

Analysis of the Solid Phase Copolymerization Grafting Process

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Abstract-Solid phase grafting, which is an emerging process for the production of graft copolymers, was analyzed and reviewed as an environmentally friendly and inexpensive graft copolymerization process. The effect of the process variables; amount of initiator, catalyst, interfacial agent, monomer, reaction temperature and reaction time were examined. Two graft copolymers, produced by solid phase grafting, were used to show differences in graft percentage by changing the process conditions. The two graft copolymers used were maleic anhydride graft onto polypropylene and acrylic acid graft onto polystyrene. A proposed mechanism was given for each example and characteristic bonds proposed in the PP-g-MA mechanism was positively identified by NMR spectroscopy. Graft levels of 4 wt% PS-g-AAc and 9.6 wt% PP-g-MA were obtained providing comparable or superior graft levels to other grafting processes. Successful scale-up of the solid phase technique proved that this process is efficient and marketable.

Key words : Solid Phase, Graft Copolymerization, Compatibilizer, Graft Level, Copolymer Analysis

INTRODUCTION

The use for polymers in every aspect of life continues to grow at an incredible rate each year. To keep up with this rapid growing need and sophisticated consumer desires these new polymers are being developed to perform in various applications. In recent years, polymers have replaced more traditional materials in industrial applications such as consumer products, packaging, electronics, automobiles, and furniture. Initially, researchers synthesized or tried to synthesize new polymers with desired unique properties such as electrical conductivity, photosensitivity, and reactivity. Due to the growing cost of synthesizing new polymers as well as the low success rate of new polymer development, research has begun to focus on the modification of commodity polymers for specialty applications. This technique of modifying the polymer has led to an increased interest in the field of polymer modification as an easy and cost-effective method to produce polymers with new and diverse properties. Several different modes of polymer modification may be considered viz., chemical, physical, and physicochemical modification.

In order to supply consumers with these new products, compatibilizers need to be developed to facilitate in the engineering of new polymer materials with desirable properties, when attempts are made to blend two distinct polymeric materials for synergistic resultant properties. A novel process that is being used to produce compatibilizers is solid phase copolymerization grafting. This technique grafts various monomers onto a solid polymer backbone using little or no solvent. Graft copolymers may be used as is or as secondary ingredients in various polymer processing operations. This study will review the research that has been conducted in this area and critically assess and analyze the solid phase graft copolymerization process.

COPOLYMERS

One of the first techniques used to chemically modify a polymer was in the area of copolymerization. Copolymers are defined as polymers containing two or more structural units on the backbone. A copolymer can have several different structures random, alternating, block, and graft. A random copolymer is when the polymer chain has an unspecified sequence as shown.



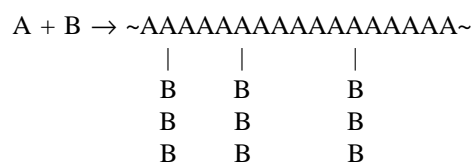
An alternating copolymer has a backbone chain in which the comonomers occur in an alternating sequence.



A block copolymer is when the comonomers are joined in long sequences of another comonomer.



When a comonomer chain is pendent from a backbone of another comonomer a graft copolymer is formed.



In the formation of a graft copolymer, the method of sequential polymerization of the monomer as a side chain is used on the backbone of the existing polymer. Traditionally, graft copolymers have been synthesized by radical or ionic polymerization. Radical polymerization involves a radical site being generated on the backbone of a polymer. This radical is accomplished by means of a free-radical initiator, irradiation, increased temperature, or by applying stress to the polymer. Irradiation can only be accomplished on polymers that are sensitive to irradiation. In radical polymerization, a free-radical initiator

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can be added. Once the free-radical site is created on the backbone, the monomer chemically attaches to the main polymeric backbone at the radical site. Graft copolymers can also be synthesized by ionic polymerization, which utilizes the method of creating a reactive ionic site on the polymer backbone. Depending on the ionic site formed, this process can be categorized as anionic or cationic polymerization.

The main problem with blending two polymers is generally that most polymer mixtures are immiscible. This leads to poor physical and mechanical properties resulting in unstable morphologies. The unstable morphology of the polymer blend is due to the lack of desired interaction between the dispersed phase (minor component of the blend) and the matrix (major component of the blend). From this inability to produce a homogeneous phase stress concentration, weak polymer to polymer interfaces and poor mechanical properties occur. Since the cost of synthesizing new polymers is on the rise this immiscibility problem needs to be overcome. It is possible to introduce new physical and chemical properties into a polymer by grafting the appropriate monomer onto the backbone of the polymer. With the help of graft copolymers, two once immiscible polymers can be blended to have favorable mechanical properties along with miscibility. The most common form of graft copolymers are compatibilizers that are formed in-situ during the blending process [Datta and Lohse, 1996]. There have been a great number of attempts to manufacture more targeted graft copolymers for various advanced applications.

GRAFT COPOLYMER PROCESSES

Currently, the techniques employed to produce graft copolymers can be categorized into several processes; solution phase grafting, reactive extrusion grafting, high temperature thermal grafting, radiation grafting, vapor phase grafting, supercritical phase grafting, and solid phase grafting. When the solution process is used to form the graft copolymer, the polymer is dissolved along with the monomer and initiator into a common solvent. Such a solvent is normally environmentally hazardous, if improperly handled. With this process the desired graft levels and desired location of the graft on the backbone polymer can be attained. Although higher levels of graft can be attained, disadvantages arise from long reaction times and in the environmental concern of solvent recovery.

Reactive extrusion has relatively short reaction times compared with the solution phase process. This process involves melting of the polymer in a mill or extruder. The process largely depends on the residence time, temperature and free-radical initiator. The main advantage is the simplicity of the process application and operation, since the equipment needed is normally available to polymer manufacturer. The major drawback of this process is that the low residence time in the extruder does not allow adequate time to obtain high levels of graft. Another disadvantage that arises is in the final product of the polymer having discoloration due to the temperature and pressure.

When the high temperature thermal grafting process is applied the polymer experiences high temperatures that result in thermal decomposition of the polymer. This thermal decompo-

sition generates a free radical on the polymer backbone, which is required for the graft reaction. However, multiple disadvantages occur during this process. At these high reacting temperatures the molecular weight of the polymer decreases producing non-favorable graft copolymers for many applications. Other drawbacks include the yellow pigmentation that occurs from the chain scission coupled with the elevated temperatures and energy requirements making the process uneconomical.

