



Modification and Properties of Polyolefin with Maleic Anhydride as a Functional Monomer

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관능성 단량체로서 Maleic Anhydride를 이용한 Polyolefin의 개질 및 물성

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ABSTRACT : Surface modification of macromolecules renders a progressive and favorable method to enhance the properties of polymeric materials and improves conductivity, wettability, stability, adhesion, antibacterial properties, etc. of polymeric surfaces without deterioration of the polymer bulk properties. Polyolefins such as polyethylene and polypropylene were grafted with maleic anhydride(MAH) as a functional monomer in solution. Evidence for grafting was shown with FTIR measurement. The grafting ratio was determined from chemical titration. The higher MAH loading, the lower contact angle(θ) was obtained. With the increasing content of MAH, melting temperature(T_m) of maleic anhydride grafted polymer decreased while decomposition temperature(T_d) of maleic anhydride grafted polymer increased.

요약 : 거대분자의 표면개질은 고분자재료의 물성을 향상시키기 위한 점진적이고 바람직한 방안을 제공하며 고분자의 주요 물성을 손상시키지 않고 고분자 표면의 전도도, 젖음성, 안정성, 접착 및 항박테리아성 등을 개선시킨다. PE 또는 PP 등의 polyolefin을 관능성 단량체로서 MAH와 용액상에서 그래프트시켰다. FTIR측정을 통하여 그래프팅이 일어났음을 확인하였다. 그래프팅율은 화학적정에 의하여 결정하였다. MAH량이 많아질수록 접촉각은 낮은 값을 얻었다. 또한 MAH량이 증가함에 따라 polyolefin-g-MAH의 용점(T_m)은 감소하는 한편 분해온도(T_d)는 증가하는 경향을 보였다.

Keywords : modification, polyolefin, functional monomer, graft polymerization, maleic anhydride, wettability

I. Introduction

In order to expand the applications of polyolefins and produce useful substances which have improved mechanical, thermal, and chemical properties chemical modification of polyolefins is usually employed as an important alternative. In the modification of polyolefins free radical graft polymerization of maleic anhydride(MAH) with base polymer employing an initiator is paid much attention over the past decades. With the incorporation of glow discharge, ultraviolet (UV) irradiation, x-ray and photografting, modifications of useful product such as film, fiber, and powder etc. were also examined and intensified mainly by surface grafting reactions.^{1,2} Through the

interfacial interaction between the components in polymeric materials PP-g-MAH or PE-g-MAH has been widely used for improving of the physical properties.³⁻⁵ By utilizing of melts,⁶⁻⁸ solution⁹⁻¹¹ and solid-state¹²⁻¹⁴ modifying of polyolefins has been successfully performed. Surface treatment is required for most polymer materials which are chemically inert to improve their adhesion properties to other materials. In addition graft polymerization is a fascinating means to render a various functional groups to a polymer. In the past several years, emphasis on applications of modified polymers through grafting has been increased.¹⁵ There has been significant research in techniques of graft polymerization of different monomers on backbone polymers.¹⁶

Surface modification techniques including chemical,^{17,18} plasma^{19,20} treatments, flame,²¹ ultraviolet (UV) irradiation and corona discharge^{22,23} which improve interfacial adhesion by changing surface energy to increase wettability have been ex-

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tensively employed. Feasible introduction of graft chains with a high density and exact localization of graft chains with invariable bulk properties to the surface makes grafting attractive in its benefits compared to other methods. Radical polymerization is suggested as a useful method for polymer grafting on the surface.

In this experiment, graft polymerizations of PE and/or PP with MAH were performed and the effect of maleic anhydride on the spectroscopic, thermal properties and contact angle in the maleic anhydride grafted polyethylene (PE-g-MAH) and/or maleic anhydride grafted polypropylene (PP-g-MAH) were examined.

II. Experimental

PE used was low density PE (Daehan Petrochemicals, E-308, $d = 0.956$, $MI = 0.8$ g/10min). PP ($d = 0.9$, $M_n = 5,000$, Brookfield viscosity 6,000 poise at 190 °C) was purchased from Sigma-Aldrich, USA. Maleic anhydride (MAH), benzoyl peroxide and xylene used in this experiment were purchased from Junsei Chemical Co. The typical formulations of the polymerization are given in Tables 1. Grafting of MAH onto PE or PP was carried out in xylene with benzoyl peroxide (BPO).^{24,25} A mixture of BPO and MAH dissolved in xylene was added dropwise to the solution of PE in xylene for the first 3 hr of 5 hr reaction. The reaction was carried out at 120 °C with mild agitation in nitrogen gas purging. At the end of reaction, the mixture was cooled to room temperature and washed with acetone several times and dried in vacuum overnight. Evidence for grafting was obtained from FTIR measurement. The grafting ratio (GR) of PE-g-MAH was determined from chemical titration.²⁶ The chemical titration is such as the following procedure. Purified PE-g-MAH (0.3–0.4 g) was dissolved completely in 120 ml of xylene at 120 °C, and after addition of 0.2 ml of deionized water, the mixture was refluxed for 1 hr. Adding dropwise 10.0 ml of a 0.1 M isopropanolic KOH solution, the mixture was refluxed for another 2 hrs to ensure complete reaction with the MAH groups. With 0.1 ml of a

