

Solid Phase Graft Copolymerization: Effect of Interfacial Agent

SUNGGYU LEE,* RAMESH RENGARAJAN,[†] and VETKAV R.
PARAMESWARAN,[‡] *Department of Chemical Engineering,
University of Akron, Akron, Ohio 44325*

Synopsis

Solvents or interfacial agents have been used as media to perform various polymerization reactions. The selection of solvents to provide the appropriate medium for the reaction has opened up a totally new area for research. In the present study, three solvents, viz., toluene, decalin, and tetralin, were investigated in the preparation of polypropylene–maleic anhydride copolymers by solid phase graft copolymerization. The graft level was quantitatively determined by wet chemical methods and qualitative confirmations were made by Fourier transform infrared spectroscopy. It was found that toluene and decalin increased the surface area for reaction by swelling the polymer. The graft level increased with an increase in concentration of toluene and decalin. In the case of tetralin, the graft level decreased as the concentration of the solvent in the reactant mixture increased. It was experimentally observed that unlike toluene and decalin, tetralin did not cause swelling of the polymer at the reaction conditions. Therefore, the surface area available for reaction would be less when tetralin is used. Moreover, since tetralin dissolves the polymer rather than causing it to swell, the contact area for the reaction is further diminished by the formation of a monomolecular layer of solvent insulating the monomer from the polypropylene.

INTRODUCTION

Polypropylene–maleic anhydride copolymers were first synthesized by grafting maleic anhydride to polypropylene in the early 1960s. The synthesis was performed in the liquid phase using benzene or toluene as the reaction medium. Several free radical initiators were used to initiate the reaction. The reactions were performed in solution at the boiling point of the solvent. The duration of the reaction varied from 1 h to over 20 h. The comonomer content in the graft copolymer varied from 0.3 to 40%. The resultant polymer was dark brown in color. In certain cases, salts of the above polymers were prepared by further reacting with calcium or zinc salts.

The graft copolymers were also produced by extrusion processes. Studies performed by Hogt¹ revealed very low levels of graft (ca. 0.4%) by the twin screw extrusion process. The graft level was primarily determined by the residence time in the extruder. The reaction was performed at high temperatures (> 250°C). High shear developed in the twin screw extruder ensured uniform mixing in the extruder. The free radical initiator used had an extremely low

* To whom all correspondence should be addressed.

[†] Currently with A. Schulman Inc.

[‡] Currently with The Goodyear Tire and Rubber Company.

half-life at the processing temperatures, which partially accounted for the low graft levels.

Several researchers^{2,3} have studied the graft copolymerization of PP and maleic anhydride in single screw extruders. The primary objective of their study was to investigate the feasibility of producing graft copolymers in an extruder and to improve the surface properties, especially, the adhesion of the copolymer to other substrates.

Currently the copolymer of PP and maleic anhydride is being used as an adhesive layer in laminates. These adhesives have been used to bond two non-adhering polymers. The adhesive is either coated on one substrate and then melt bonded onto the other or a thin layer of adhesive film is coextruded and laminated to form a permanent bond. The peel strength of the laminate increased with the amount of reactive component in the copolymer.

In the current process under investigation, the grafting was performed in the solid phase, well below the melting point of the polymer and just above the tack point of the polymer. The interfacial agent was used to etch and swell the polymer surface, to provide reaction sites for the graft reaction. (The quantity of toluene, decalin, and tetralin used in this process was small when compared to conventional solution processes. Therefore, they may be considered as "interfacial agents" rather than as solvents.) This novel technique was advantageous over other processes since it utilized smaller amounts of solvent. The solvent was adsorbed on the polymer surface which could not be recovered. The reaction was performed at low temperatures, low pressures, and with low residence times unlike solution phase grafting where the reactions took as long as 10 to 40 h. This novel process also utilized a conventional low shear mixer which was modified to perform the solid phase graft copolymerization reaction.

EXPERIMENTAL PROCEDURE

The choice of formulations for this study was based on the following considerations:

1. Solubility of the polymer in the interfacial agent
2. Ability of the interfacial agent to etch and swell the polymer
3. Solubility of the reactive monomer in the interfacial agent at the processing temperatures
4. Effect of the boiling point of the interfacial agent on the degree of graft achieved.

Decalin and tetralin are the suggested solvents for the homopolymer isotactic polypropylene at temperatures greater than 120°C. These two solvents were therefore chosen for our analysis. Toluene was also known to swell polypropylene at elevated temperatures, however, it does not dissolve polypropylene. It was also selected for our current analysis.

Benzoyl peroxide was selected as the free radical initiator for our study. In addition, a catalyst RRKB-1 (supplied with a purity of 99.5% by K. B. & Associates), was used to promote the formation and stabilization of the free radicals.