The use of radiation to graft copolymers is gaining popularity due to the low cost involved in obtaining beam sources. This technique of radiation grafting utilizes high energy or frequency beams such as gamma rays or X-rays to chemically modify the polymers. Desired lengths and placement of the graft can be achieved with great flexibility by this process. As with many other techniques long reaction times have limited this process in industrial use. Control of the process and applicability of the process to various types of polymers are often lacking.

Vapor phase grafting is when the reactive monomer is introduced, in the vapor phase, into the reaction chamber with the parent polymer. A catalyst is used to facilitate in the chemical reaction. This method has reportedly improved adhesion and dyeability properties of polymer fibers. The major drawback to this process is that the reactive monomer vapors used are generally hazardous. This leads to higher costs by requiring specialty reactors.

Supercritical fluid grafting uses the unique properties of supercritical fluids to swell the polymer as well as to dissolve the reactive monomers. This provides high mass transfer rates for the reactive monomer to diffuse into the polymer matrix within the reactor system. This swelling of the polymer has been deemed to help increase levels of graft by providing better contact between the polymer and the reactive monomer. One of the main advantages to this process is the use of non-toxic fluids such as carbon dioxide to facilitate in the reaction. Since the polymer remains in powder form throughout the reaction, there are minimal problems in isolating and recovering the graft copolymer [Trevedi, 1997].

Another novel approach that utilizes the polymer in the powder form is solid phase grafting. Lee and co-workers invented this technique in 1989. The process of solid phase grafting is unique in the fact that the polymer remains as a powder during the reaction. Not only does this process incorporate low equipment cost coupled with low operating temperatures but it is also environmentally safe. Since this process uses no or minimal solvent it is referred to as an "interfacial agent" and does not require recovery. Additionally, the reaction times are relatively short and levels of grafting are at least comparable to most of the other processes explained previously [Lee and Rengarajan, 1992].

SOLID PHASE GRAFT COPOLYMERIZATION

In 1975, Fujii used the solid phase grafting technique to graft maleic anhydride onto powdered polyolefins. The reaction was conducted using benzoyl peroxide as the free radical initiator with small amounts of acetone as the solvent at 150 °C [Fujii, 1975]. Two research groups investigating independently of each

other reported the use of this process again in 1986. Nemecek et al. mixed benzoyl peroxide, chloroform, and acrylic acid monomer at 100 °C to powder polypropylene to get a polypropylene-acrylic acid graft copolymer [Nemecek, 1986]. In that same year, Fumio et al. reported a feasibility study of grafting maleic anhydride monomer onto polypropylene [Fumio, 1986]. This graft of polypropylene-maleic anhydride was confirmed possible in 1989 by Lee and co-workers and 10 % graft levels were achieved with their patented process [Rengarajan et al., 1989; Lee and Rengarajan, 1992]. Graft copolymers of polycarbonate-methyl methacrylate (PC-g-MMA) [Sobocinski, 1991], poly(vinyl chloride)-vinyl acetate (PVC-g-VAc) [Zhang, 1992], polystyrene-acrylic acid (PS-g-AAc) [Subramanian, 1995], polystyrene-butyl acrylate (PS-g-ButAcryl) [Shah, 1997], and polystyrene-maleic acid (PS-g-MA) [Subramanian, 1998] have since been successfully produced by solid phase grafting by Lee and coworkers. Pan and coworkers have also used the solid phase grafting process to graft glycidyl methacrylate onto polypropylene (PP-g-GMA) [Pan et al., 1997]. They found that for PP-g-GMA the ultimate grafting level achieved was higher than that obtained by other processes. Sulfonation of nylon 6 and AMODEL® has also been successfully accomplished using the same process concept [Bashir, 1994].

This technique utilizes the principle of free radical polymerization to create a free radical site on the polymer backbone allowing the graft monomer to chemically bond to that polymer. The free radical initiators used to produce the free radical sites on the polymer backbone are usually organic peroxides or azo compounds. The polymer remains in the solid form throughout the entire reaction. This is achieved by keeping the operating temperatures below or around the glass transition temperature. The polymer is ground into a fine particle size to provide uniform mixing of the monomer/polymer in the reactor and to provide larger surface area for chemical reaction to occur [Subramanian, 1998].

Although the graft levels achieved by solid phase grafting may not be the highest, it is becoming advantageous to use this process over other grafting techniques. Features such as little or no solvent use resulting in minimal or no recovery, low pressure and temperatures, short reaction times, and ease of equipment modification along with adaptability to different polymer-monomer systems are making this process very lucrative for industrial use [Rengarajan, 1993]. The remaining part of this review will focus on analyzing mechanistic issues, minimization/control of homopolymerization, rate-controlling step, maximum graft levels achieved, optimal operating conditions, and graft copolymer purification techniques for analysis purposes.

SOLID PHASE GRAFT PROCESS EQUIPMENT

The process of solid phase grafting is relatively simple in design. It does not require solvents, vapor, or radiation. The main apparatus for experimental investigation consists of a cylindrical vessel with specially designed mixing blades and a 1.5-hp driving motor. A schematic diagram of this reactor appears in Fig. 1. The reactor vessel consists of an 800-ml stainless steel batch reactor and sits horizontally on the reactor shaft. The mix-

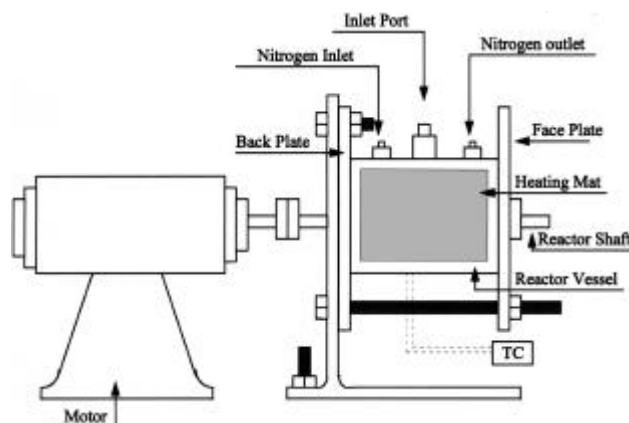


Fig. 1. Solid phase graft copolymerization reactor system [Subramanian, 1995].

ing blades are specially designed at specific angles to facilitate uniform mixing of the reactants. Ports for addition of polymer are located at the top of the reactor vessel. A separator funnel is used for initiator addition while a syringe is used to inject the monomer into the reactor system. Initiator and monomer injection systems may differ depending on the phases of initiator and monomer at the operating temperature. In order to maintain constant temperature the reactor is electrically heated by silicon heating tapes wrapped around the vessel. Accurate control of the temperature is accomplished through an Omega proportional-integral-differential (PID) solid-state relay [Subramanian, 1995]. A larger batch of graft copolymer can be conveniently made using an oil-heated reactor/equipped with shear mixing. Such as a Processal reactor or a Brabender type reactor.

ANALYTICAL ASPECTS OF SOLID PHASE GRAFTING PROCESS

To analyze the graft levels achieved after the reaction process the product needs to be purified of all impurities. The product not only contains the graft copolymer but also unreacted monomer, initiator, products due to the decomposition of the initiator, and the homopolymer of the monomer. Soxhlet extraction is used to remove these impurities from the graft copolymer. This technique uses a solvent extraction to dissolve the unwanted products leaving only the graft copolymer. The extracted polymer is then vacuum dried for 12 to 24 hours at 80 °C. Often the monomer might dissolve into the polymer matrix making it necessary to reflux the polymer in an appropriate solvent and then precipitate the polymer out by the addition of a non-solvent. This procedure is necessary due to the fact that during the reaction, the polymer is heated to its glass transition temperature (T_g) or its softening point. Above this softening point, the thermoplastic polymer changes from being a glass at low temperatures to a rubbery or flexible plastic above the T_g . The glass transition temperature is a measure of the ease of torsion of the backbone bonds rather than of the ease of separation of the molecules. As the polymer cools down, the mobility of the chain decreases and the monomer is thus trapped

inside the polymer matrix. The dissolved monomer interferes in the accurate determination of the graft content and hence needs to be removed. The polymer is then again vacuum dried. The extracted solution from the reflux step was analyzed by GC/MS to identify water-soluble species remaining in the polymer after the grafting reaction. The polymer was washed in a reflux vessel with solvent and the extracted solution was filtered and injected into the GC/MS. During the extraction/purification process, copolymers such as maleic anhydride may go through further chemical reactions resulting in ring-opening products of dicarboxylic functional groups. To preserve the original functional groups on the polymeric backbone, care must be exercised.

Once the polymer is purified several analytical methods can be run to test for graft level in the polymer. FTIR spectroscopy is used to identify the presence of the graft material on the polymer backbone. This is done by comparing the non-graft homopolymer spectra with the graft copolymer spectra. By comparing characteristic peaks of the monomer and homopolymer in the graft copolymer spectra grafting can be identified. Quantitative analysis of the graft can be achieved by FTIR by utilizing the IR absorbance technique [Bartick et al., 1982]. In this technique, the two homopolymers are mixed at different ratios to establish a calibration curve. The IR absorbance ratios are then compared to the mixture ratios and a calibration curve is created for the binary polymeric mixture, whose results are analogously used for the graft copolymer system.

The graft content can also be quantified by using a wet chemical method such as titration. Subramanian [Subramanian, 1995] using this method determined the amount of graft in the PS-g-AAc copolymer. He dissolved 1 g of the graft polymer in 100-ml of toluene then titrated with a 0.01 N solution of NaOH in methanol with phenolphthalein as the end-point indicator. The equations used to determine the acid content in the graft copolymer and then the percent graft are given by [Subramanian, 1995].

$$\text{Acid Number (AN)} = \frac{\text{ml NaOH} \times \text{Normality of NaOH Solution} \times \text{Molecular Weight of NaOH}}{\text{Grams of Polymer}}$$

$$\% \text{ Grafting} = \frac{\text{AN} \times \text{Molecular Weight of Acrylic Acid}}{\text{Molecular Weight of NaOH} \times 10}$$

Another method that can be used to determine if grafting has taken place is to use solid and liquid state NMR. In previous work by Rengarajan et al. [Rengarajan et al., 1990], maleic anhydride graft to the backbone of polypropylene was examined. Their results showed that solid state NMR showed a peak at 175-ppm indicating maleic anhydride on the polymer backbone. This peak was not observed in the homopolymer spectra. When liquid state NMR was used, the peak of maleic anhydride could not be detected. This is due to the dipolar broadening of resonances near branch points that have restricted mobility. This did not occur in the solid-state method because the dipolar broadening is removed by high power ^1H decoupling [Rengarajan et al., 1990].

After the polymer has been extracted and dried the material

was analyzed using a Differential Scanning Calorimeter (DSC) and Thermogravimetric Analyzer (TGA). The DSC measures the energy necessary to establish zero temperature difference between a substance and a reference material against either time or temperature. This was done to quantify the change in melting point and glass transition temperature. TGA was performed to determine the onset of decomposition and to measure the volatile content in the polymer.

The glass transition temperature is defined as the peak point of the first derivative curve of the heat flow. Typically, the two homopolymers that are constituent polymers of the graft copolymers are immiscible to each other. If these immiscible polymers were physically blended then two separate T_g 's would be identified. This is not the case for a graft copolymer. For example, when polystyrene (T_g of 94 °C) and acrylic acid (T_g of 106 °C) are blended, the DSC indicated two separate glass transition temperatures for the blend. Fig. 2 shows a unique T_g , which is not a characteristic of a blend, for the graft copolymer PS-g-AAc. All the graft levels showed a T_g between the T_g 's of polystyrene and acrylic acid, indicating that acrylic acid polymer chains are chemically bonded to the polystyrene backbone [Subramanian, 1995].

VARIABLE EFFECTS OF SOLID PHASE GRAFT COPOLYMERS

For each graft copolymer synthesized by solid phase grafting the optimal conditions vary depending on the type of polymer and monomer used. After choosing the graft materials, the operating conditions such as, amount of initiator, choice of interfacial agent, amount of catalyst, reaction temperature, reaction time, and amount of polymer charged into the reactor need to be determined in order to achieve maximum graft levels as well as to minimize any waste. Variations in these variables can cause drastic changes in graft levels. Since many graft copolymers have been synthesized by this process polypropylene-g-maleic anhydride and polystyrene-g-acrylic acid will be examined to explain how the changing of parameters affects the weight percent of the graft.