1.0% phenolphthalein ethanol solution as an indicator, the hot solution was titrated with a 0.1 M isopropanolic HCl solution. A blank solution also was treated under the same conditions. The grafting ratio (%) was calculated by the equation

$$\text{Grafting Ratio(\%)} = 100 \times N(V_0 - V) \times M_0 / (2 \times W \times 1000) \quad (1)$$

where N is the acid concentration of the isopropanolic HCl solution (mol/L), W is the weight of PE-g-MAH (g), V and V_0 are the volumes (ml) of the isopropanolic HCl solution added to the PE-g-MAH and blank solutions, respectively, and M_0 is the molecular weight of MAH (98.06). The press-moulded films of the PE-g-MAH were immersed into acetone at room temperature to remove the unreacted monomer and other secondary products. The FTIR spectra of the PE-g-MAH and PP-g-MAH films were recorded with a Nicolet MAGNA-IR 750 spectrometer. The grafted polyethylenes with different GR were obtained by changing MAH concentrations in the presence of BPO. The contact angle (θ) data were obtained from an angle subtended at the triple line by the tangents onto the solid/liquid and liquid/vapor interfaces in a system with solid/liquid/vapor phases being a thermodynamic equilibrium.²⁷ The contact angle of distilled water on the PE-g-MAH and PP-g-MAH film was measured using a contact angle meter (VCA-2500, ASC products, USA). Each contact angle θ measured was the average value of five runs with a maximum error of $\pm 2^\circ$. The polymer plates of dimensions $10 \times 10 \times 1$ mm³ were used in the contact angle measurement. To get rid of unreacted MAH on the sample surface, the plates were first put into acetone followed by washing with distilled water and dried. DSC thermogram data were provided with DSC-2010 (TA Instruments Co.) differential scanning calorimeter. 2–3 mg samples were crimp-sealed in 30 μ l aluminum pans and first heating scan was performed from 20 to 250 °C. In order to cancel the thermal history effects, sample was held at this temperature for five minutes before starting the cooling and the second heating sweeps, and then cooled with the rate of 10

Table 1. Experimental Conditions in Graft Polymerization of Polyolefin with Maleic Anhydride

	T-1	T-2	T-3	T-4	T-5	T-6	T-7	T-8	T-9	T-10
PE	44	44	44	44	44	-	-	-	-	-
PP	-	-	-	-	-	44	44	44	44	44
MAH	10	12.5	15	17.5	20	10	12.5	15	17.5	20
BPO	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
xylene	436	436	436	436	436	436	436	436	436	436
reaction temp	120 °C									
reaction time	5 hrs									

°C/min to room temperature. The thermal analysis was carried out under a nitrogen purge (20 ml/min) and degree of crystallinity (X_c) of the grafted PE samples was calculated by the following equation:

$$X_c = \Delta H_c / \Delta H^0 \quad (2)$$

where ΔH_c is the overall enthalpy of crystallization acquired from the integral area(S) of the cooling thermogram, ΔH^0 is given to 293 J/g exhibiting the enthalpy of 100% crystallinity of polyethylene.²⁸ In order to get information on its degree of crystallinity, ΔH values were usually normalized to the amount of the phase under consideration. In addition the processing temperature of polymeric materials is generally determined by the T_m 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. Thermogravimetric analysis(TGA) was provided with TGA 1500 manufactured by Polymer Laboratories Co. at the heating rate of 20 °C/min under nitrogen purge. Thermal stability of specimen was investigated from TGA data. For quantitative evaluation of its thermal stability, the temperature at which two tangents are intersected is used as the decomposition temperature(T_d) of a specific component.

III. Results and Discussion

It is usually believed that grafting of maleic anhydride (MAH) to polyolefins proceeds through a free radical mechanism.²⁹ Free radicals produced from thermal decomposition of a peroxide abstract hydrogen atoms from polyethylene backbones, thus polymer free radicals are resulted. Polymer radicals then attack monomer(MAH) and then results in grafting of monomer to polymer backbones. The specimen for grafting ratio of PE-g-MAH is free from the residual monomer by dissolving the grafted polyethylene with xylene, precipitating with acetone.

Figure 1 illustrates the effect of MAH content on grafting ratio. The graph indicates that grafting ratio increases with the increase of MAH content. This is attributed to the fact that higher MAH content increases the feasibility which reacts with PE macroradicals to graft in the present experiment.

Figure 2 shows the variation of BPO concentration with MAH content in grafting ratio. The experiment conditions are T-5 and T-10 in Table1. Generally the grafting reaction involves initiation to form macroradicals through abstraction of hydrogen atoms from the polymer chain by the initiator radicals, and addition of the unsaturated monomer to the macroradicals. Also grafting of MAH onto PE was carried out normally at a high temperature to generate free radicals from the thermal decomposition of the initiator. With the increasing

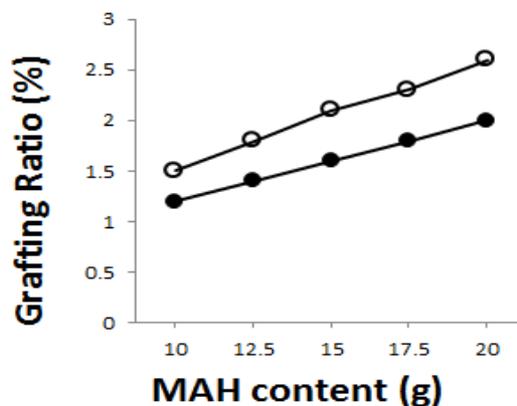


Figure 1. Effect of MAH content on grafting ratio : PE-g-MAH(○), PP-g-MAH(●).

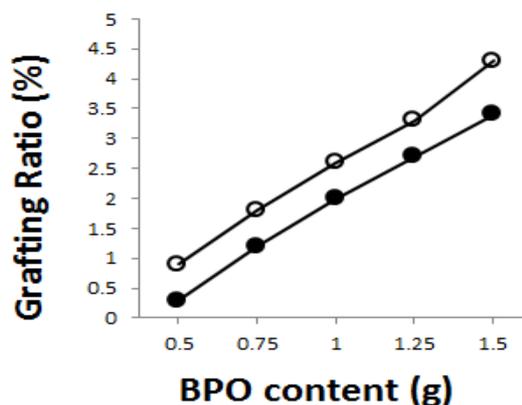


Figure 2. Effect of BPO content on grafting ratio : PE-g-MAH (○), PP-g-MAH(●).

loading of initiator, more PE radicals are produced, leading to a higher grafting ratio. So the grafting ratio increases with the increasing of BPO concentration as shown in Figure 2.

Figures 3 and 4 show FTIR spectra of PE-g-MAH and PP-g-MAH. An infrared spectrum is obtained by passing infrared radiation through a sample and determining which fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of vibration of a part of the sample molecule. Most infrared spectroscopy is carried out by using Fourier-transform infrared(FTIR) spectrometers. This method is based on the interference of radiation between two beams to yield an interferogram, i.e. a signal produced as a function of the change of path length between the two beams. The two domains of distance and frequency are interconvertible by the mathematical method of Fourier transformation. The radiation emerging from the source is passed through an interferometer to the sample before reaching a detector. Upon amplification of the signal, in which high-frequency con-

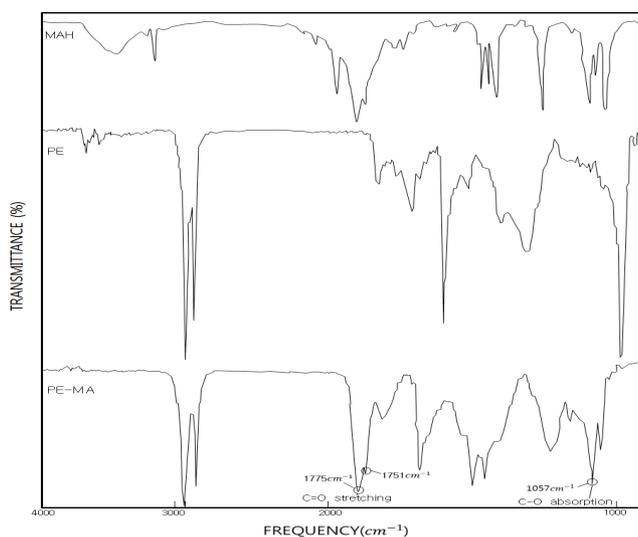


Figure 3. FTIR spectra of PE and PE-g-MAH.

