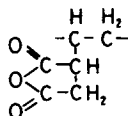


Adhesive Property of Polypropylene Modified with Maleic Anhydride by Extrusion Molding

INTRODUCTION

It is known that maleic anhydride (MAH) reacts with polymers in the presence of radical reagents when mixed at the molten state.¹ This reaction was applied to various kinds of vinyl polymers, in particular polypropylene (PP).¹⁻⁴ Ide and his co-workers studied the reaction mechanism of MAH and PP at the molten state² and in solvents.² It was also reported that ionomers were obtained from reaction products.^{2,3,5} The structure of modified PP as shown in Scheme 1 suggested that it was reasonable to use it as an adhesive⁶:



Scheme 1

Although the reaction mechanism of PP with MAH has already been investigated,^{1,3} the physicochemical properties of PP modified with MAH have not yet been reported. Accordingly, in this study, modification of PP using MAH in the presence of benzoyl peroxide (BPO) was carried out in an extrusion molder. Thermal behavior and adhesive strength of modified PP were investigated in connection with the amount of reacted MAH.

EXPERIMENTAL

Sample Preparation

Isotactic PP powder (melt index = 0.5) made by Mitsui Petrochemical Co. was used as an original sample. In order to evaluate the isotactic content, the atactic portion was extracted from the original powder using chloroform with a Soxhlet extractor for period of 8 h. Unextracted residue was 99.0% by weight. The PP powder (ca. 100 g) was mixed well with MAH and BPO, which were made by Wako Pure Chemical Inc. The amounts of MAH and BPO are shown in Figure 1.

The mixtures were introduced into an extrusion molder equipped with a pelletizer. The temperature of the molder was maintained at $200 \pm 2^\circ\text{C}$. MAH was reacted with PP as the mixture passed through the extruder.¹ The length of the molder was ca. 100 cm and the diameter was 3 cm. The reaction time was ca. 3 min. In order to extract untreated MAH, the obtained pellet was dissolved in xylene in a flask equipped with a condenser and a stirrer. An oil bath was maintained at a temperature of 140°C , and the flask was placed in it for 5 min. Following that the solution was cooled to room temperature. The recrystallized PP was filtered, washed by acetone three times, and dried at room temperature under the reduced pressure of 10^{-2} mm Hg.

The modified PP was sandwiched between metal plates covered with Teflon sheets and pressed at 100 kg/cm^2 for 2 min. Immediately after, plates cooled at 20°C under the same pressure. The thickness of the films was at around 0.1 mm.

For comparison, PP powder was irradiated by γ -rays at 20°C in air with the dose rate 0.1 Mrad/h. The total dose and amount of reacted MAH are given in Figure 1. After the irradiation, the sample was treated in the same way as the sample which reacted when mixed with BPO.

The obtained films were measured without further treatments by infrared spectroscopy, X-ray diffractometry, and differential scanning calorimetry. For the peeling test, a film was sandwiched between two fresh aluminium sheets (0.1 mm thickness) and pressed the same way as previously mentioned.

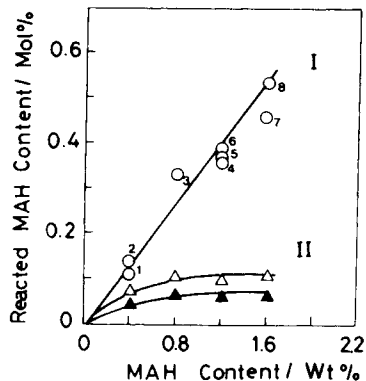


Fig. 1. Relationship between MAH content in the reaction mixture and reacted MAH content: (○) BPO content (wt %), 1 = 0.4, 2, 3, 4, 7 = 0.8, 5, 7 = 1.2, 6, 8 = 1.6; (▲) γ -ray irradiation (2.5 Mrad); (△) 5 Mrad.

MEASUREMENTS

Infrared Spectroscopy (IR)

A Japan Electro Optic Laboratory Fourier transform infrared spectrometer (FT-IR) Type JIR-40X was used. The amount of reacted MAH was calculated using the following equation which was made based on the results reported previously¹:

$$\text{reacted MAH} = 1.32 \times D_{1785}/D_{840} \quad (1)$$

where D_{1785} shows the optical density of the band at 1785 cm^{-1} due to the acid anhydride group. D_{840} shows that of the band at 840 cm^{-1} due to the stretching of the alkyl chain. This band was used as an internal standard.