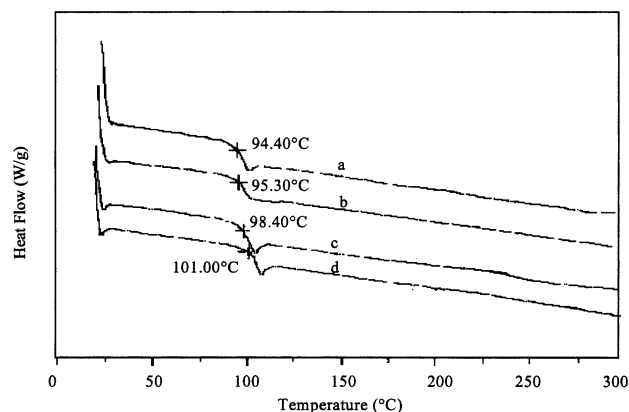


Fig. 2. DSC thermograms of (a) homopolymer PS, (b) PS-g-AAc (1 wt% grafting), (c) PS-g-AAc (2.31 wt% grafting), and (d) PS-g-AAc (3.48 wt% grafting) at 10 °C/min [Subramanian, 1995].

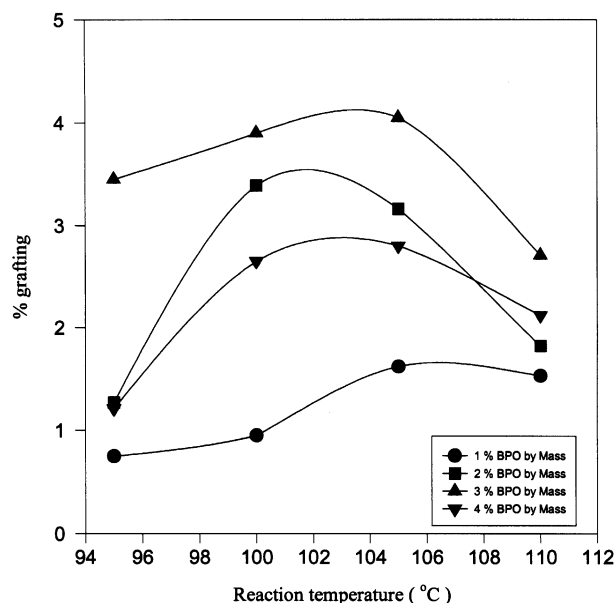


Fig. 3. Effect of temperature on the percent grafting. Reaction time=20 min ; monomer concentration= 7.37×10^{-4} mol/g PS ; monomer to solvent ratio=0.265 mol AAc/mol H₂O [Subramanian and Lee, 1998].

1. Effect of Reaction Temperature

The reaction temperature of solid phase grafting depends largely on the choice of polymer. For the case of polystyrene-g-acrylic acid the temperature range that gave the maximum graft level was determined to be 104-106°C. Fig. 3 shows the weight percent grafted versus four different reaction temperatures. In this figure, four different amounts of initiator were used to obtain four sets of data points for each temperature. In each case, the weight percent of grafting shows a maximum between 104 and 106°C. Operating above the glass transition temperature of polystyrene (95°C) provides better diffusion of the monomer into the polymer matrix allowing for higher graft levels. At temperatures above 106°C the half-life of the initiator exponentially decreases resulting in the number of free radicals available for polymerization to be high at the onset of the reaction. If the free radical initiation reaction is too fast, both depolymerization and cross-linking reactions are strongly favored. This behavior of temperature effect on initiator half-life can be examined with BPO. The half-life of BPO at 105°C is about 10 minutes. At lower temperatures BPO does not decompose to the same extent, resulting in reduced availability of radicals providing lower graft levels. At temperatures higher than 105°C, the half-life of BPO decreases to 4 minutes causing the BPO to reduce to a negligible amount in the first 8 to 10 minutes of the reaction also resulting in lower graft percentage. Another cause could be attributed to the monomer (acrylic acid) at elevated temperature has a strong tendency to homopolymerize resulting in lower graft levels [Subramanian, 1995].

When maleic anhydride was grafted onto polypropylene similar results were reported. Operating at 100°C did not provide as high of a graft percent as that of operating at 120°C. In the work by Rengarajan the graft level doubled from 4% graft at 100°C to 8% graft at 120°C. To attain the highest graft lev-

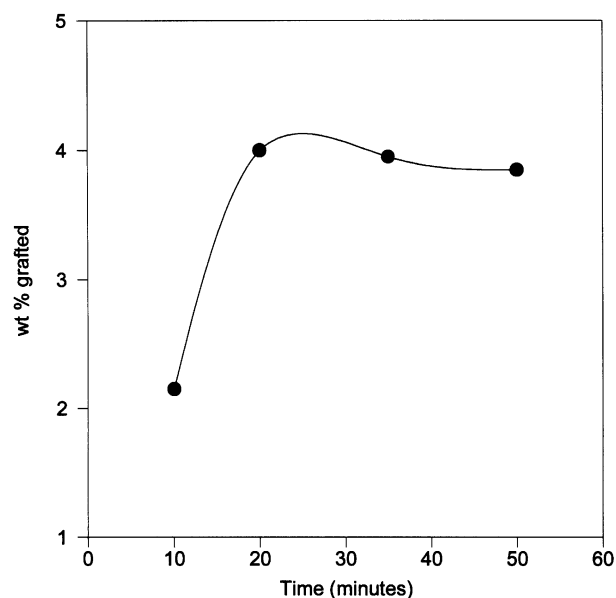


Fig. 4. Effect of reaction time on wt% grafted : initiator conc. 3 g/100 g polymer ; conc. of monomer soln. 50% w/w aq acrylic acid ; amount of monomer 5.25 g/100 g polymer ; reaction temperature 105°C [Subramanian, 1995].

els desired temperature for the solid phase process would be to operate above the softening point or T_g of the polymer. This allows the free radicals to be formed at the surface and within the polymer matrix providing greater surface area for higher graft levels to be achieved [Rengarajan, 1993].

The time of reaction needs to be determined in order to achieve the maximum productivity out of the initiator at the reactor operating temperature. The effect that time has on the graft level is shown in Fig. 4. As the reaction time is allowed to continue the active sites on the polymer backbone are being exhausted. After 20 minutes, only small amounts of initiator remain, due to its half-life, to initiate grafting. This lack of reactants results in no further increase in grafting but instead leads to homopolymerization of the monomer [Subramanian, 1995]. If the initiator and the monomer are fed into the reactor continuously at controlled feed rates, the optimal reaction time will be also different.

