Preparation and Properties of Polyolefin Graft Polymer available as a Primer for Polyurethane Adhesive

(I) Synthesis of polyolefins with cyclic acid anhydride by free radical graft polymerization

Ki Jung Ryu, Min Jung Kim, Seong Kee Min, Won Kee Lee, and Chan Young Park[†]

Department of Polymer Engineering, Pukyong National University, Busan 608-739, Korea

Abstract: Because of their low surface free energy and absence of polar groups at the surface, polyolefins are substrates whose wetting and adhesion are very difficult. Free radical grafting of monomers to backbone polymer is one of the most attractive ways for the chemical modification of polymers. Synthesis of graft copolymer through graft polymerizations of PE and/or PP with phthalic anhydride (PhAn) was made and FTIR spectra of the graft polymer were the examined. And also the effects of phthalic anhydride content on the grafting ratio, thermal properties and contact angle of the graft polymer were examined.

Keywords: polyolefin, surface free energy, polar group, free radical, contact angle

Introduction

Polyurethanes (PU)s are usually employed in coating technology for their versatility and wide range of properties. They are frequently used for adhesive applications, e.g. on wood, leather, rigid plastics such as PVC, thin, flexible plastics such as BOPP and polyester (PET), glass, metals and textiles, because of the possibility to steer their mechanical properties and the possibility to incorporate functional groups for that can interact with the functional groups at the surface of a substrate.[1] Good adhesion to non-polar adherend such as polyethylene and polypropylene is required in a number of technologies including printing, painting and food packaging technology. However, for good adhesion between polyolefins and other materials it is usually necessary to pretreat the polyolefinic substrate.[2] Now that polyolefins have low surface free energy and do not have polar groups at the surface, they are substrates whose wetting and adhesion are very difficult. Improved adhesion increases retention and improves the marginal sealing of fixed partial parts. To enhance the adhesion, polyolefins are treated by corona discharge or flame treatment.[3-5] This treatment creates many oxygenated functional groups on the substrate surface such as carboxylic

acid, aldehyde, ketone and alcohol groups.[6,7] Also this can be achieved by (co)polymerization of new monomers or by modification or blending of existing polymers. From a research and development point of view, the latter methods are usually more efficient and less expensive.

Primers are useful because they provide various functional groups that are potentially able to ensure a number of covalent and non-covalent interactions with the treated polyolefinic substrate. In coating technology, primers are commonly used to improve adhesion between substrates and topcoats. The type of primer to be used depends on the substrate and topcoat. Primer allows the adherend to come in contact with the adhesive, and adequate mechanical bonding is obtained. Good adhesion in adherend can be obtained by mild surface scouring followed by application of a primer. Primers play an important role in adhesive procedures since the untreated surface of adherend is not readily reactive to adhesive. Primers are capable of bonding nonpolar surfaces, and their use could be to increase the bond strength between adherends after surface treatment.[8,9] This primer must be able to penetrate into the leather grain layer increasing the cohesion of the collagen fibers and also, it has to be compatible with the adhesive. And primer was also applied to avoid roughening of leather and to improve adhesion and mechanical properties of adhesive. Thereafter a primer is applied to the treated sub-

strate by brush or roll coating. One class of primers that are suitable for polyolefins treated in this way consists of graft polymer through modification of polyolefins. Free radical grafting of monomers is one of the most attractive ways for the chemical modification of polymers. It involves the reaction between a polymer and a vinyl containing monomer, which is able to form grafts onto the polymer backbone in the presence of free radical generating chemicals, such as peroxides.[10,11] Such reactions can be performed in solution, yielding a relatively homogeneous medium because the reactants are easily mixed and the polymer and monomer are usually soluble. However, carrying out these reactions in the melt, i.e. via reactive extrusion, has economic advantages, as the modification is very fast and the need for solvent recovery is avoided.[12-14] Free radical grafting of maleic anhydride (MA) onto polyolefins has gained wide industrial application.[15-17] MA modified polyolefins are an essential part of many plastics formulations. They are used as chemical coupling agents, impact modifiers, and compatibilisers for blends and filler reinforced systems.[10,11]