X-Ray Diffractometry

A Philips PW 1710 diffractometer was used. The sample was measured at a scanning rate $1^\circ/\text{min}$. The crystalline structure was determined with the reference of previous report.⁷⁻⁹

Differential Scanning Calorimetry (DSC)

A Shimadzu DSC Type DT-40 was used. The sample was measured at scanning rate $10^\circ\text{C}/\text{min}$ under N_2 atmosphere. The sample weight (ca. 8 mg) was measured using a Zartorius balance precision of which was $\pm 0.001 \text{ mg}$. Temperature of the phase transitions and the heat of fusion were calibrated using Indium as a standard. The sample was heated at the rate $10^\circ\text{C}/\text{min}$ to 200°C and maintained for 5 min and then cooled to room temperature at the rate $10^\circ\text{C}/\text{min}$. The DSC curves of the first heating were used for the calculation of the heat of fusion. The heat of fusion was determined following the ASTM¹⁰ and JIS¹¹; a straight baseline was assumed between the starting temperature of melting (T_{mi}) and finishing temperature of melting (T_{me}). The errors inherent in the estimation of the base line were taken into consideration, as previously reported.¹²

Mechanical Measurements

A Toyo Baldwin Tensilon UTM-100 was used for the peeling test. The drawing speed was $50 \text{ mm}/\text{min}$, and the gauge length was 35 mm. The peeling test was carried out at 20°C .

RESULTS AND DISCUSSION

Figure 1 shows the relationship between the concentration of mixed MAH and reacted MAH. As shown in Figure 1, reacted MAH content increased with increasing amount of MAH when BPO was used as an initiator. In contrast, the amount of reacted MAH leveled off at around 0.06

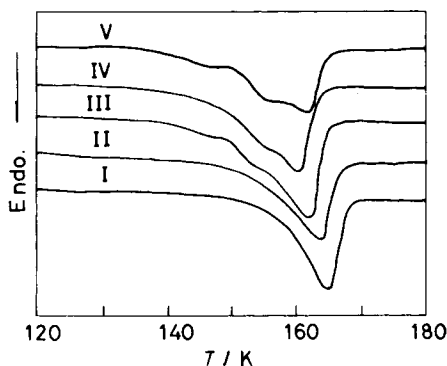


Fig. 2. DSC heating curves of modified PP films: (I) original PP; (II) reacted MAH = 0.100; (III) 0.327; (IV) 0.462; (V) 0.538.

(0.25 Mrad) and 0.1 (0.5 Mrad) in the irradiation method. This suggests that the radicals which were made during irradiation immediately terminated in the extrusion molder at 200°C.¹³ It is thought that the reaction between PP and MAH was initiated from hydroperoxide groups or carbonyl radicals, being created by the thermal decomposition of main chain of PP in the extrusion molder. The amount of reactive group seems to depend on the total dose. This corresponded to the fact that the reacted MAH was constant regardless of the increase of added MAH.

The PP decomposed during the reaction in the extrusion molder.¹ If the amount of mixed MAH and BPO increased higher than ca. 2.0, the viscosity of the sample at 200°C markedly decreased, and it became difficult to apply the extrusion molding. The situation was the same for the sample irradiated by γ -rays. As Ide and his co-workers have already reported,¹ the viscosity decreased, depending on reaction temperature, time, amounts of MAH and BPO, the combined ratio of MAH and BPO, and so on. In our reaction conditions, 200°C and 5 min, the viscosity decreases 50% when MAH content was higher than about 0.2.¹

Figure 2 shows the DSC melting curves (the first heating curve) of modified PP films. The original PP films started to melt at 155°C, and peak temperature was observed at 165°C. When the amount of reacted MAH was small, DSC melting curves showed a similar pattern to the original sample. When the amount of reacted MAH exceeded 0.15, the starting temperature of melting (T_{mi}) shifted to the low temperature side. Moreover, several small shoulders appeared as shown in curves IV and V. These shoulders were observed more clearly when the heating rate decreased. The X-ray diffractograms of both unreacted and reacted samples showed monoclinic crystallite,⁷ which was characterized by the peak at $2\theta = 14.2$. It is known that PP forms a smectic structure after rapid quenching.^{8,9} However, the cooling rate used in this experiment (20°C/min) was insufficient to form a lower order structure, such as a smectic modification or

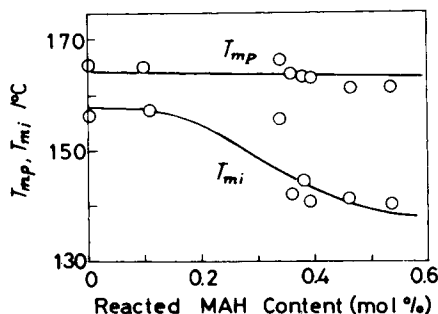


Fig. 3. Relationship between peak temperature of melting (T_{mp}), starting temperature of melting (T_{mi}), and reacted MAH content.

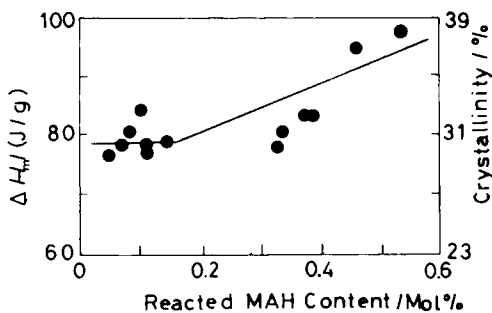


Fig. 4. Relationship between heat of fusion (ΔH_m), crystallinity, and reacted MAH content.

glassy phase. On this account, the shoulder peaks observed at the low temperature side of the main melting peak cannot be attributed to the melting of smectic structure. Moreover, the effect of other types of tacticity can also be ignored, since 99% of the sample is isotactic, as already mentioned in the Experimental section. It is reasonable to consider that the disordered molecular chain was rearranged during the heating process, forming a crystallite as small shoulder peaks were observed in the DSC curves.

Figure 3 shows the relationship between the amount of reacted MAH, the temperature of melting peak (T_{mp}) and also the starting temperature of melting (T_{mi}). It is clear that the melting peak moves slightly to the low temperature side, while the starting temperature decreases markedly at the point where reacted MAH equals 0.15.

Figure 4 shows the relationship between the heat of fusion (ΔH_m) and the amount of reacted MAH. The heat of fusion remained at the initial stage and then increased from ca. MAH = 1.5. Although the increase in ΔH_m was relatively small, it exceeded the extent of experimental error.¹² The increase corresponds well with the results shown in Figures 2 and 3. Crystallinity increased corresponding to the growth of crystallite. It was found that the temperature range of melting was directly related to the increase of the heat of fusion. The heat of fusion of 100% crystalline PP is reported to be 259 J/g.¹⁴ The crystallinity of the sample calculated, assuming the two-state model, is also shown in the longitudinal axis on the right.

Figure 5 shows the peeling strength (σ) as a function of the amount of reacted MAH. The strength increases linearly correspond to an increasing amount of reacted MAH, and, from the point of MAH = 0.15, the strength levels off at around $\sigma = 1.5$ kg/cm². The increase of σ in the first stage may be explained by the increase of active reaction sites caused by the introduction of MAH. It is reasonable to think that the adhesive force increases with the increasing number of the active reaction site, even if the molecular mechanism of the peeling has not been fully explained.¹⁵ The DSC curves of the sample having MAH content up to 0.15 were almost the same as the original sample, in spite of the chemical modification. This suggests that the higher-order structure of the sample does not change until MAH content reaches MAH = 0.15.

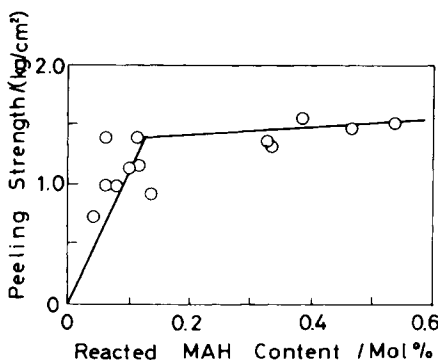


Fig. 5. Relationship between peeling strength and reacted MAH content.

The value of σ was maintained at a constant value, after the MAH was exceeded 0.15. As shown in Figure 4, the crystallinity increased in the second stage, and the crystallite appeared, as shown in Figure 2, due to the partial decomposition of the main chain. Shoulder peaks which appeared at a temperature lower than the main peak indicated the distribution of crystalline size. The molecular weight of the active reaction site of the acid anhydride group is larger than that of the monomer unit of PP. It is difficult for a portion of molecular chain attached to the reactive site to be folded into the lamellae. This means that the reactive site always exists in the amorphous region of the sample.

If the crystallization is assumed to start from the aluminium surface during pressing, it is considered that the lamellae side positions itself parallel to the aluminium surface, since the surface energy of the lamellae side is smaller than that of edge surface of the folded chain.¹⁶ It can be considered that the probability of crystallization on the surface increases when the molecular weight decreases. At the same time, the probability that the active reaction site comes into contact with the aluminium surface also decreases, because the active reaction site is always included in the amorphous region. This may be explained by the fact that the adhesive force leveled off when MAH content exceeded 0.15. The increase in amount of reacted MAH and the decrease in the amorphous region might have caused the leveling off of the adhesive force.

References

1. F. Ide, K. Kamade, and A. Hasegawa, *Kobunshi Kagaku*, **25**, 107 (1968).
2. F. Ide, A. Hasegawa, and T. Kodama, *Kobunshi Kagaku*, **25**, 167 (1968).
3. M. Ueda, S. Mizunuma, M. Oba, and Y. Minoura, *Kogyokagaku Zasshi*, **71**, 432 (1968).
4. Jpn. Pat. 53-1319.
5. F. Ide, K. Kamade, and A. Hasegawa, *Kobunshi Kagaku*, **25**, 298 (1968).
6. Jpn. Pat. 54-99193.
7. G. Natta and P. Corradini, *Nuovo Cimento*, **15**, 40 (1960).
8. G. Natta, *Makromol. Chem.*, **35**, 93 (1960).
9. S. Nishimoto, T. Kagiya, Y. Watanabe, and M. Kato, *Polym. Degradation Stabil.*, **14**, 199 (1986).
10. ASTM D 3417-83.
11. JIS K7122.
12. Japan High Polymer Centre, Ed., *Report on the Investigation Based on the Subvention to Testing and Evaluation New Organic Composites in Fiscal 1985*, Japan High Polymer Centre, Tokyo, 1986.
13. S. Nara, H. Kashiwabara, and J. Shoma, *J. Polym. