Solid phase graft copolymerization: 2. Effect of toluene

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Toluene was used as the interfacial agent to enhance the graft level in the solid phase graft copolymerization of polypropylene and maleic anhydride. The effect of catalyst and interfacial agent on the graft efficiency was investigated. It was found that the interfacial agent enhanced the graft level significantly at high initiator concentrations. At low initiator concentrations, however, only a slight increase in graft level was observed. In the absence of catalyst and interfacial agent, at high initiator concentrations (12.5%), the graft obtained was only 3.9%. In the presence of 5% catalyst and 10% interfacial agent the graft level doubled to 7.9%. This significant increase in graft level was attributed primarily to the catalyst which increased the graft level at an average from 3.9% to 6.8%. The final colour of the reaction product was influenced only by the type and amount of catalyst and not by the interfacial agent. The addition of interfacial agent resulted in agglomerates and lumps in the final product. This product had a tendency to adhere to the mixing blades in the reactor. This may be attributed to the uneven addition of the interfacial agent into the reactor. Quantitative determination of the graft level was performed by wet chemical methods and FTi.r.was used to determine the presence of maleic anhydride in the copolymer.

(Keywords: solid phase graft copolymerization; interfacial agents; graft levels)

INTRODUCTION

The technology of using solvents to effect graft copolymerization has been around for many years. Conventional techniques used excessive amounts of solvent (about ten times the weight of polymer) to dissolve the polymer and then effect the graft in solution. This technique was efficient and able to produce copolymers with high comonomer content. The type of copolymer (either block, random or graft) obtained was varied by the catalyst and initiator used. In the case of polypropylene–maleic anhydride copolymer, the solvents traditionally used were benzene and toluene. Extremely high loadings of these solvents were used to dissolve the polymer and then effect the graft with the aid of a free radical initiator. The coppolymer was later precipitated from the solution using another solvent.

With this technology the solvents had to be distilled for separation. The grafted copolymer had to be dried free of solvent before use. The solvents, such as benzene and toluene, which had been traditionally used were suspected to be carcinogenic. Therefore, pollution had to be avoided at all costs. This made the process extremely expensive and made it uneconomical in either large volume, low cost applications or in low volume, high cost, specialty applications.

Several other techniques including thermal, radiation, and extrusion grafting were also used to prepare copolymers. These techniques have their advantages and disadvantages. The main disadvantage is high equipment cost and low graft efficiency. Each of the above techniques was used in selected areas that warrant their application.

The technology of solid phase graft copolymerization is novel from the following processing engineering standpoints:

(1) Low solvent use
(2) No solvent recovery
(3) Low cost process
(4) Low pressure process
(5) Low temperature process
(6) Easy adaptability
(7) Easy equipment modification

In addition, a high level of comonomer can be grafted to the parent polymer by the use of proper catalyst, free radical initiators, and interfacial agents.

EQUIPMENT

A twin blade heated low shear mixer was used for the solid phase grafting process. The top of the mixer was modified with an injection port to spray liquids into the reactor. A liquid metering pump was used to meter and inject the liquid into the reactor. Inert atmosphere was maintained by purging the reactor with nitrogen. The exhaust from the reactor was passed through a stripping column and vented to the atmosphere.

REACTANTS

Polypropylene was cryogenically ground to a fine powder (US standard 150 mesh). This was performed to increase the surface area for grafting. Maleic anhydride briquettes were broken into small particles (US standard 10 mesh) for easy handling. Benzoyl peroxide was obtained in a flake form. It was refrigerated for stability.

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Toluene was used as the interfacial agent for the current study. It was chosen primarily due to its relatively high boiling point and low volatility. It swelled the polypropylene to promote surface reactions. The solubility of maleic anydride in toluene was approximately 23 g in 100 ml at room temperature.

A catalyst (RRKB-1) to promote the formation and stabilization of free radicals was added to investigate its effect on the graft levels.