MIXING PROCEDURE

The polypropylene and the maleic anhydride were weighed and added into the reactor along with the catalyst. The interfacial agents were metered and injected into the reactor. Reaction temperatures were measured by a thermocouple and controlled within $\pm 2^\circ\text{C}$ using an Omega PID temperature controller.

The reactor was purged with nitrogen initially to remove all the air from the reactor. The polymer was allowed to attain the reaction temperature before the other additives were added. The products were removed from the reactor and extracted with water for 24 h. The extracted products were washed and dried in an oven. The comonomer content was determined by titration.

RESULTS AND DISCUSSION

The factors investigated in this study were (a) effect of type of interfacial agent and (b) effect of amount of interfacial agent. The results have been compiled in Figure 1.

It is evident from the figure that the graft level increased as the concentration of toluene in the reaction medium increased. The graft level increased linearly from 6.0% at 0% toluene to 9.2% at 20% toluene. As the solvent concentration increased, it swelled the polymer providing additional reaction sites.

A similar increase was observed when decalin was used as an interfacial agent. However, the graft level obtained at 20% tetralin concentration was lower than that obtained with toluene. It was noticed that decalin did not cause as much swelling of the polymer as toluene did. This resulted in fewer reaction

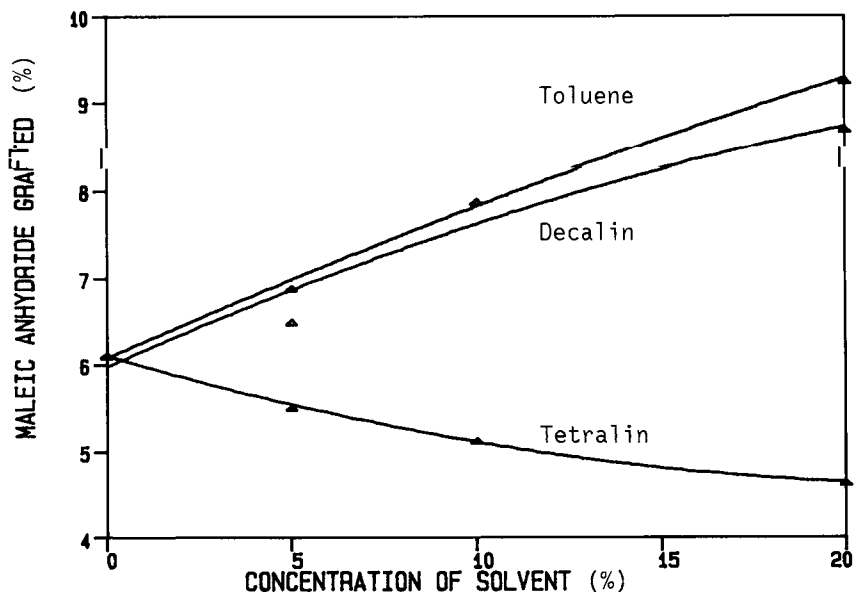


Fig. 1. Effect of solvent concentration on the graft level at 120°C with 5% catalyst.

sites than those generated by toluene. The lower graft level can also be attributed to the lower solubility of the comonomer in decalin.

Surprisingly the graft level decreased as the concentration of tetralin in the formulation increased. The graft achieved with tetralin was lower than that obtained with the standard without any solvent. This was attributed to the following factors:

1. Dissolution rather than swelling of the polymer by the solvent resulted in lower surface area.
2. Formation of a monomolecular layer of the solvent on the surface of the polymer inhibits the reaction.
3. It is also possible that the reactivity and stability of the free radicals generated by the initiator in the presence of tetralin play an important role. This needs to be further investigated.

CONCLUSION

It was clear that toluene and decalin enhanced the graft level of maleic anhydride in the PP-MA copolymer. Toluene performed better than decalin. In the absence of the interfacial agent, the graft level achieved was only 6%. About a 50% increase in graft level was observed in the presence of 20% solvent in the formulation.

It was also found that the ability of the interfacial agent to swell the polymer played a role in the determination of graft level. Reduction in the surface area was observed when the solvent dissolved the polymer.

The authors would like to express their sincere thanks to all the members of their research group for assisting in the progress of this study. Special thanks should be given to A. Schulman Inc. for providing polymer samples and access to analytical instruments.

References

1. A. Hogt, *Modification of Polypropylene with Maleic Anhydride*, Proceedings of the Annual Technical Conference, Society of Plastic Engineers 1988, pp. 1478-1480.
2. A. Robert Steinkamp, U.S. Pat. 3,862,265 (1975).
3. G. Norman Gaylord, U.S. Pat. Appl. 4,506,056 A (1985).

Received January 24, 1989

Accepted December 14, 1989