

Preparation of Grafted Copolymers via Oxidized Polypropylene

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ABSTRACT: A new and novel class of oxidized polypropylene containing bound peroxide functionalities can be used as polymerization initiators to produce polypropylene-grafted copolymers. Upon heat treatment, the peroxide functionalities in the oxidized polypropylene act as a source of free radicals, reacting with the unsaturated double bonds of the monomer and initiating polymerization. The grafting reaction is carried out in the solid state in a reactor. The advantage of grafting via this new class of oxidized polypropylene is the elimination of expensive and environmentally unfriendly organic peroxides. A number of monomers have been grafted using oxidized polypro-

pylene, including vinyl acetate, vinyl pyrrolidinone, methacrylic anhydride, and maleic anhydride. Oxidized polypropylene-grafted copolymers are effective compatibilizers for PP/ETP blends and good coupling agents in glass-reinforced formulations. Preparation, characterization, and mechanical properties of terpolymers prepared from sequential grafting of oxidized polypropylene are also discussed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3018–3028, 2007

Key words: oxidized polyolefins; initiators; graft copolymers; peroxides; irradiation

INTRODUCTION

Graft copolymers of polypropylene have been of growing interest because they have the combined properties of the grafted polymer and the polyolefin backbone. When compared to physical blends of polymers, graft copolymers, owing to the intersegment chemical bonds therein, exhibit a finer heterophasic morphology, in which the domain size of the dispersed phase is stable and may be smaller by about an order of magnitude.¹ It is reported that these graft copolymers can be used as compatibilizers for normally immiscible polymer systems. Physical blends of immiscible polymers, e.g., polypropylene and polystyrene, often require the inclusion of a compatibilizer, which can alleviate to some degree the problems associated with the high interfacial tension and poor adhesion between the immiscible polymers in the blend.² The benefits of grafted copolymers to improve polymer–polymer interaction and morphology of a PP-g-PMMA and PC blend were reported by Phan and Shu.³ Phan et al. in 2002 demonstrated the use of a compatible PP-g-PMMA/nylon blend in a coextruded, multiplayer tubing application.⁴ Im-

provements in compatibility and interfacial adhesion were also reported in 2001 by DeNicola and Phan in a grafted PP and polyamide-6 blend.⁵

Grafted copolymers are also used to enhance interaction and interfacial adhesion of polymer–filler systems. Mai in 2001 showed that acrylic grafts increased limited oxygen index as well as improved dispersion of aluminum trihydroxide in a polyolefin-filled system.⁶ A similar observation was also reported by Young for maleated grafted polymers with antimony oxide or aluminum trihydrates.⁷

The preparation of graft copolymers by creating active sites on the polymer backbone, and initiating graft polymerization of a polymerizable monomer at these sites, is well-known. Procedures that have been used for introducing such active sites include treatment of the polymer backbone with an organic compound that is capable of generating radicals. Peroxides or azo compounds are commonly used as the source of radicals. Upon decomposition, peroxides or azo compounds generate free radicals. These radicals form active grafting sites on the polymer and then initiate polymerization of monomer. Radiation can be used in place of peroxides or azo compounds as a source of generating active grafting sites on the backbone. In the grafting process, utilization of the bulk technique in which the polymer particles are contacted directly with initiator and monomer without the use of a liquid suspending medium or a solvent is advantageous due to simplicity of execution

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and the avoidance of side-reactions caused by the presence of solvents or suspending media, such as water.⁸

Grafted copolymers were produced via a living free radical polymerization mechanism.⁹ First, a complex copolymer, poly[propylene-*co*-1-(4-but-1-enylphenyl)-1-(2'', 2'', 6'', 6''-tetramethylpiperidinoxy)ethane], was prepared. The polymer was then heated in the presence of styrene, butadiene, and *t*-butyl acrylate to produce the mono- and di-block graft copolymers.

Creating grafting copolymers using functionalized polyolefins was also reported by Han and Chung.¹⁰ They showed that grafted copolymers could be prepared by creating free radicals from postpolymerized borane-containing polyolefins. Under oxidative conditions, the borane group acted as a source of free radicals to initiate polymerization of methyl methacrylate and acrylic acid.

In this article, we report a new class of oxidized polypropylene, which contains bound peroxide functionalities capable of generating radical active sites on the polyolefin backbone. Therefore, grafting can take place without the need for the synthesis of a borane complex or a nitroxide intermediate. Nor does it need the treatment of a polyolefin backbone with an expensive and hazardous organic peroxide or azo compound. In this article, we also demonstrate that the oxidized polypropylene-grafted copolymer can be an effective compatibilizer for PP/ETP blends and a good coupling agent in a glass-reinforced formulation.

EXPERIMENTAL

Materials

Two grades of homopolymer polypropylene (PP) available from Basell Polyolefins were used in this study: PP 1 (fractional MFR) and PP 2 (12 MFR). Fiber glass coated with silane sizing, PPG3973, was obtained from PPG Industries. All monomers (methyl methacrylate, vinyl acetate, vinyl pyrrolidinone, styrene, methacrylic acid anhydride, and maleic anhydride) were commercially available products obtained from Aldrich. PA-6 (nylon-6) used in the study was Capron 8202NL from Honeywell. Prior to blending, the PA-6 was dried in a desiccant drying oven at 120°C for 2–3 h.

Oxidized polypropylene was prepared by Basell Polyolefins via the radiation method.^{11,12} Unless specified, oxidized polypropylene-initiated polymerization was carried out in a jacketed autoclave equipped with an air-driven agitator. The sequentially and randomly grafted polypropylene with butyl acrylate (or methyl methacrylate) and styrene were prepared via oxidized polypropylene. Peroxide concentration in the oxidized polypropylene was

measured via a titration method.¹³ For the organic peroxide-grafted reaction, Lupersol 11 (available from Atochem) was used as an initiator, and the polymerization was carried out at 110°C.

Characterization

IR mapping

Sphere thin sections (15 μm) of the oxidized polypropylene-grafted copolymers were obtained by Ultramicrotomy using a diamond knife. The Fourier transformed infrared (FTIR) scans were performed on a Nexus 470 FTIR from Nicolet.

Differential scanning calorimetry

The DSC experiments were carried out on a DSC 7 from Perkin–Elmer at a scan rate of 2°C/min.

Morphology

Scanning electron microscopy (SEM) was done on injection-molded tensile bars. Samples were fractured in liquid nitrogen, and observations were made using a Hitachi 3500 scanning electron microscope. Micrographs were taken in several areas perpendicular to the direction of flow, including the center of the tensile bar and the area near the skin.

Molecular weight determination

The grafted copolymer was extracted with trichlorobenzene. The weight-average molecular weight was then determined by gel permeation chromatography (GPC), RI detector in THF (tetrahydrofuran) mobile phase using a polystyrene MW-calibration.

Blend preparation

All compounded materials contained a stabilizer package and processing aid for extrusion. Compounding was performed in a corotating intermeshing Leistritz LSM 34 GL twin-screw extruder. All pelletized materials were then molded in a 5 oz Battenfeld injection molding machine.

Mechanical properties

All properties were measured at room temperature, including notched Izod impact strength (ASTM-D256 - Procedure A), tensile properties (ASTM-D638-89), and flexural strength (ASTM-D790-92). Heat distortion temperature at 264 psi was measured using 1/8" thick flex bars. The melt flow rate (MFR) was run as per ASTM D-1238 at 230°C using 2.16 g weight.

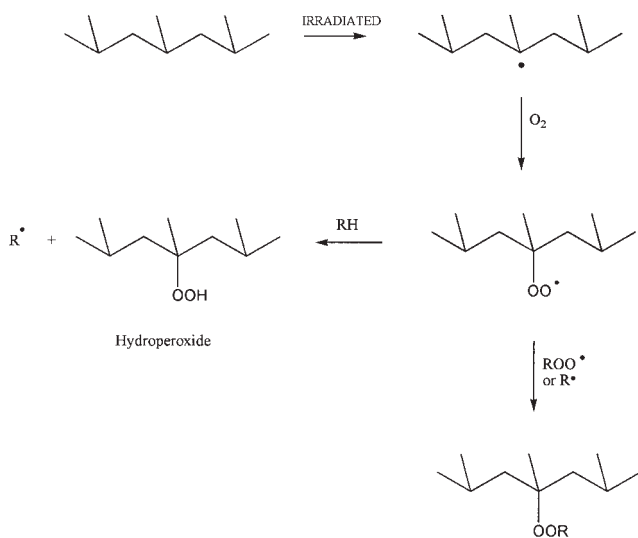


Figure 1 Formation of peroxide functionalities in the oxidized polypropylene.

RESULTS AND DISCUSSION

Oxidized polypropylene initiated polymerization

Oxidized polypropylene is a high MFR, functional polypropylene.^{14,15} We were able to make oxidized polypropylene in a wide range of MFRs, from 100 to 2700 dg/min. The concentration of functionalities present in the oxidized polypropylene is correlated with the polymer MFR. In general, a high MFR oxidized polypropylene contains a high concentration of functionalities. Typical functionalities present in the oxidized polypropylene include ketone, acid, ester, alcohol, lactone, peroxide, and vinyl groups. One application of oxidized polypropylene is the dispersion and coupling of both halogenated and nonhalogenated flame retardants.¹⁶ Benefits include enhancement of flame retardant performance, and improvement in physical properties, processability, and surface appearance. Oxidized polypropylene and its ionomers thereof were also evaluated as compatibilizers for polypropylene/nylon-6 (PP/PA-6) blends.¹⁷ Oxidized polypropylene is reported as an excellent carrier for filler (e.g., flame retardant) master batches.¹⁸ Benefits are seen in the areas of processability, mechanical properties, and morphology.

The benefits of using oxidized polypropylene in these applications are attributed to the polar functionalities present in the polymer.

The functionalities that are most important to grafting reactions are peroxides. The mechanism for peroxide formation in the oxidized polypropylene is shown in Figure 1. Irradiation of polypropylene yields polypropylene radicals, which then react with oxygen to form peroxy radicals. The peroxy radicals then undergo a hydrogen abstraction reaction or a reaction with other peroxy radicals to yield peroxide species that are chemically bound to the polypropylene backbone. A high peroxide concentration polymer is obtained if the polymer is prepared in an environment of a high radiation dosage and a high level of oxygen treatment. We have not identified all of the peroxide species present in the oxidized polypropylene, but we believe that alkyl peroxide and hydroperoxide are the dominant species present in the final product. Total peroxide concentration is determined by a simple titration method, whose reactions are shown in Figure 2. Using this technique, the peroxides in the oxidized polypropylene oxidize iodide to yield iodine. The concentration of iodine is then determined by a simple titration with a known concentration of thiosulfate. The peroxide concentration is the same as the concentration of iodine, since they have equivalent stoichiometry as shown in Reaction 1 of Figure 2.

The chemically bound peroxide species in the oxidized polypropylene can be used as polymerization initiators to produce polypropylene-grafted copolymers. Upon heat treatment, the peroxide functionalities in the oxidized polypropylene act as a source of free radicals, reacting with unsaturated double bond of the monomers. Since polymerization is an exothermic reaction, differential scanning calorimetry (DSC) is used to demonstrate the polymerization capability of the new oxidized polypropylene. Figure 3 shows the results of three polymerization reactions monitored by DSC. The x -axis indicates the temperature that the polymer is heated to, and the y -axis shows the normalized heat flow of the reaction. Increasing heat flow demonstrates an endothermic reaction, while decreasing heat flow indicates an exothermic reaction. In the first experiment, which



Figure 2 Determination of peroxide concentration via titration.

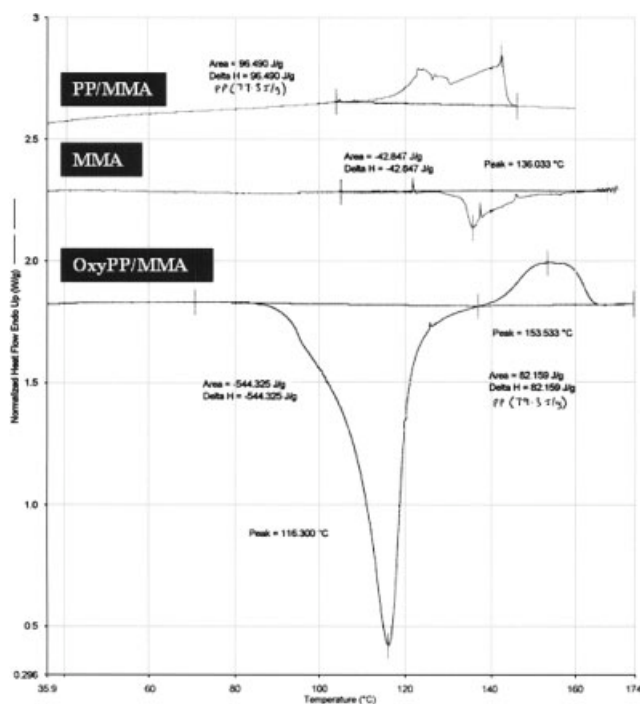


Figure 3 DSC polymerization reactions via oxidized polypropylene.

contains methyl methacrylate (MMA) and a polypropylene homopolymer without the presence of an initiator or a peroxide species, we observe no exotherm peak, as there is no polymerization taking place. In fact, we see a small endothermic peak, which is attributed to the heat needed to melt the polymer. Methyl methacrylate by itself undergoes a thermal polymerization, and a small exotherm peak is seen at 140°C in the second DSC experiment. A large exotherm peak is seen in the sample containing the methyl methacrylate and the oxidized polypropylene. The exotherm peak starts to appear at 90°C and reaches the maximum at 116.3°C. Enthalpy for the MMA polymerization initiated by the oxidized polypropylene is -544 J/g, which is similar to the value that is reported in the literature, -560 J/g.¹⁹ The result of this DSC experiment shows that the oxidized polypropylene initiates polymerization below its melting point of 160°C. Therefore, the polymerization takes place with the polypropylene in the solid state. Melting or use of solvents is not required. In a second set of DSC experiments, similar exotherm peaks are observed for the polymerization of vinyl acetate and styrene using oxidized polypropylene as an initiator to produce the corresponding polypropylene-grafted copolymers (Fig. 4). Again, oxidized polypropylene acts as a “self” initiating backbone molecule to promote polymerization without the addition of any expensive and environmentally unfriendly organic peroxide or azo compounds.

For both vinyl acetate and styrene polymerization reactions, it is interesting to note that we do not see an endothermic peak at 153–160°C for the melting of the polypropylene-grafted copolymers. Since polymer melting and the polymerization of vinyl acetate or styrene takes place at a similar temperature, the final heat flow will be the balance of the energy given off from the polymerization and the energy needed to melt the polymer. The result indicates that more heat is given off from the polymerization than the heat required to melt the polymer. Therefore, we can only detect the exothermic peak, but not the endothermic peak.

As expected, the overall rate of polymerization initiated by the oxidized polypropylene is dependent on the concentration of peroxide species present in the polymer. One would assume that a higher peroxide concentration will lead to a faster polymerization rate and a larger exotherm peak. In a series of experiments shown in Figure 5, MMA polymerizations are carried out isothermally at 90°C using three different oxidized polypropylenes that contain three levels of peroxide. The goal of the experiment is to measure the amount of time for the reaction to reach the maximum exotherm. Results shown in Figure 5 indicate that the experiment, which used the oxidized polypropylene with the highest peroxide concentration, requires the shortest time to reach the exotherm maxima. At 63 mmol/kg peroxide concentration, we detect the exotherm peak within 25 min as compared to 80 and 120 min for the experiments containing 12 and 9.1 mmol/kg of peroxide, respectively. The experiment with the highest peroxide

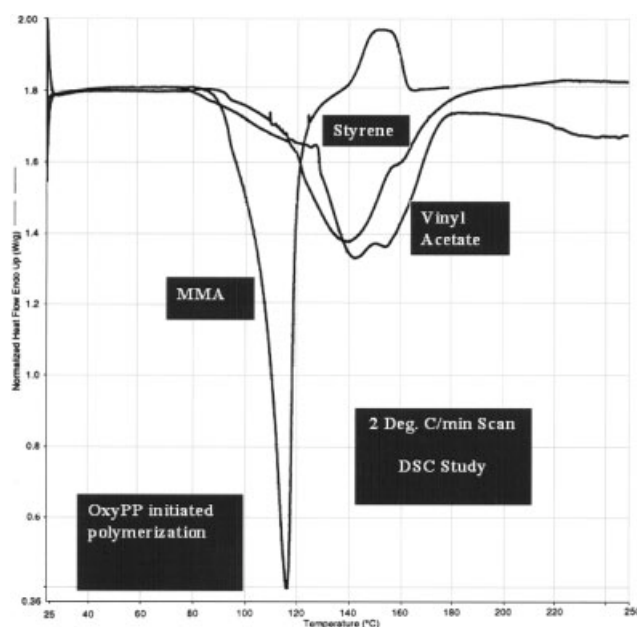


Figure 4 Oxidized polypropylene initiates polymerization of vinyl acetate and styrene.

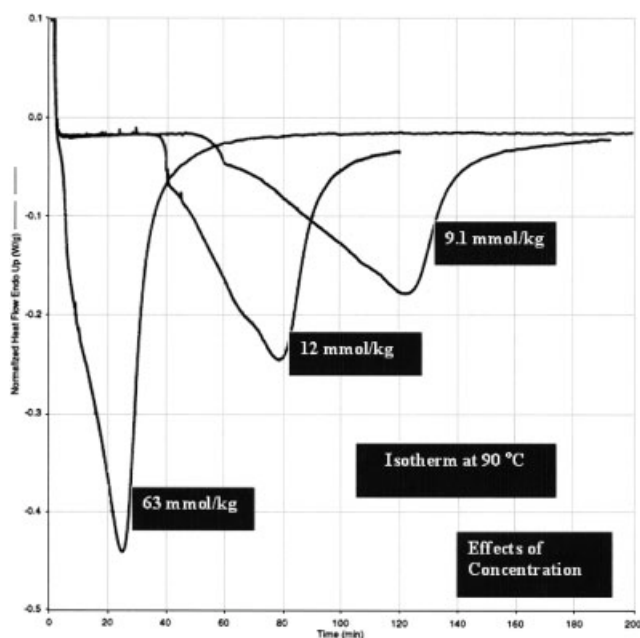


Figure 5 DSC isotherm experiments of various peroxide concentration oxidized polypropylene.

concentration oxidized polypropylene has the sharpest and most intense exotherm peak, while the experiment with a lower peroxide concentration has a broader and less intense exotherm peak. In general, the results above indicate that a faster polymerization rate is achieved for a peroxide-rich oxidized polypropylene.

Mechanism of the oxidized polypropylene grafted reaction

The mechanism for the oxidized polypropylene-initiated polymerization reaction is shown in Figure 6. Decomposition of the alkyl peroxide species in the oxidized polypropylene by heat yields alkoxy radicals on the polyolefin backbone. These alkoxy radicals then undergo a chain scission or initiate a polymerization. If a monomer is nearby it will undergo polymerization to form a copolymer grafted on the backbone. If the alkoxy radicals undergo a chain scission, other radicals will be formed on the backbone, which can also act as active grafting sites. The final products will be polypropylene-grafted copolymers with polypropylene as the backbone and grafted copolymer as the side chain. In the case of hydroperoxide present in the oxidized polypropylene, its decomposition yields both alkoxy and hydroxy radicals. One can foresee the possibility of obtaining both grafted and ungrafted polymers made in the same process. The hydroxy radical can abstract a hydrogen atom to form a radical on the backbone, which then can initiate the grafting reaction. The hydroxy radical itself can initiate polymerization to allow homopolymerization.

Using oxidized polypropylene, we are able to carry the grafting reactions with the oxidized polypropylene in the solid state, without the need for solvent or organic peroxides. The polymerization and grafting reactions were carried out at 140°C with various monomers including methacrylic acid

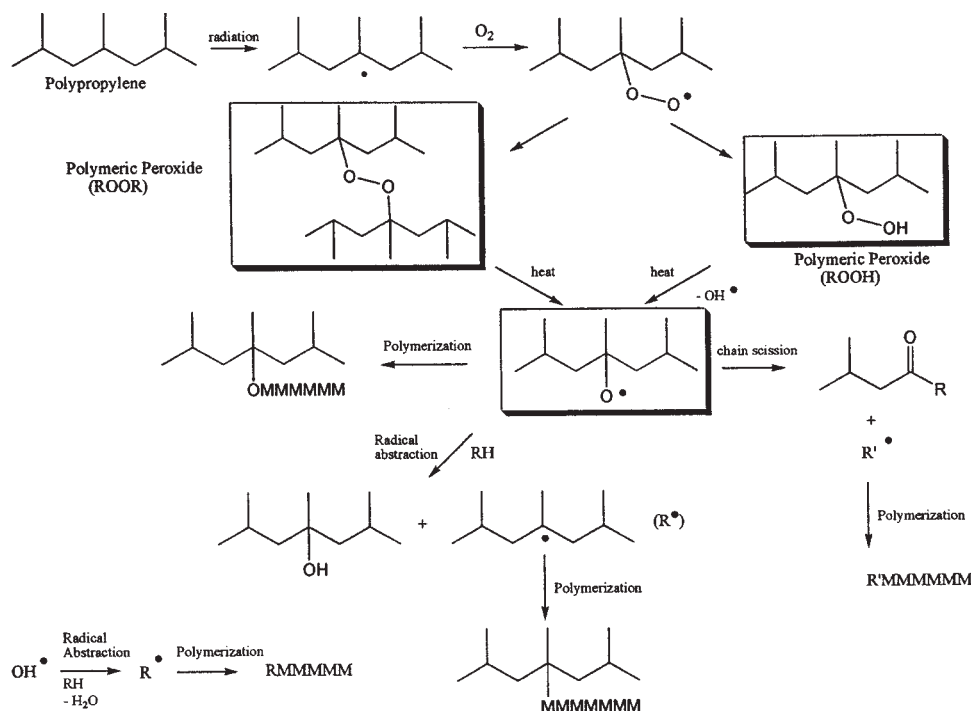


Figure 6 Mechanism of the oxidized polypropylene initiated polymerization.

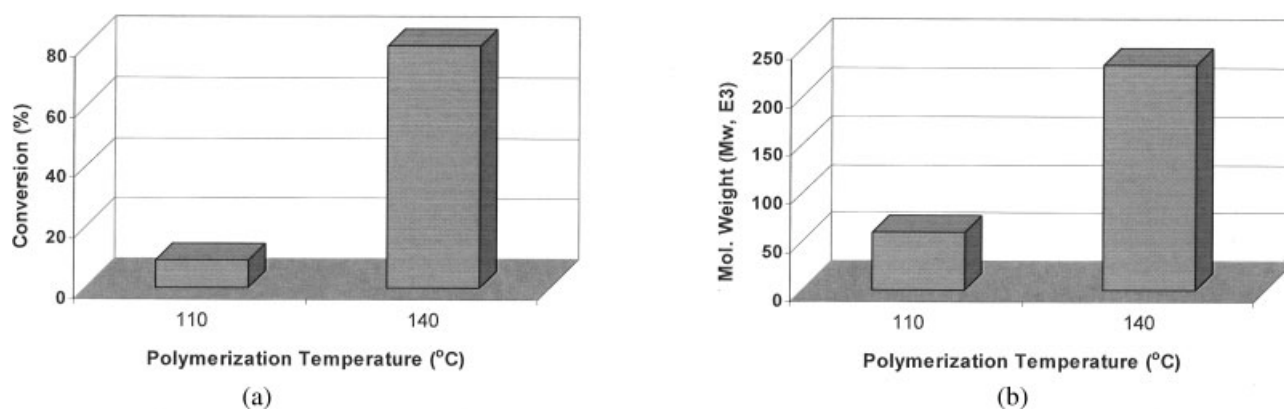


Figure 7 Effects of polymerization temperature on conversion and molecular weight of the grafting chain of polypropylene-grafted copolymers prepared from oxidized polypropylene.

anhydride, vinyl pyrrolidinone, styrene, vinyl acetate, methyl methacrylate, and butyl acrylate. For oxidized polypropylene with a high porosity, we can load up to 70 pph of monomer to the oxidized polypropylene with a 80–95% conversion. For oxidized polypropylene with a low porosity, a typical monomer loading level is about 10–15 pph. The grafting reaction is carried out at 140°C for two reasons: firstly, the temperature is lower than the melting temperature so that it can be carried out in the solid state, and secondly, the temperature is high enough to decompose peroxides and activate the polymerization. A lower conversion is obtained if the grafting reaction is conducted at a temperature lower than 140°C due to limited radical concentration available for polymerization. Results in Figure 7 show that only 10% of vinyl acetate monomer is polymerized when the reaction was conducted at 110°C as compared to 80% for the reaction carried out at 140°C. As a consequence, the grafted chain length and the weight-average molecular weight of the low conversion reaction are several times shorter than that of the high conversion reaction (Fig. 7).

The radicals formed in the oxidized polypropylene have a higher molecular weight and are less volatile than the radicals formed from the organic peroxide. Thus, the oxidized polypropylene grafting reaction is generally cleaner and results in less fouling on the reactor. For the organic peroxide reaction, the peroxide and monomer are volatile, and the polymerization can take place outside of the polymer sphere, which can lead to significant fouling. Such phenomena are significant issues in commercial production, often resulting in manufacturing interruptions to clean the reactor. Pictures given in Figure 8 show that significant fouling is accumulated at the agitator shaft for the organic peroxide-initiated reaction, while very little polymer fouling is found in the same region for the reaction initiated by oxidized polypropylene.

As mentioned earlier, competing reactions occur when grafting via oxidized polypropylene, particularly chain scission versus polymerization. The final MFR of the graft copolymer is dependent on the amount of monomer grafted on the oxidized polypropylene. Our experience indicates that at the 20 pph monomer grafting level, the grafted copolymer MFR is about the same as the starting MFR of the oxidized polypropylene. As shown in Table I, the oxidized polypropylene has a MFR of 890 dg/min. After grafting with 20 pph of polyvinyl pyrrolidinone (PVP) or polymethacrylic acid (PMAA), the grafted copolymers have MFRs of 950 or 900 dg/min, respectively. For a lower grafting level, since there is not much monomer to polymerize, the chain scission reaction becomes dominant. As a consequence, the final MFR of the grafted copolymer increases. The 3 pph polymethacrylic acid anhydride-grafted polypropylene has a MFR at 2700 dg/min (Table I). In contrast, the MFR of the final grafted copolymer decreases when the graft level is 40 pph and higher. For example, the MFR of the oxi-

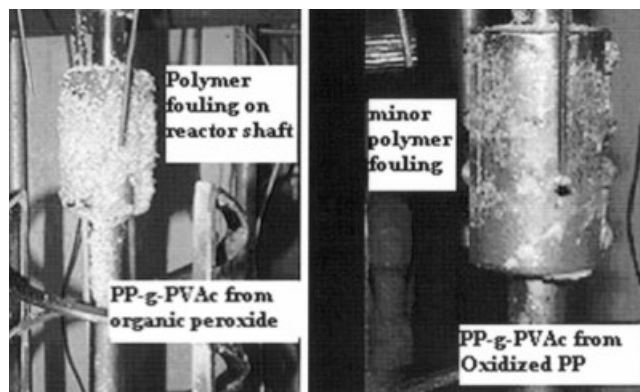


Figure 8 Polymerization fouling of organic peroxide reaction versus oxidized polypropylene.

TABLE I
MFR of Grafted Copolymers Prepared via Oxidized Polypropylene

Types	Monomer (pph)	MFR (dg/min)
PP-g-PVP	20	950
PP-g-PMAA	20	900
PP-g-polymethacrylic acid anhydride	3	2700
Oxidized PP1	None	890
PP-g-PS	66	18
PP-g-PS	40	38
Oxidized PP2	None	130

dized polypropylene before grafting is 130 g/min, and the MFR of the copolymers are 40 and 18 dg/min after grafting with 40 and 66 pph of polystyrene (PS), respectively. The reason attributed is formation of a higher MW and a longer grafted chain length.

The graft polymerization reaction via oxidized polypropylene is not monomer-diffusion dependant. For oxidized polypropylene bulk polymerization, free radicals and grafting sites are distributed inside the polymer sphere; therefore, the polymerization takes place evenly within the polymer sphere, leading to good particle morphology and excellent flow ability. In contrast, in the peroxide grafting process, free radicals first form in the liquid monomer phase; thus, the polymerization often takes place before the monomer has a chance to diffuse into the polymer particle. As a consequence, the peroxide-grafted copolymer normally has a surface layer with a high grafting content, which we call shelling ("shelling"). This shelling phenomenon can yield a sticky, tacky surface on the particles and are not desirable in manufacturing processes because it can cause storage and transport problems. Figure 9 shows the results of Fourier transform infrared (FTIR) analysis along the radius of particles of vinyl acetate-grafted copolymer (PVAc) on polypropylene using either peroxide or oxidized polypropylene as an initiator. The *x*-axis represents the distance from the surface to the center of the polymer sphere and the *y*-axis shows the ratio of the concentration of polyvinyl acetate to polypropylene. Particles with a low degree of shelling would have a lower ratio of polyvinyl acetate to PP. As noted in the results shown in Figure 9, the oxidized polypropylene-initiated reaction to produce PP-g-PVAc does not have a surface rich with polyvinyl acetate compared to the polymer initiated by the peroxide process. The surface PVAc/PP ratio is only 0.6 as compared to 1.3, respectively. There is at least two times more PVAc present on the surface of the organic peroxide grafting sphere than on the oxidized polypropylene.

Applications of oxidized polypropylene grafted copolymers

Using the oxidized polypropylene as a radical initiator, we prepared polypropylene-grafted polyvinyl pyrrolidinone at three different grafting levels, 3, 5.6, and 16.5 pph. The polypropylene-grafted polyvinyl pyrrolidinones (PP-g-PVP1, PP-g-PVP2, and PP-g-PVP3) were then evaluated as a compatibilizer for a PP/PA-6 blend. The PP/PA-6 blend contains 25 wt % PA-6 and 5 wt % of the PP-g-PVP described above. The rest of the formulation consists of a polypropylene homopolymer. The results shown in Table II indicate that the mechanical properties of the blends containing the PP-g-PVP are superior to the control blend, which contains no compatibilizer. The blends using PP-g-PVP have higher tensile strength at yield and at break, and higher flexural strength and modulus. Tensile strength of a noncompatible PP1/PA-6 blend is 4537 psi and increases to 6719 psi with the addition of 5 wt % of PP-g-PVP3. Similarly, flex modulus also increases from 259 kpsi to 309 kpsi, respectively. Property improvement is attributed to effective compatibilization by the polypropylene-grafted copolymers prepared from oxidized polypropylene. As expected, a higher grafting level leads to a more compatible system. It is evident from the data shown in Table II that the PP1/PA-6 blend that has the most improved overall physical properties contains the highest level of polyvinyl pyrrolidinone grafts. When the grafted copolymers have lower graft levels, the effectiveness of the compatibilizer is also reduced. Tensile strength decreases from 6719 psi to 6546 psi and 6360 psi as the PVP level is reduced from 16.5 pph to 5.6 pph and 3 pph, respectively. Similarly, flex strength also decreases from 9953 psi to 9578 psi and 9297 psi, respectively.

Improvement in physical properties seen in Table II reflects an enhancement in blend morphology promoted by the presence of a compatibilizer. As shown in Figure 10(a), the SEM image of the PP1/PA-6 blend (75/25) shows large domains, irregular size and shape of the PA-6 phase in the PP1 matrix, indi-

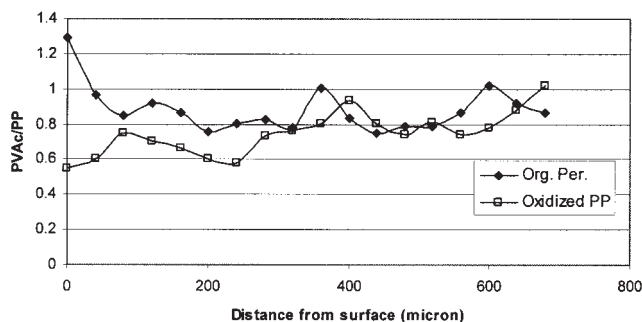
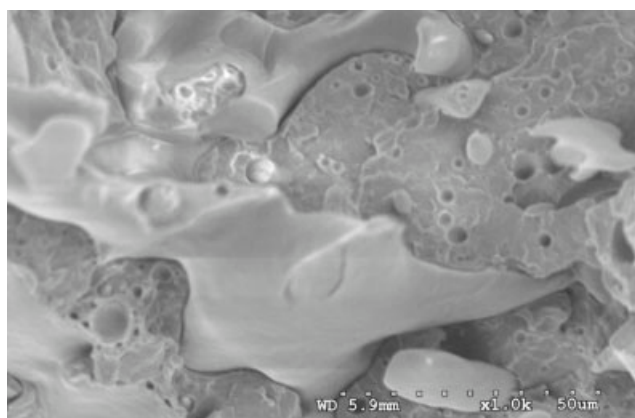


Figure 9 Particle morphology of PP-g-PVAc prepared from the oxidized polypropylene and organic peroxide.