Phthalic anhydride is produced by the partial oxidation from ortho-xylene. At room temperature it forms white crystal like flakes. In contact with water it results phthalic acid. And then phthalic anhydride is widely used to make phthalate esters used as plasticizers in polyvinyl chloride (PVC) processing. The effect of phthalic anhydride as a new coupling agent on the properties of low density polyethylene composites was studied.[18]

In the present article, in order to modify polyolefins we synthesized both PE-g-PhAn and PP-g-PhAn as an available primer from the free radical polymerization of PE and PP with phthalic anhydride. And we extensively consider the effects of phthalic anhydride content on the FTIR analysis, grafting ratio, thermal properties and contact angle of the graft polymer.

Experimental

The properties of the commercial low density polyethylene (LDPE), such as density = 0.956, melt index = 0.8 g/min, were given from Daehan Petrochemicals Co. (E-308). PP (d = 0.9, M_n = 5,000, Brookfield viscosity 6,000 poise at 190°C) supplied by Aldrich Co., phthalic anhydride (PhAn) and benzoyl peroxide supplied by Junsei Chemical Co. were used as received. The solvents (xylene and 1-butanol) used in this experiment were laboratory reagent grade. The recipes and experimental conditions used in each experiment are given in Table 1. The grafting reactions of MAH onto PE or PP were carried out in xylene with benzoyl peroxide (BPO).[19,20] First of all, the monomer PhAn and the initiator BPO were dissolved and stirred until completely dissolved in 1-butanol. And then a mixture of BPO and PhAn was added dropwise to the solution of PE or PP in xylene for the first 30 min of 5 hr reaction. Free radical grafting experiments were carried out at 120°C with mild agitation in N_2 atmosphere. After the reaction was completed, the reaction mixture was chilled to room temperature and washed with acetone three to four times and then dried in a vacuum oven for 24 hr at 60°C.

The occurrence of grafting was confirmed by FTIR measurement. FTIR spectrometers employ a Michelson interferometer, which splits the radiation beam from the IR source so that it reflects simultaneously from a moving mirror and a fixed mirror, leading to interference. After the beams recombine, they pass through the sample to the detector and are recorded as a plot of time versus signal intensity, called an interferogram. The overlapping wavelengths and the intensities of their respective absorptions are then converted to a spectrum by applying a mathematical operation called

Table 1. Formulation of Graft Polymerization of Polyolefin with Phtalic Anhydride (unit : g)

Experiment	EXP-1	EXP-2	EXP-3	EXP-4	EXP-5	EXP-6	EXP-7	EXP-8
PE	20	20	20	20	-	-	-	-
PP	-	-	-	-	20	20	20	20
xylene	150	150	150	150	150	150	150	150
BPO	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PhAn	5.0	6.5	8.0	9.5	5.0	6.5	8.0	9.5
1-butanol	40	40	40	40	40	40	40	40
reaction temp	120°C							
reaction time	5 hr							

a Fourier transform. The FTIR method eliminates the need to scan slowly over a range of wavelengths, as was the case with older types of instruments called dispersive IR spectrometers, and therefore FTIR spectra can be acquired very quickly. The FTIR method also allows greater throughput of IR energy. The combination of these factors gives FTIR spectra of strong signals as compared to background noise (i.e., a high signal to noise ratio) because radiation throughput is high and rapid scanning allows multiple spectra to e averaged in a short period of time. The result is enhancement of real signals and cancellation of random noise. Now that infrared spectroscopy is a valuable tool for the identification of grafted polymer, grafted polymer films were recorded on a Nicolet 520 FTIR using the KBr pellet technique imposed for the sample texture.

The grafting ratio (GR) of graft polymer (PE-g-PhAn, PP-g-PhAn) was measured with varying PhAn and initiator content. And Quantitative analysis was done by a titration method as follows.[21] One gram of modified polymer (PE-g-PhAn) was put in 150 mL refluxing xylene/1-butanol mixture at 120°C for 60 min. The hot solution reaction was then titrated without permitting it to cool with 0.05 N ethanolic KOH using thymol blue as indicator. Then an excess of KOH was added and a deep blue color was back-titrated to a yellow endpoint by addition of 0.05 N isopropanolic HCl to the hot solution. Results were expressed as weight percentage. A blank solution also was treated under the same conditions. The grafting ratio (%) was calculated by the equation

Grafting Ratio (%) = $100 \times N(V_o - V) \times M_o / (2 \times W \times 1000)$ (1)

where N : the acid concentration of the isopropanolic HCl solution (mol/L)

W : weight of graft polymer (g)

V, V_o : volume (ml) of the isopropanolic HCl solution added to the graft polymer and blank solutions, respectively

M_o : molecular weight of PhAn (148.12).

When a liquid contacts a second fluid phase and a solid surface, there is produced a force imbalance orienting the liquid-fluid interface by causing it to assume a characteristic equilibrium orientation with respect to the solid surface, reflected in the so-called contact angle (θ). At equilibrium, the contact angle may be considered to be an intensive material constant depending only on the natures of the three component phases, but independent of the quantities present.

Being an experimentally accessible quantity, the contact angle can be a very useful tool for examining interfacial effects. By contact angle meter, contact angle (θ) of distilled water on the PE-g-PhAn and PP-g-PhAn film was determined with apparatus (VCA-2500, ASC products, USA). The film plates were first put into acetone followed by washing with distilled water and dried to remove unreacted PhAn on the sample surface, In contact angle measurement, dimension of polymer plates was $10 \times 10 \times 1$ mm^3. Average value of five samples was provided with contact angle.

Thermal properties were obtained from differential scanning calorimeter (DSC-20l0, TA Instruments Co.). A small quantity of the sample (2~3 mg) is confined within an aluminum pan and subjected to controlled temperature variation. A reference material is placed in an equivalent pan and the two pans are heated simultaneously. The temperature of the two pans are monitored continuously and the rate of heat flowing to the sample is adjusted to keep the temperatures of the two pans equal. The heat flow is proportional to an electrical current in a resistive heating element, so it is straightforward both to control and to monitor. Whenever the sample undergoes a thermal transition, so that there is a change in heat capacity, the DSC registers both the amount and the direction of the additional heat flow. In addition the processing temperature of polymeric materials is generally determined by the Tm of the matrix polymer. For smooth manufacture of final product, the processing temperature of polymer was set about 10 to 30°C higher than that of polymer.

Results and Discussion

In order to characterize the obtained modified polymer, firstly a qualitative study was done by using FTIR. FTIR spectra of grafted copolymer (PE-g-PhAn, PP-g-PhAn) are shown in Figures 1 and 2. It could be observed that two new absorption peaks produced by PhAn grafting exhibit bands at ~1,860 cm^{-1} and ~1,770 cm^{-1} corresponding to asymmetric and symmetric C=O stretching modes from the PE-g-PhAn and PP-g-PhAn sample. Other strong bands appear in the region ~1030 cm^{-1} and can be attributed to ring stretching vibrations of the grafted sample. Therefore the presence of bands corresponding to both the polyolefin backbone and anhydride residues in the grafted copolymer confirms the occurrence of grafting by FTIR measurement.

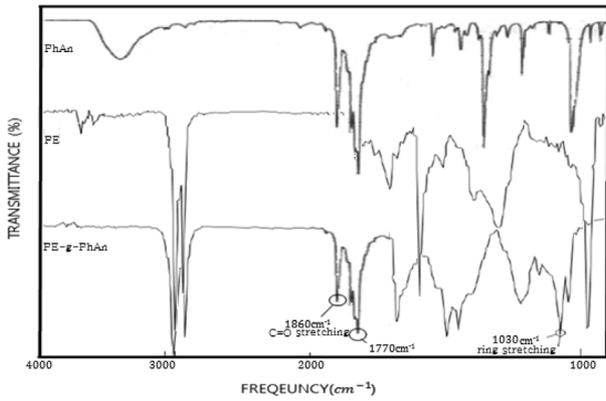Correlation of grafting ratio and contact angle versus vary-

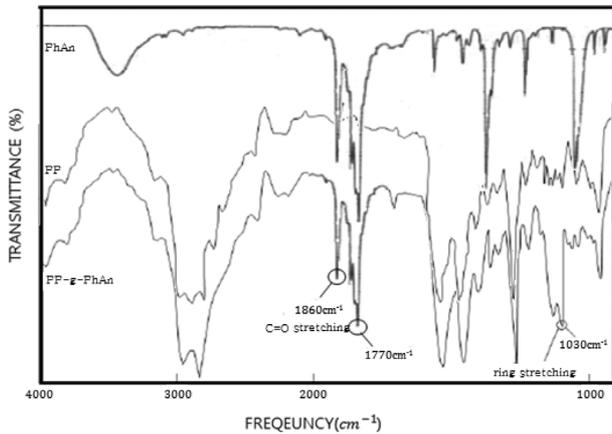**Figure 1.** FTIR spectrum of PE, PhAn and PE-g-PhAn.

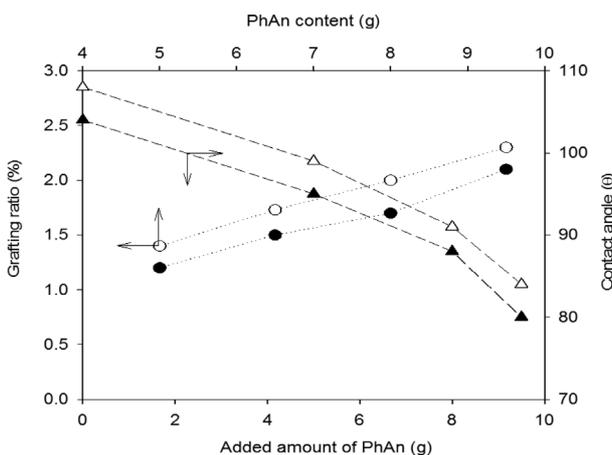**Figure 2.** FTIR spectrum of PP, PhAn and PP-g-PhAn.

Figure 3. Correlation of grafting ratio and contact angle versus varying phthalic anhydride concentration for a modification process of PE-g-PhAn and PP-g-PhAn [grafting ratio ; PE-g-PhAn (○), PP-g-PhAn (●), contact angle; PE-g-PhAn (▲), PP-g-PhAn (△)].
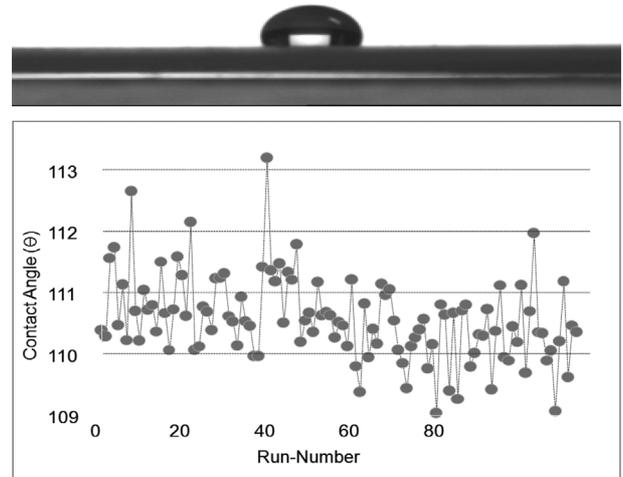
Figure 4. Measurement of contact angle by sessile drop method.

examined. The graph illustrates the variations in the grafting ratios of PE-g-PhAn and PP-g-PhAn with the BPO initiator fixed at 0.5 phr and PhAn concentrations of 5.0, 6.5, 8.0, and 9.5 g. From Figure 3 it can be concluded that the higher phthalic anhydride level the higher grafting ratio obtained. However, the grafting ratio of PE-g-PhAn surpasses that of PP-g-PhAn. Adding more PhAn to the media would have the tendency to react with PE macroradicals to graft accounts for the reason why the grafting ratio of PE-g-PhAn and PP-g-PhAn increases with an increasing PhAn concentration.