2. Effect of Initiator and Catalyst

The initiator is one of the most important factors to the solid phase grafting process. It can be used to initiate both the grafting of the monomer onto the polymer backbone and the homopolymerization of the monomer. Along with the initiator the presence of catalyst may play an important role in enhancing the graft level [Lee and Rengarajan, 1992]. The effect of adding catalyst to the process can be seen in Figs. 5 and 6 [Rengarajan, 1993; Rengarajan et al., 1990]. In both figures the degree of graft increased with initiator concentration regardless of amount of catalyst. However, the highest level of maleic anhydride graft was achieved when the catalyst concentration was the greatest. This increase in graft from addition of catalyst could be attributed to the decreasing molecular weight of the side chains caused by free radical initiator and the decreased tendency of maleic anhydride towards homopolymerization.

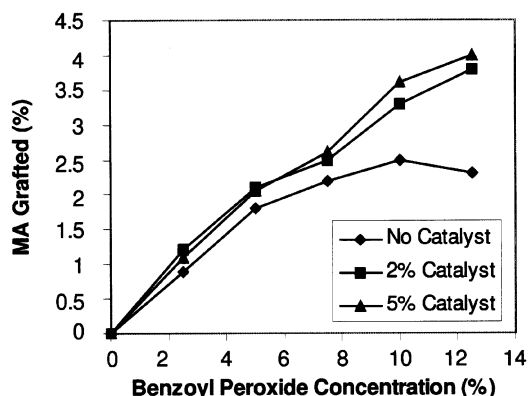


Fig. 5. Effect of temperature and catalyst concentration (100 °C) [Rengarajan, 1993].

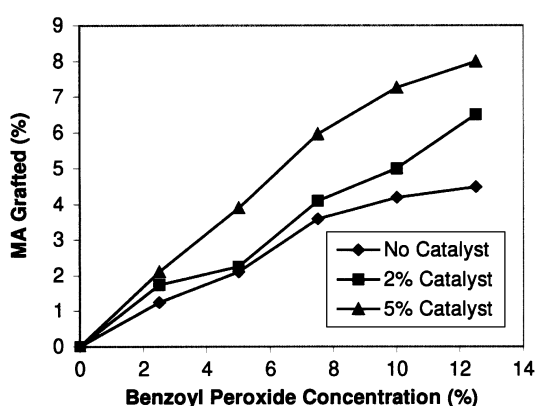


Fig. 6. Effect of temperature and catalyst concentration (120 °C) [Rengarajan, 1993].

It was found that the addition of a catalyst increased the stability of the free radicals and thereby increasing the graft level. The role of catalyst, if properly utilized, is to enhance the graft reaction (monomer attachment reaction) while suppressing the homopolymerization reaction.

The effect of the initiator as explained depends on the catalyst, time, and the temperature of the reaction. At higher temperatures the half-life of the initiator decreases providing less time for the free radicals to interact between the polymer matrix and monomer. In an article by Subramanian and Lee [Subramanian and Lee, 1998] of grafting acrylic acid onto polystyrene, the effect of BPO was studied in the range of 4.13×10^{-5} – 1.65×10^{-4} mol/g polystyrene at four different temperatures. The results can be seen in Fig. 7. The percent grafting increased with increase in concentration of initiator at every temperature. This phenomenon was explained by the fact that the amount of free radicals generated increases on increasing the concentration of BPO, resulting in an increase in graft level. However, at higher concentrations of initiator the graft level begins to decrease because the acrylic acid monomer is apt to homopolymerize instead of grafting onto the polymer backbone [Subramanian and Lee, 1998].

3. Effect of Interfacial Agent

The solid phase graft copolymerization process seeks to eliminate or minimize the use of solvents in graft copolymerization reactions. However, another way to soften the polymer sur-

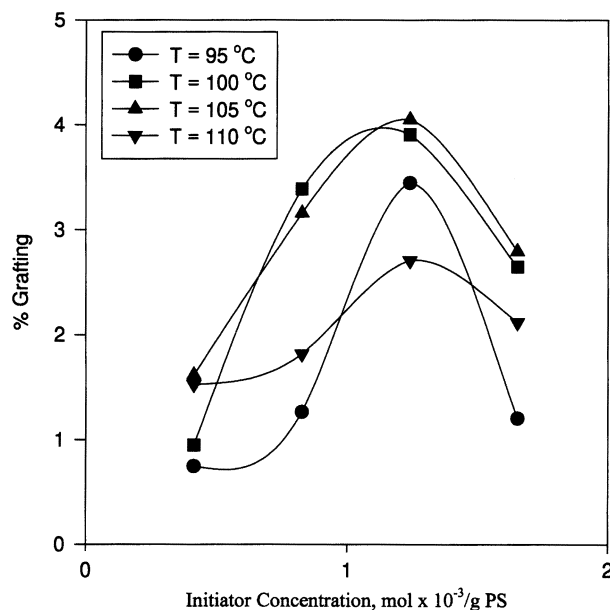


Fig. 7. Effect of initiator concentration on the percent grafting. Reaction time=20 min ; Monomer concentration= 7.37×10^{-4} mol/g PS ; Monomer to solvent ratio=0.265 mol AAc/mol H₂O [Subramanian and Lee, 1998].

face other than temperature is to add an interfacial agent. Use of interfacial agents also helps in the smooth processing of highly viscous reaction mixtures at the reaction temperature. Three effects need to be examined for the interfacial agent. The type of interfacial agent, the amount of interfacial agent added to the reactive system, and the monomer to solvent concentration ratio need to be determined to achieve maximum graft levels.