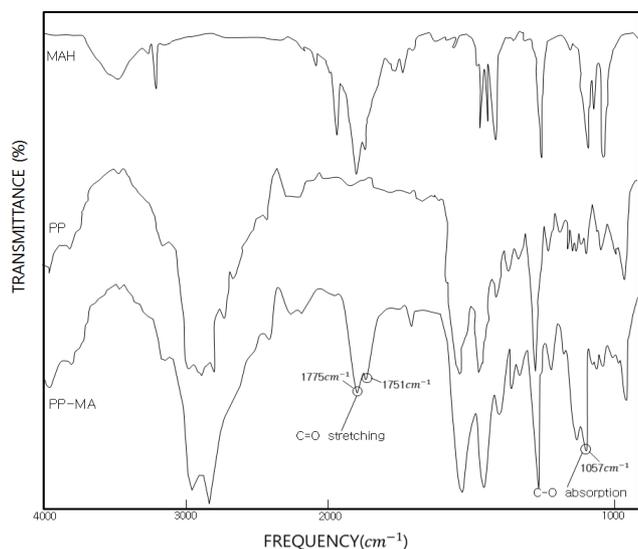


Figure 4. FTIR spectra of PP and PP-g-MAH.

tributions have been eliminated by a filter, the data are converted to a digital form by using an analog-to-digital converter and then transferred to the computer for Fourier transformation to take place. From Figures 4 and 5 it can be seen that two new absorption peaks appear at 1775 and 1751 cm^{-1} , which are attributed to the stretching of the carbonyl from the PE-g-MAH and PP-g-MAH sample. On the other hand the new peak which appeared at about 1057 cm^{-1} is associated with the C-O absorption of the grafted sample. Therefore it was inferred that MAH grafting on the backbone of PE and PP chain occurred.

Surface tension and contact angle are correlated with each other and in this experiment as the content of MAH is in-

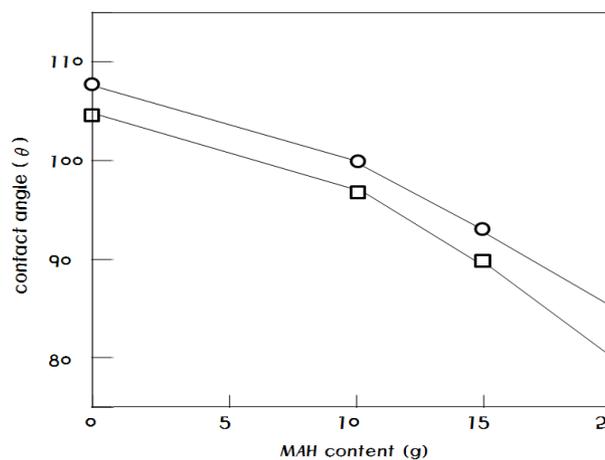


Figure 5. Effect of MAH content on contact angle : PE-g-MAH(○), PP-g-MAH(□).

creased surface tension is expected to be decreased. The effect of MAH content on contact angle is shown in Figure 5 with PE-g-MAH and PP-g-MAH. It can be seen that the contact angle decreases with increasing MAH content. The reduction in the contact angles is probably attributed to the increase of the polarity of the grafted polymer.

The thermal analysis describes a number of techniques which involve measuring a physical property of a material as a function of temperature. Differential scanning calorimetry (DSC) is such a thermal method that may be used to compare and evaluate polymer samples. It is a technique which records the energy necessary to establish a zero temperature difference between the sample and a reference material as a function of time or temperature. In this method, the two specimens are subjected to identical temperature conditions in an environment which is heated or cooled at a controlled rate. DSC curves are plotted as a function of time or temperature at a constant rate of heating. In the DSC graph a shift in the baseline results from the change in heat capacity of the sample. Figures 6 and 7 show the effect of MAH content on melting temperature (T_m) in PE-g-MAH and PP-g-MAH. Introduction of anhydride grafting decreases melting temperature (T_m). Bulky grafted moiety on maleic anhydride grafted polymer limits the folded chain arrangement of segments and may act as defects in its crystalline structures. The crystallite size of this polymer is therefore reduced and with weakening of the crystalline structure the melting temperature decreases.³⁰ Polar group on the grafted PE increases the nucleation and percent of crystalline sections,³¹ therefore the melting enthalpy of grafted polyethylene is higher than PE. From Figures 6 and 7 it can be seen that melting temperature decreases with increasing MAH content. The degrees of crystallinity were obtained with 24.9%, 23.4%, 22.1% and 20.4% respectively for PE and PE-g-MAH (MAH : 2 wt%, 3 wt% and 4 wt%) calcu-

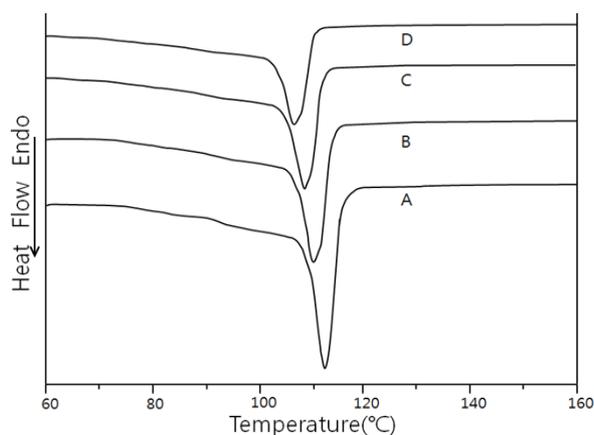


Figure 6. DSC thermograms of (A) PE, (B) PE-g-MAH (MAH : 2wt%), (C) PE-g-MAH (MAH : 3wt%) and (D) PE-g-MAH (MAH : 4wt%).

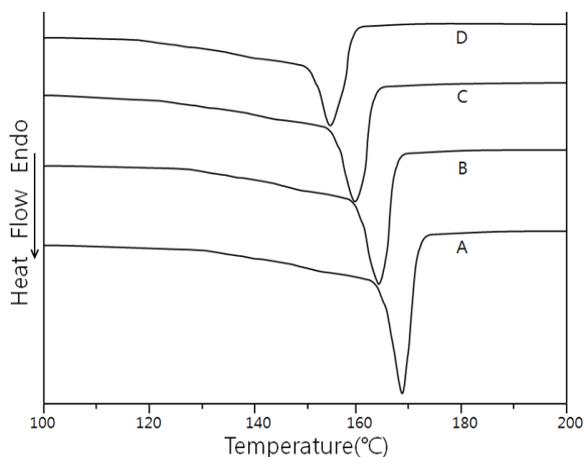


Figure 7. DSC thermograms of (A) PP, (B) PP-g-MAH (MAH : 2wt%), (C) PP-g-MAH (MAH : 3wt%) and (D) PP-g-MAH (MAH : 4wt%).

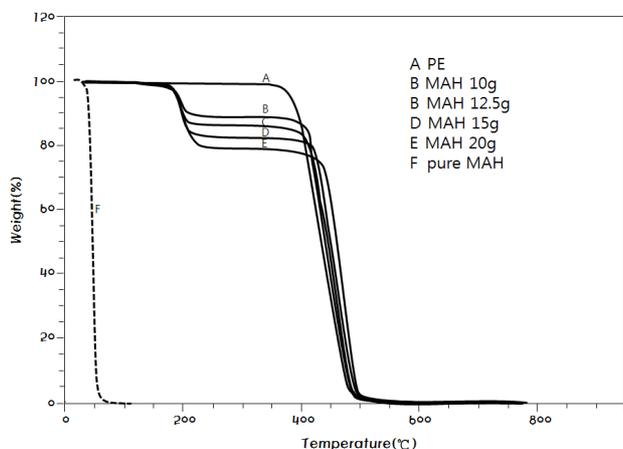


Figure 8. TGA thermograms for PE and PE-g-MAH with different amount of MAH.

lated by eq (2). As the contents of MAH were increased X_c were decreased. A similar result was also observed in PP-g-MAH.

The thermal stability of PE-g-MAH was evaluated using thermogravimetric analysis (TGA). The temperature at which two tangents are intersected is used as the decomposition temperature (T_d) of a particular component to quantitatively evaluate its thermal stability. The onset temperature of main weight loss in TGA is used as an indication of thermal stability. Figure 8 shows the weight loss curves for the PE-g-MAH. It represents that the second decomposition temperature of PE-g-MAH was increased obviously as the MAH content was increased. So the more MAH content in PE-g-MAH, the better thermal stability is obtained.

IV. Conclusions

The grafting ratio increases with the increasing of MAH content. This is attributed to the fact that higher MAH content increases the feasibility which reacts with PE macroradicals to graft. With the increasing loading of initiator, more PE radicals are produced, leading to a higher grafting ratio. So the grafting ratio increases with the increasing of BPO concentration. It can be seen that contact angle decreased from 104° for pure PE to 82° for PE-g-MAH. The reduction in the contact angles is probably attributed to the increase of the polarity of the grafted polymer. DSC results indicate that melting temperature decreases with increasing of MAH content. From TGA thermogram the more MAH content in PE-g-MAH, the better thermal stability is obtained.

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