MIXING PROCEDURE

Polypropylene was added into the reactor and the mixer was turned on. The polymer was allowed to attain the reaction temperature. During this period nitrogen was purged into the reactor. The additives were added into the reactor in four stages. The comonomer, catalyst and the free radical initiators were divided into four equal parts and each part was added into the reactor at 15 minute intervals. The comonomer was added to the solvent and it was injected into the reactor. The preweighed catalyst and the free radical initiator were added in that order. A similar sequence was followed three times at 15 minute intervals. The batch was dropped from the reactor after 1 h of reaction.

RESULTS AND DISCUSSION

The following factors were investigated in the current study: effect of solvent type and amount; the effect of catalyst type and amount and effect of initiator concentration. It was found that all of these factors contributed significantly to the determination of the graft level of the copolymer.

The effects of initiator, residence time, and catalyst were investigated prior to the current analysis[1,2]. The duration of the reaction, the type and amount of catalyst, and the type and amount of free radical initiator were optimized from the previous analysis.

Effect of free radical initiator

It was found from the initial trials that only very low levels (0.5%) of graft could be achieved in the absence of a free radical initiator. Free radicals generated by the initiator provided reaction sites on the polymer. In the absence of a free radical initiator, the formation of free radicals was only by the heat provided for the reaction. At the low processing temperatures very low amounts of free radicals could be formed in the absence of a free radical initiator. These radicals are, in general, shortlived and possess low energy. They are insufficient to promote the graft reaction.

It is clear from *Figures 1, 2, 3, 4* and *5* that the graft level increased with the initiator content. Though this phenomenon was expected, the process is unique because the reaction was performed in a solid phase, well below the melting point of the polymer.

The stability of the free radical initiator at the reaction temperature determined the reaction time. At 120°C the half-life period of benzoyl peroxide was about 4 minutes. It was found that most of the initiator decomposed in about 15 minutes. This primarily determined the reaction time.

Effect of interfacial agent

At low levels of free radical initiator practically no difference in graft level was observed as can be seen from

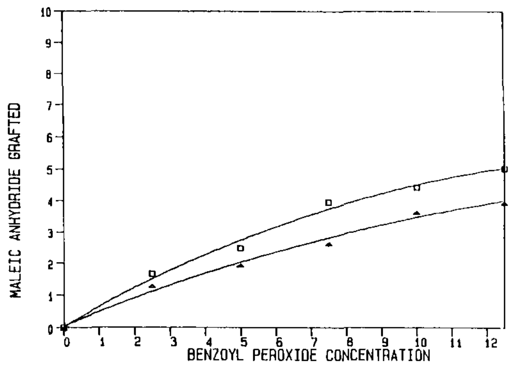

Figure 1 Effect of solvent and initiator on graft level (120°C, 0% catalyst). △, 0% solvent; □, 10% solvent

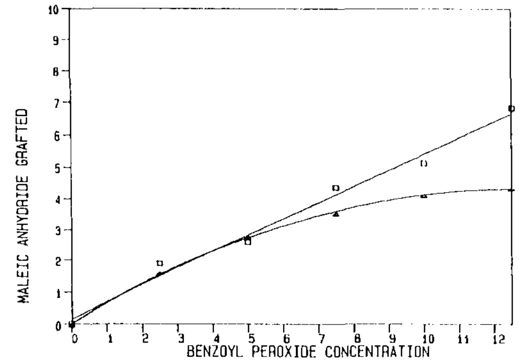

Figure 2 Effect of solvent and initiator on graft level (120°C, 2% catalyst). △, 0% solvent; □, 10% solvent

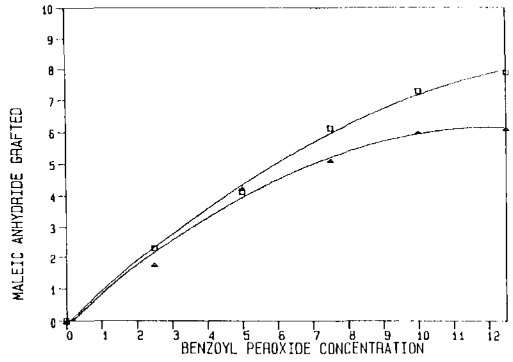

Figure 3 Effect of solvent and initiator on graft level (120°C, 5% catalyst). △, 0% solvent; □, 10% solvent