Secondly the effect of PhAn content on contact angle is examined. Measurement of contact angle by sessile drop method is shown in Figure 4. When a drop of liquid is placed on a solid surface, the liquid will either spread across the surface to form a thin, approximately uniform film or spread to a limited extent but it remains as a discrete drop on the surface. The final condition of the applied liquid on the surface is taken as an indication of the wettability of the surface by the liquid or the wetting ability of the liquid on the surface. The quantitative measure of the wetting process is taken to be the contact angle, θ, which the drop makes with the solid as measured through the liquid in question. In Figure 3 it can be noticed that contact angle versus PhAn concentration is represented with PE-g-PhAn and PP-g-PhAn. The PE and PP exhibited contact angles of 104° and 108°, respectively underlining its hydrophobic character. With increasing PhAn content to the reaction medium a significant decrease of the measured contact angle was observed. This results could be related to the increased wettability and decreased surface tension as well as the increased polar group of grafted copolymer (PE-g-PhAn, PP-g-PhAn). Therefore the increased

ing phthalic anhydride concentration for a modification process of PE-g-PhAn and PP-g-PhAn is represented in Figure 3. First of all the effect of PhAn content on grafting ratio is
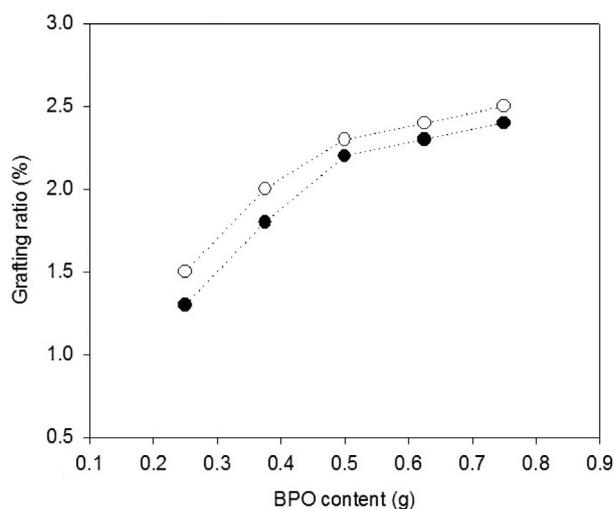
Figure 5. Evolution of grafting ratio versus varying initiator concentration for a modification process of PE-g-PhAn (O) and PP-g-PhAn (△).

amount of PhAn seems to cause the decrease of contact angle.

Figure 5 represents grafting ratio versus varying peroxide concentration for constant initial PhAn concentrations. The initiating sites can be incorporated by copolymerization, can be incorporated in a post polymerization reaction, or can already be a part of the polymer. If the number of active sites along the backbone participate in the formation of one branch, then the number of chains grafted to the macromolecule can be controlled by the number of active sites. Radical initiators can produce radical species under mild conditions and promote radical reactions. Organic peroxides such as BPO have a peroxide bond (-O-O-), which is readily cleaved to give two oxygen-centered radicals. The oxyl radicals are unstable and believed to be transformed into relatively stable carbon-centered radicals. Thus BPO generates benzoyloxyl radicals, each of which loses carbon dioxide to be converted into a phenyl radical (Ph•). Therefore the results of grafting ratio versus BPO content are shown in Figure 5. As BPO content increases, more PE radicals which introduce active sites capable of initiating functionality results in a higher grafting ratio. We can see that grafting ratio generally increases as the BPO content is increased. Thus it can be concluded that the higher initiator level the higher grafting ratio as given in Figure 5. Similar behavior for PP-g-PhAn is also noticed in Figure 5.