Lee et al. [Lee et al., 1990] analyzed the effect of using three different interfacial agents for polypropylene-g-maleic anhydride and the graft levels that were achieved. In the study, toluene, decalin, and tetralin were used and the results on the graft levels achieved are given in Fig. 8. It is evident from this figure that the interfacial agent that provided the highest level of graft was toluene. On the other hand the interfacial agent that provided the lowest level of graft was tetralin. For solid phase grafting the correct interfacial agent to facilitate in the graft-

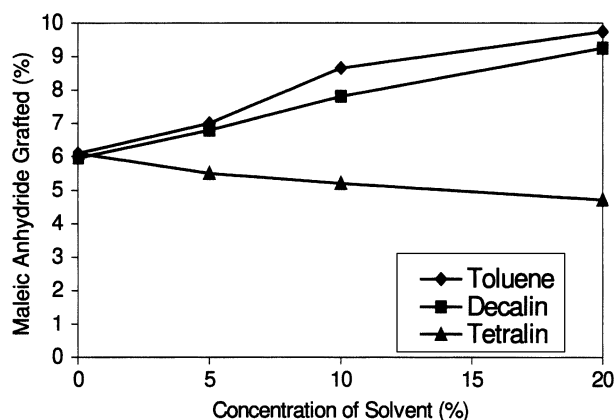


Fig. 8. Effect of solvent concentration on the graft level at 120 °C with 5 % catalyst [Lee et al., 1990].

ing process is crucial. This can be seen in the comparison of toluene and tetralin for PP-g-MA. As the concentration of solvent is increased the graft level for toluene increases from 6 % graft at 0 % solvent concentration to 9.2 % graft at 20 % solvent concentration. The opposite is true for tetralin. As the solvent concentration is increased the percent graft decreases from 6 % to 4.7 %. This can be attributed to several factors. The dissolution rather than swelling of the polymer by the solvent resulted in lower surface area or the formation of a monomolecular layer of the solvent on the surface of the polymer inhibited the reaction. 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, but this was not examined in the study.

The amount of interfacial agent used to soften the polymer surface largely depends on the polymer and the quantity of graft copolymer being produced. From a study by Rengarajan et al. [Rengarajan et al., 1989], the amount of initiator added to the reaction system was studied. It was found that the addition of solvent to the system resulted in increased graft percentage yields. When the solvent concentration of toluene was 20 %, the graft level achieved was 9.6 % this is 102 % higher than that when no interfacial agent was used, as seen in Fig. 9. Although a small amount of solvent is added to the system, this process is still environmentally friendly, where the solvent does not need to be recovered like traditional grafting processes [Rengarajan et al., 1989]. It is to be noted that the solid phase grafting process can be very successfully operated without interfacial agent and/or without catalyst. Lee and coworkers have synthesized a variety of graft copolymers using this process without interfacial agent and catalyst.

The final effect that needs to be examined for interfacial agents is that of the monomer to solvent concentration. This is the ratio of monomer in a solution that is added to the polymer. Examining PS-g-AAc results given by Subramanian and Lee [Subramanian and Lee, 1998] the effect of adding monomer and the effect of monomer to solvent ratio can be examined. For each graft copolymer there is an optimal amount of monomer needed to reach the highest graft level. Once this level is reached continuing to add monomer will result in a decrease in the final graft percent. This is due to the excess presence of monomer in the reaction system causing homopoly-

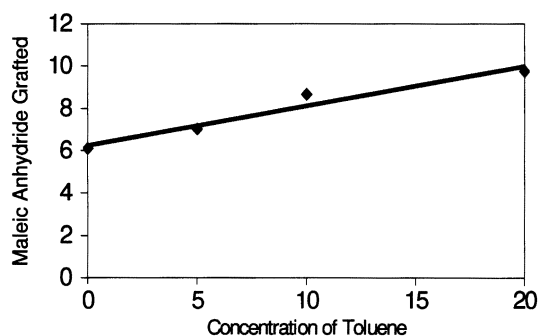


Fig. 9. Effect of solvent concentration (concentration of toluene) on graft level (120 °C, 5 % catalyst) [Rengarajan et al., 1989].

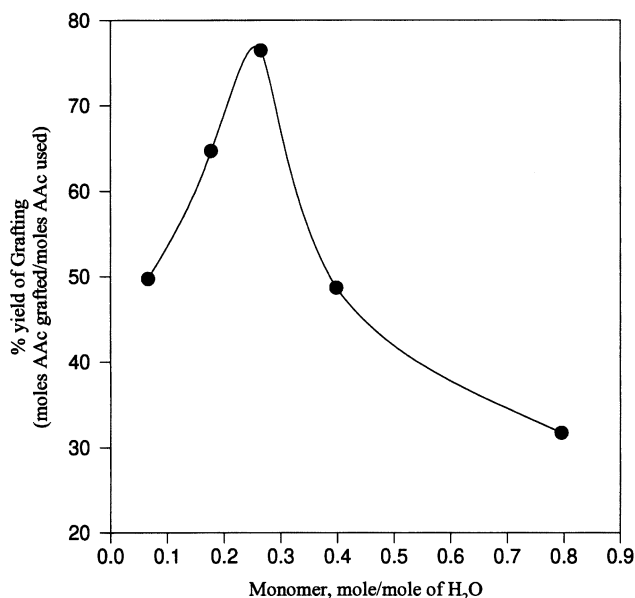
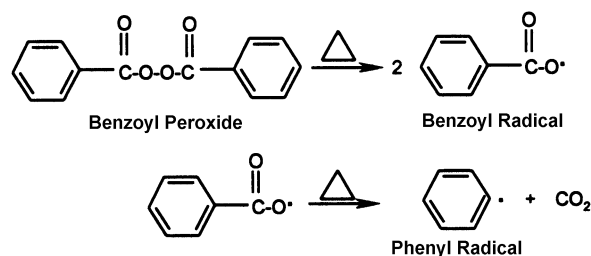


Fig. 10. Effect of the ratio AAC/H₂O on grafting. Reaction time= 20 min ; temperature=105 °C ; initiator concentration= 1.24×10^{-4} mol/g PS [Subramanian and Lee, 1998].

erization to be favored. Once the optimal amount of monomer has been determined the amount of interfacial agent can be determined. Fig. 10 shows the effect of the monomer-to-solvent ratio on the percentage yield of grafting. This ratio is defined as the amount of monomer grafted to the polymer backbone to the amount of monomer used in the reaction. From this figure it can be seen that the maximum graft yield was achieved at 0.265 mole AAC/mole H₂O. As the amount of monomer solution increased, the amount of monomer in the reaction increased, resulting in higher graft levels. However, at very high concentrations of monomer solution, an excess of monomer is present competing for the free radicals on the polymer backbone. This leads to homopolymerization of the monomer resulting in lower graft levels [Subramanian and Lee, 1998].

