid phase. The increase in graft level was also seen as an increase in the intensity of the peaks at 1790 and 1865  $\text{cm}^{-1}$  from the FTIR spectrum.

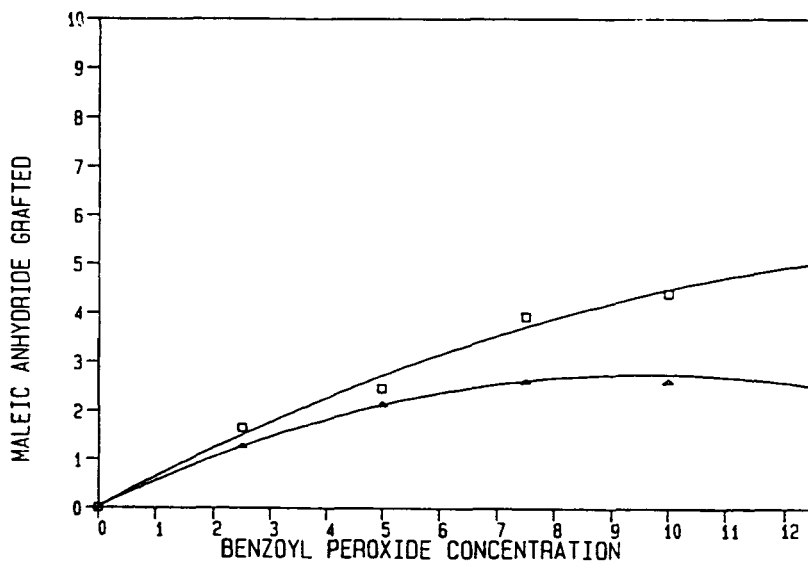


Fig. 5. Effect of temperature and initiator concentration on graft level without catalyst: ( $\Delta$ ) 100°C; ( $\square$ ) 120°C.

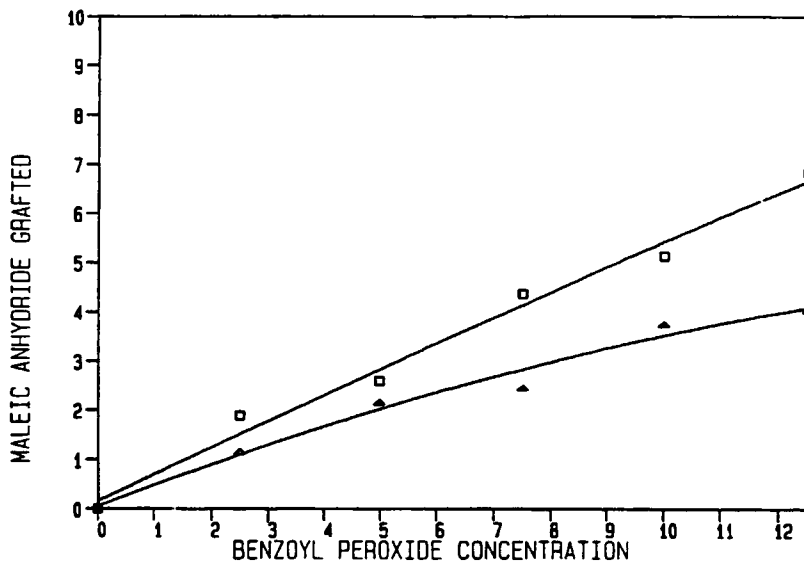


Fig. 6. Effect of temperature and initiator concentration on graft level at 2% by weight of catalyst A: ( $\Delta$ ) 100°C; ( $\square$ ) 120°C.

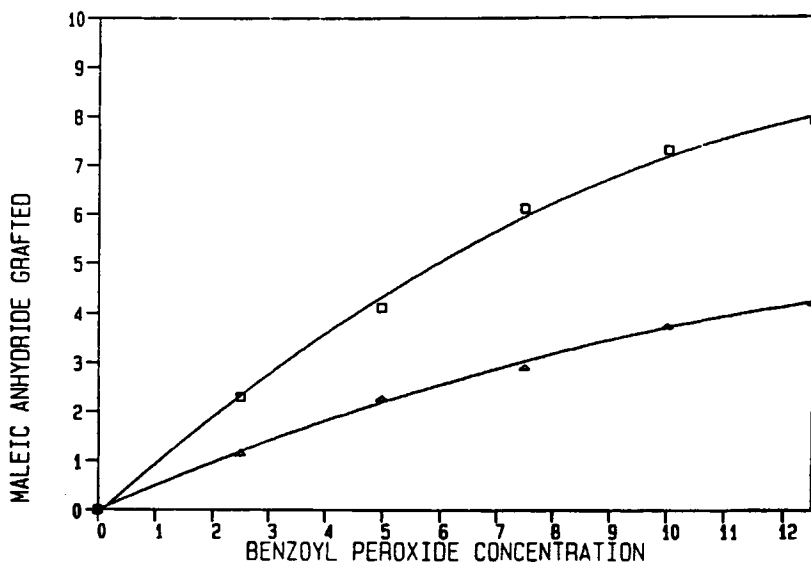


Fig. 7. Effect of temperature and initiator concentration on graft level at 5% by weight of catalyst A: ( $\Delta$ ) 100°C; ( $\square$ ) 120°C.

### CONCLUSIONS

It is clear that graft copolymers of polypropylene and maleic anhydride can be manufactured utilizing this energy-efficient, low-cost, low-temperature, low-pressure process. This process eliminated expensive solvent recovery and purification. This process also enabled us to prepare high comonomer levels unlike other processes.



The effect of catalyst in the graft level was not felt at low initiator (below 7.5%) and catalyst (2%) concentration. In order to achieve an 8–9% graft level, a minimum of 12.5% initiator and 5% catalyst was required. The process and its results were found to be very reproducible.

A high level of maleic anhydride (8–9%) can be grafted to polypropylene by this solid phase graft copolymerization process. This process utilized low amounts of solvent and can be performed at low temperatures 100–120°C and at atmospheric pressure. This free radical process required inexpensive reactor setup. By utilizing this technology the manufacture of copolymers of PP–MA is made easy and less expensive.

The authors wish to thank Dr. Vetkav Parameswaran and Dr. Sunil Kesavan for their assistance in the reactor design. The authors also would like to thank the management of A. Schulman Inc. for their support.

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Received July 29, 1988

Accepted October 17, 1988