The relation of PhAn concentration with melting temperature (T_m) in modified grafted polymers (PE-g-PhAn and PP-

g-PhAn) is seen in Figures 6 and 7, respectively. Differential scanning calorimetry (DSC) is a common expamle of a thermal analysis method. The first feature upon heating is the increase in heat flow required by the increase in heat capacity at T_g. This would be a step function for a genuine second-order transition examined at very slow rates of heating. The second feature indicated is an exothermic peak, indicating that some of the material has crystallized on heating, at a crystallization temperature Tc. This often occurs in crystallizable polymers because insufficient time was allowed on cooling for extensive crystallization; but once the glass transition is traversed, chain segments acquire enough mobility to crystallize. The area under this peak is proportional to the amount of crystallized material if the enthalpy of fusion is known and the DSC has been calibrated with a standard. Presence of polar group in the grafted copolymer resulted in reduction of melting temperature (T_m). In the DSC thermograms, endothermic peak is corresponding to the melting of all crystalline material in the sample is melting temperature
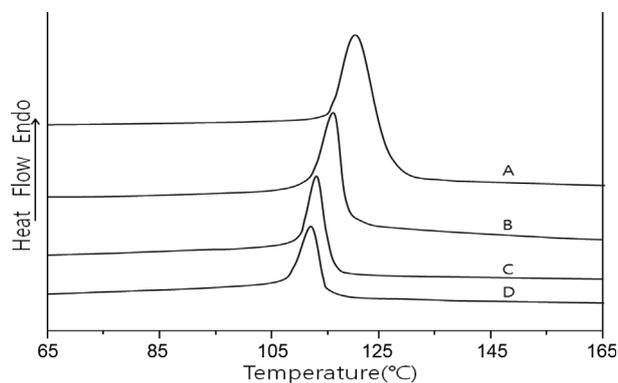

Figure 6. DSC endothermic peaks of (A) PE, (B) PE-g-PhAn (PhAn:5g), (C) PE-g-PhAn (PhAn:6.5g) and (D) PE-g-PhAn (PhAn:8g).
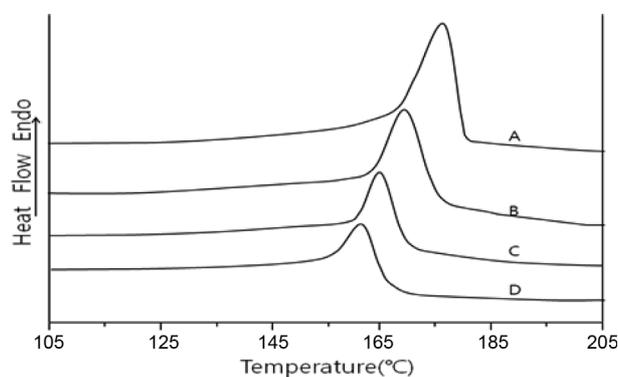

Figure 7. DSC endothermic peaks of (A) PP, (B) PP-g-PhAn (PhAn:5g), (C) PP-g-PhAn (PhAn:6.5g) and (D) PP-g-PhAn (PhAn:8g).

T_m. It has been reported that polar group of grafted copolymer that may act as defects in its crystalline structures leads to weak crystalline structure and thus reduction of melting temperature.[22] The thermograms of all the grafted copolymers in this research showed the endothermic melting peaks as shown in Figures 6 and 7. Moreover Figures 6 and 7 show that phthalic anhydride concentration increases with decreasing of T_m for the grafted copolymer. PP-g-PhAn also shows similar behavior as shown in Figure 7. The T_ms generally decrease as the content of PhAn is increased. This might be due to the hindered crystallization and reduced crystal perfectness in the presence of polar group.[23]

Conclusions

The presence of two new absorption peaks at 1,860 cm^{-1}, 1,770 ~ 1030 cm^{-1} confirms the occurrence of grafting by FTIR measurement. The grafting ratios of PE-g-PhAn and PP-g-PhAn increase with increasing PhAn concentration. However, the grafting ratio of PE-g-PhAn surpasses that of PP-g-PhAn. With increasing PhAn content to the reaction medium a significant decrease of the contact angle was observed. This results could be related to the increased wettability, decreased surface tension and the increased polar group of grafted copolymer. It is seen that grafting ratio generally increases as the BPO content is increased. Phthalic anhydride concentration increases with decreasing of T_m for the grafted copolymer. This might be due to the hindered crystallization and reduced crystal perfectness in the presence of polar group. Consequently the introduction of polar group to the polyolefin backbone polymer might decrease contact angle and increase the wettability.

Acknowledgement

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