PROPOSED REACTION MECHANISM

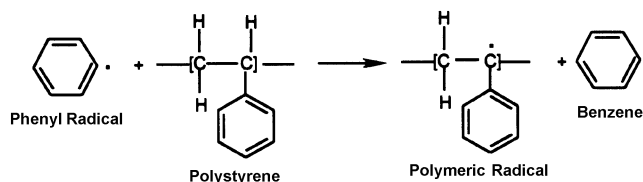
The reaction mechanism for graft copolymerization has been proposed for several of the various techniques used. Typically, organic peroxide initiators are used to generate free radicals on the polymer backbone, due to their unstable nature at moderate temperatures. The free radical is formed by the decomposition of the initiator as given.



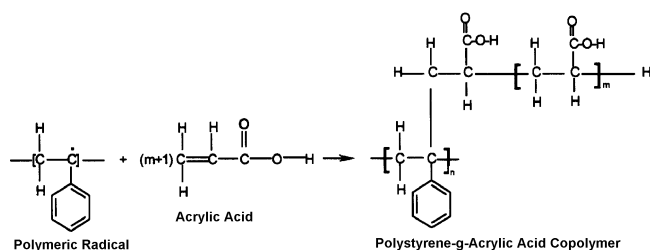
Once the free radical is formed it can initiate the polymerization by directly attacking the polymer backbone or by initi-

ating the homopolymerization of the monomer. The homopolymerization produces a grafting site on the backbone polymer by chain transfer or terminates the reaction yielding homopolymer of the monomer. This reaction can be shown as follows for the initiation, propagation, and termination of acrylic acid when graft to polystyrene [Subramanian, 1995].

Initiation of Reaction :



Propagation and Termination of Reaction :



Minoura proposed the chain scission free radical mechanism for the production of polypropylene-g-maleic anhydride shown in Fig. 11 [Rengarajan, 1993]. This work was later confirmed by experimental work by Rengarajan et al. [Rengarajan et al., 1990]. The resultant products were determined by solid-state ^{13}C -NMR studies. This proposed mechanism of chain scission is shown in Fig. 12.

SOLID PHASE GRAFTING PROCESS SCALE-UP

The scale-up of the solid phase graft copolymerization process is in an exploratory stage. One set of experiments that

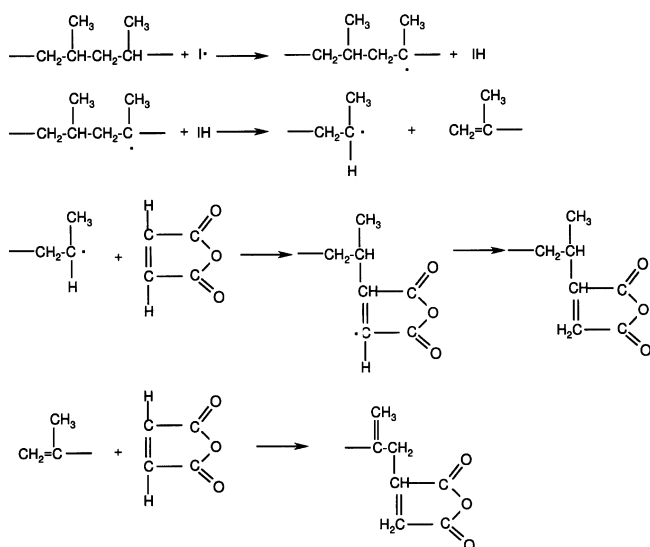
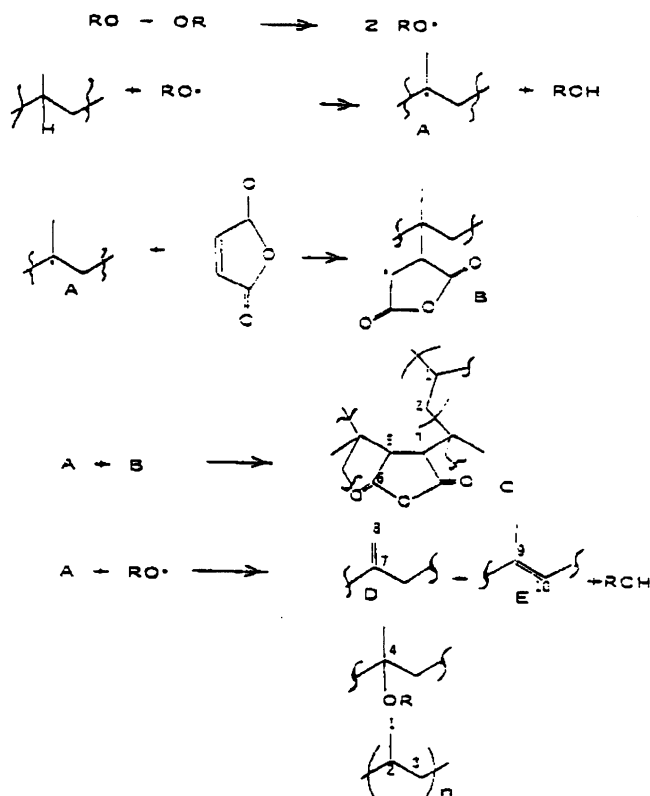


Fig. 11. Mechanism of chain scission as proposed by Minoura for polypropylene-g-maleic anhydride [Rengarajan, 1993].



Resonance Assignments

Structure	ppm Observed
1	16
2	35
3	53
4	70
5	not resolved
6	175
7, 8, 9, 10	130

Fig. 12. Proposed mechanism for grafting of polypropylene with maleic anhydride. Confirmed by solid state NMR resonance [Rengarajan et al., 1990].

have been conducted in this area was on the graft copolymer PS-g-AAc. The experimentation was conducted in a 2-liter reactor built by Processal, Inc. The Processal reactor system is similar to the 800-ml reactor explained earlier. It is a jacketed vessel that is heated with Dowtherm fluid. The optimal conditions that were determined for 100-grams of polymer were scaled up to 1000-grams of polymer. These conditions are given in Table 1.

The graft results achieved from this study are shown in Table 2 [Subramanian, 1998]. It can be seen that this process can achieve similar levels of grafting at 100-grams or 1000-grams

Table 1. Optimal experimental conditions for PS-g-AAc [Subramanian, 1998]

Temperature :	105 C
Reaction time :	20 minutes
Initiator (BPO) :	3 g per 100 g of polymer
Monomer (AAc) :	5 g per 100 g of polymer
Solvent (Water) :	5 g per 100 g of polymer

Table 2. Experimental conditions for Ps-g-AAc scale-up [Subramanian, 1998]

Run number	Amt. of polymer (grams)	Temp. (C)	Amt. of initiator (grams)	Amt. of monomer (grams)	Amt. of solvent (grams)	Graft level by FTIR %	Graft level by titration %
1	100	105	3	5.20	5	4.05	3.90
2	200	105	6	10.40	10	4.75	4.58
3	300	105	9	15.60	15	2.90	2.70
4	500	105	15	26.00	25	2.65	2.50
5	1000	105	30	52.00	50	3.50	3.38

of polymer. The reason for the decrease in grafting when 500 grams of polymer was run is due to very small amount of polymer used in a large volume reactor. This inhibits proper mixing of the initiator, polymer, and monomer. As the amount of polymer increased to 1000 grams, better mixing of the reaction constituents occurred leading to higher graft levels.

CONCLUSIONS

The novel process of solid phase grafting was analyzed for its application to produce graft copolymers for use as compatibilizers and property-enhanced polymeric materials. Various studies have proven that the technique of solid phase grafting can be used to synthesize graft copolymers. This process has been successfully applied to a variety of base polymers, producing PP-g-MA, PS-g-MA, PS-g-AAc, PP-g-AAc, PVC-g-PS, PP-g-PS, PC-g-PMMA, PVC-g-Lactic Acid, PVC-g-VAc, HDPE-g-MA, LDPE-g-MA, PET-g-AA, PS-g-Butyl Acrylate, etc.

The graft copolymer was characterized by several methods such as titration, FTIR, DSC, TGA, GC/MS, and N.M.R. In each case the results were positive in indicating the presence of the monomer functional group on the polymer backbone indicating grafting had occurred. The DSC provided interesting results indicating how the T_g of the copolymer had changed in comparison to both polymers used in the blend. The single glass transition temperature indicated that the copolymer was definitely not a blend of the two polymers but was indeed a copolymer. The characteristic bonds of the graft copolymer were positively identified and confirmed by the NMR spectroscopy.

The effects of the process variables such as temperature, initiator, interfacial agent, catalyst, and reaction time were analyzed and examined. The increase in catalyst resulted in an increase in graft level where the continued increase in initiator and interfacial agent did not produce higher graft levels. It was found that there was an optimal condition and further increases in these variables resulted in a decrease in graft levels. This was attributed to the monomer homopolymerizing instead of chemically attaching to the backbone of the base polymer. The optimal time and temperature were also determined for the two examples used in this study, PS-g-AAc and PP-g-MA. It was found that the optimal temperature is slightly above the softening point of the matrix polymer while the optimal time largely depends on the half-life of the initiator. The highest level of grafting achieved for PS-g-AAc was 4 wt %, while 9.6 wt % was achieved in the PP-g-MA. These graft levels are at least comparable or superior to many of the other processes listed. This process becomes favorable due to lower operating temperatures

resulting in less energy consumption, little or no solvent is used providing a process that is environmentally friendly, and inexpensive process modification.

From this study, the solid phase graft copolymerization process can be seen as an inexpensive and environmentally friendly way to graft polymers for a wide variety of industrial applications for value-added polymeric materials. The successful scale-up of the solid phase technique proved that this process is efficient and marketable.

REFERENCES

- Bartick, E., Corbett, J. and McClure, G., "Computerized Quantitative Analysis of Copolymer by IR Spectroscopy," *ACS Symp. Ser.*, **197**, 185 (1982).
- Bashir, S., "Production of Sulfonated Ionomers by Solid Phase Process," Ph.D. Dissertation, The University of Akron (1994).
- Datta, S. and Lohse, D., "Polymeric Compatibilizers," Hanser, New York (1996).
- Fujii, M., Japanese Patent JP 50/77493, 1975.
- Fumio et al., Japanese Patent JP 55/23134, 1986.
- Lee, S. and Rengarajan, R., U.S. Patent 5 079 302, 1992.
- Lee, S., Rengarajan, R. and Parameswaran, V., "Solid Phase Graft Copolymerization: Effect of Interfacial Agent," *Journal of Applied Polymer Science*, **41**, 1891 (1990).
- Nemecek et al., Czechoslovakian Patent CS 227840 B, 1986.
- Pan, Y., Ruan, J. and Zhou, D., "Solid-Phase Grafting of Glycidyl Methacrylate onto Polypropylene," *Journal of Applied Polymer Science*, **65**, 1905 (1997).
- Rengarajan, R., "Development of a Process for the Solid-Phase Graft Copolymerization of Polypropylene-Maleic Anhydride," Ph.D. Dissertation, The University of Akron (1993).
- Rengarajan, R., Parameswaran, V. and Lee, S., "N.m.r. Analysis of Polypropylene-Maleic Anhydride Copolymer," *Polymer*, **31**(9), 1703 (1990).
- Rengarajan, R., Vicic, M. and Lee, S., "Solid Phase Graft Copolymerization: 1. Effect of Initiator and Catalyst," *Journal of Applied Polymer Science*, **39**(8), 1783 (1990).
- Rengarajan, R., Vicic, M. and Lee, S., "Solid Phase Graft Copolymerization: 2. Effect of Toluene," *Polymer*, **30**(5) 933 (1989).
- Shah, S., "Solid Phase Graft Copolymerization of Butyl Acrylate onto Polystyrene," M.S. Thesis, The University of Akron (1997).
- Sobocinski, R., "Polycarbonate-g-Poly(methyl methacrylate) by Solid Phase Graft Copolymerization," M.S. Thesis, The University of Akron (1991).
- Subramanian, S., "Solid Phase Graft Copolymerization of Acrylic Monomers onto Thermoplastics and Their Use as Blend Com-

- patibilizers," Ph.D. Dissertation, The University of Akron (1998).
- Subramanian, S., "Solid Phase Graft Copolymerization of Acrylic Acid onto Polystyrene," M.S. Thesis, The University of Akron (1995).
- Subramanian, S. and Lee, S., "Graft Copolymerization of Acrylic Acid onto Polystyrene Using the Solid Phase Grafting Technique," *Journal of Applied Polymer Science*, **70**(5), 1001 (1998).
- Trevedi, A., "Modification of Various Thermoplastic Polymers Through Graft Copolymerization Using Supercritical Carbon Dioxide as a Solvent : Synthesis and Characterization," Ph.D. Dissertation, The University of Akron (1997).
- Zhang, W., "Graft Copolymerization of Poly(vinyl chloride)-Vinyl Acetate in Solid Phase," M.S. Thesis, The University of Akron (1992).