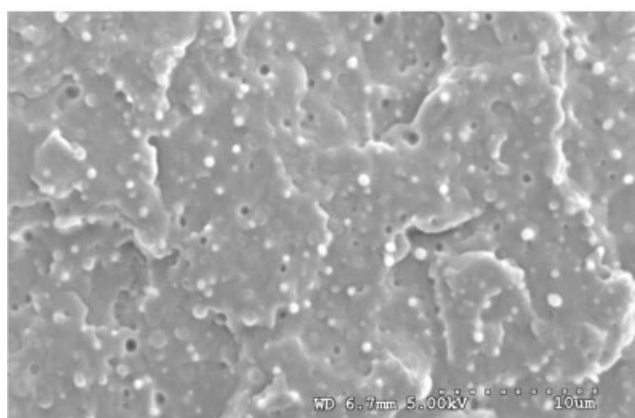
TABLE II
Mechanical Properties of PP1/PA-6 Blends Using PP-g-PVP Prepared from Oxidized Polypropylene

	Composition (wt %)			
	Ex. 1	Ex. 2	Ex. 3	Ex. 4
PP1	75	70	70	70
PA-6	25	25	25	25
PP-g-PVP1 (PVP = 3 pph)	–	5	–	–
PP-g-PVP2 (PVP = 5.6 pph)	–	–	5	–
PP-g-PVP3 (PVP = 16.5 pph)	–	–	–	5
Physical properties at 23°C				
Tensile strength at yield (psi)	4537	6360	6546	6719
Elongation at yield w/extens (%)	3.7	4.0	4.1	4.1
Flex strength at yield, 0.05"/min (psi)	7675	9297	9578	9953
Flex modulus, 1% secant (kpsi)	259	291	295	309

cating the system is incompatible. The SEM image of the same blend containing PP-g-PVP prepared from the oxidized polypropylene shows a finer, more spherical and uniform dispersion of the PA-6 phase [Fig. 10(b)]. The average particle size of the PA-6 phase is in the 2 μm range or less.



(a)



(b)

Figure 10 (a) SEM image of the PP1/PA-6 blend (75/25); (b) SEM image of the PP1/PA-6/PP-g-PVP2 blend (70/25/5).

Using oxidized polypropylene as a radical initiator, we also prepare a grafted copolymer with a polar functional group that can bind with the surface of fillers like glass. Such coupling agents improve the interfacial adhesion between the glass and the propylene polymer matrix. The result is a better dispersion of glass with improvement in mechanical properties. Polypropylene-grafted polymethacrylic acid anhydride and polypropylene-grafted maleic anhydride are prepared from oxidized polypropylene for this purpose. As is evident from the data shown in Table III, both polypropylene-grafted methacrylic acid anhydride and polypropylene-grafted maleic anhydride are effective coupling agents for a formulation containing 20 wt % of fiber glass. The physical properties of the blends containing grafted oxidized polypropylene are superior to that of the control. Heat distortion temperature increases from 109°C for the control with no cou-

TABLE III
Physical Properties of the Glass-Reinforced Blends Containing PP-g-poly(methacrylic anhydride) and PP-g-MA as Coupling Agents

	Composition (wt %)		
	Ex. 5	Ex. 6	Ex. 7
PP2	80	78.5	78.5
Fiber glass, PPG3973	20	20	20
PP-g-polymethacrylic anhydride (methacrylic anhydride = 20 pph)	–	1.5	–
PP-g-MA	–	–	1.5
Physical properties at 23°C			
Tensile strength at Yield (psi)	5675	7258	7742
Flexural strength at Yield, 0.05"/min (psi)	8640	10,720	10,940
Flexural modulus, 1% secant (kpsi)	534	558	561
HDT at 264 psi (°C)	109	136	138
MFR at 230°C, 3.8 kg (dg/min)	3	2.8	–

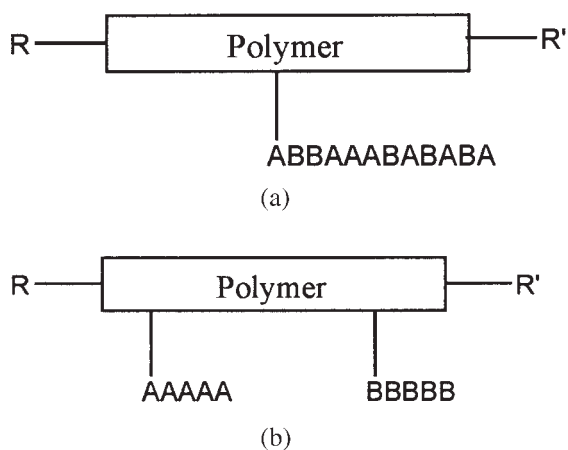


Figure 11 (a) Proposed structure of randomly grafted terpolymer; (b) Proposed structure of sequentially grafted terpolymer.

pling agent to 136–138°C for the blends containing oxidized polypropylene-grafted copolymers. Flex strength increases from 8640 psi to 10,720 psi and 10,940 psi when 1.5 wt % of grafted polymer with methacrylic anhydride or maleic anhydride (MA) included in the formulation, respectively.

Sequentially grafting polymerization via oxidized polypropylene

Sequential grafting is also possible utilizing the oxidized polypropylene as a radical initiator. The term sequential implies a method by which an olefin polymer backbone material is grafted with at least

one monomer, followed by grafting with a second monomer (or mix of monomers). In this technique, the oxidized polypropylene is grafted with a monomer-1 that is capable of being polymerized by free radicals. After a hold period for react down and removal of the unreacted monomer-1, the second monomer-2 is added to the grafted oxidized polymer. The monomer addition and react down are repeated as in the first graft polymerization reaction. The sequential grafting method allows one to prepare a terpolymer with different blocks of grafted chains on the backbone. As expected, such polymer will have a different microstructure as well as different mechanical properties than the random grafted terpolymer. A sequentially grafted terpolymer is proposed to have the structure illustrated in Figure 11(b). The sequential grafted terpolymer might also have some polymer chains that contain both blocks of copolymers on the same chain. The random grafted copolymer will have a structure given in Figure 11(a). As discussed earlier, the reactive site to initiate polymerization in the oxidized polypropylene is on the polyolefin backbone, thus the grafting chain is likely to grow from the polyolefin backbone. However, hydroperoxide is also present in the oxidized polypropylene, thus we can not completely rule out the possibility that homopolymerization of the monomer may occur.

Figure 12 shows the ^1H NMR spectra of two grafting terpolymers—sequential versus random, both of which are prepared from oxidized polypropylene. For the sequentially grafted product, the monomer-1 is methyl methacrylate at 20 pph followed by mono-

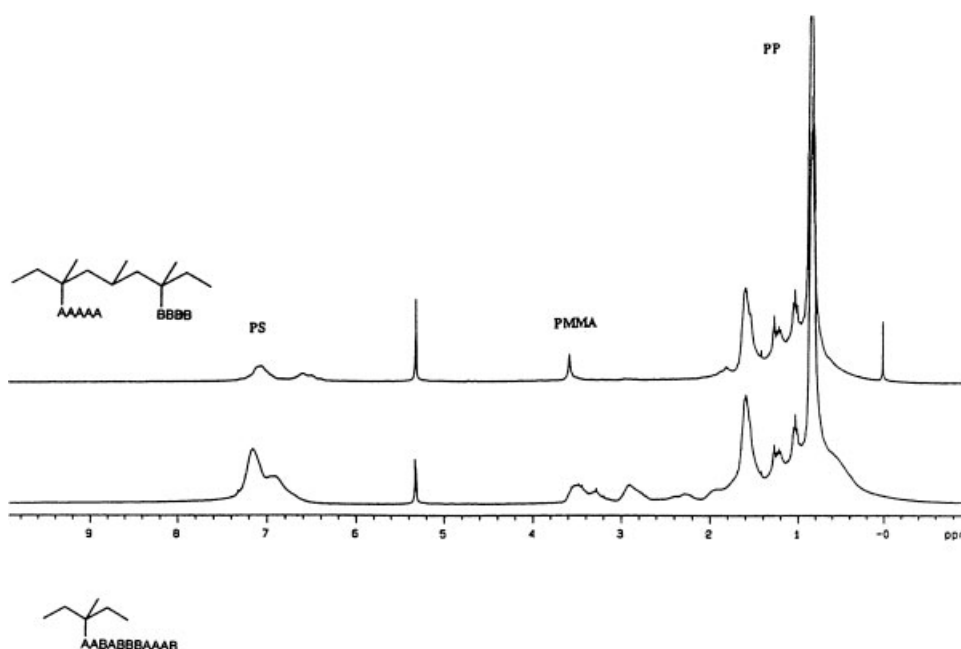


Figure 12 NMR spectra of the sequentially grafted and randomly grafted terpolymer.

TABLE IV
 T_g of Sequentially Grafted and Randomly Grafted Terpolymers

Types	T_g (°C)	Phase
Sequentially grafted terpolymer PP-g-(PBA-seq.co-PS)	-32	PBA phase
	12	PP phase
	94	PS phase
Randomly grafted terpolymer PP-g-(PBA-r.co-PS)	10.5	PP phase
	37.5	P(BA/S) phase

mer-2, styrene (20 pph). For the randomly grafted product, the styrene and methyl methacrylate (20 pph each, 1 : 1 ratio) are mixed together before the grafting polymerization. The ^1H NMR spectrum of the sequentially grafted terpolymer shows chemical shifts of the methoxy protons of the methyl methacrylate around at 3.6 ppm. Chemical shifts for these protons are sharp, and there is not much coupling going on with the neighboring protons. In contrast, chemical shifts for methoxy protons in the randomly grafted terpolymer are from 2.80 to 3.60 ppm. The peaks are broad with multiplet splitting due to complex coupling with the neighboring protons.

Table IV shows the glass transition temperature, T_g , of the terpolymer prepared from a sequentially grafted polymerization of polybutyl acrylate (PBA) and then polystyrene (PS) on oxidized polypropylene. As expected, the terpolymer should have three observable T_g s, -32°C for polybutyl acrylate, 12°C for polypropylene, and 94°C for polystyrene. In contrast, the randomly grafted terpolymer of styrene/butyl acrylate on oxidized polypropylene exhibits only two (2) T_g s: 10.5°C for PP and 37.5°C for the BA/S random copolymer chain. Noted that the T_g for the BA/S random copolymer chain is midway between the T_g s of the two single block chains—polybutyl acrylate (-32°C) and polystyrene (94°C).

Differences in microstructure between the terpolymers prepared from a sequentially grafted or a ran-

domly grafted reaction result in mechanical properties differences between the two polymers. Table V shows mechanical properties of the terpolymers prepared from the two techniques. Even though both polymers have similar tensile strength and flex modulus, their notched Izod impact properties are different. The terpolymer made by the sequentially grafted reaction is tougher and more elastic with higher notched izod impact and longer elongation at break. These properties are attributed to its lower T_g (-32°C), which the randomly grafted terpolymer lacks.

CONCLUSIONS

In summary, oxidized polypropylene is an effective initiator for polymerization. It is a "self" initiating backbone molecule that promotes polymerization to produce polypropylene-grafted copolymers. The copolymers have good particle morphology. The polymerization takes place in an autoclave reactor with the oxidized polypropylene in the solid state. Polymer melting or use of solvents is not required, and hazardous organic peroxides or azo compounds are not needed. One could foresee the possibility of carrying out the grafting reactions in the molten state in an extruder. Potential applications of the grafted oxidized polypropylene are demonstrated in the areas of polymer blends and glass-reinforced resin, but are not limited to those alone. Sequential grafting via oxidized polypropylene opens the possibility that one can alter and tailor mechanical properties of grafted copolymers to fit the requirements of applications of interest.

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TABLE V
Mechanical Properties of the Terpolymers—Random versus Sequential

Polymers	Notched			
	Izod (ft lbs/ in.)	Elongation at break (%)	Tensile strength (psi)	Flex modulus (kpsi)
Randomly grafting PP-g-(PBA-r.co-PS) (10 : 10 pph)	0.26	12.4	4920	191
Sequentially grafting PP-g-(PBA-seq.co-PS) (10 : 10 pph)	0.51	17	4910	206

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