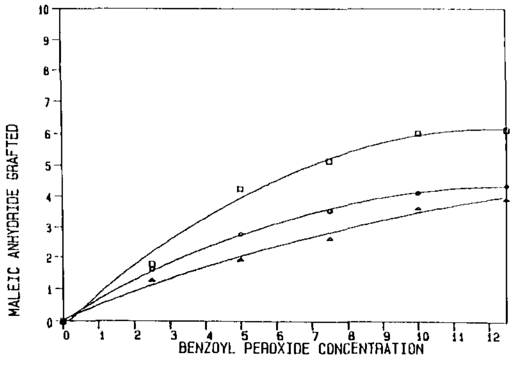

Figure 4 Effect of initiator and catalyst concentration on graft level (0% solvent, 120°C). △, 0% catalyst; ○, 2% catalyst; □, 5% catalyst

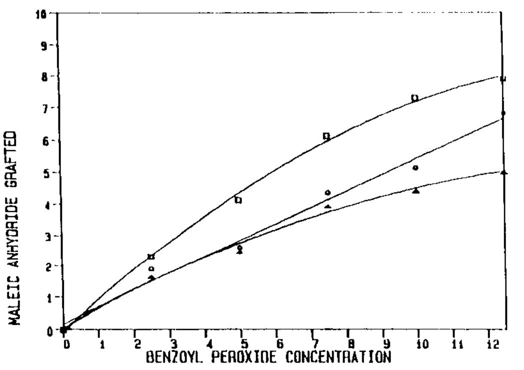

Figure 5 Effect of initiator and catalyst concentration on graft level (120°C, 10% toluene). △, 0% catalyst; ○, 2% catalyst; □, 5% catalyst

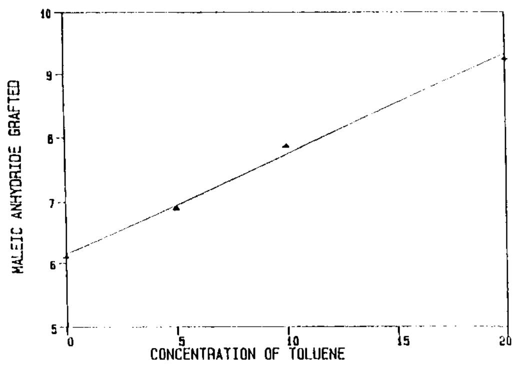

Figure 6 Effect of solvent concentration on graft level (120°C, 5% catalyst). △, concentration of toluene

Figures 1, 2 and *3*. At high initiator concentration the comonomer content in the copolymer increased by 20% in the presence of 10% toluene as interfacial agent.

It was found from the literature that the solvent was primarily used to remove the heat generated from the reaction. This prevented run-away reactions and provided more accurate temperature control

Effect of solvent concentration

The effect of the amount of interfacial agent on the graft level was also investigated (*Figure 6*). This analysis was performed at the highest level of peroxide content and catalyst level. From *Figure 6* it is evident that the graft level increased with the increase in interfacial agent concentration in the reactant mixture. It was found that the interfacial agent provided more surface area by swelling the surface of the polymer. The increase in graft level with the increase in concentration of the interfacial agent was attributed to the solubility of maleic anhydride in the solvent. The ability of the solvent to etch and swell the polymer surface was also attributed to the increase in graft levels. Though there is no data to support this statement, it is believed that this phenomenon could be explained by the mutual solubility of the polymer and the comonomer in the solvent.

Effect of catalyst amount

It is evident from *Figures 4* and *5* that the graft level increased with the catalyst concentration. It was found that the catalyst improved the graft efficiency by stabilizing the free radicals and lowering the activation energy for the graft reaction. The graft level increased significantly in the presence of interfacial agent.

CONCLUSION

The interfacial agent enhanced the graft level at high initiator concentrations. A 20% increase in graft level was observed in the presence of the interfacial agent. The catalyst enhanced the graft level significantly in the presence of the interfacial agent.

The percent graft achieved was only 3.9% in the absence of a catalyst and interfacial agent, whereas the maximum graft level achieved with the catalyst and the interfacial agent was 9.6%. The graft efficiency increased as the interfacial agent concentration increased.

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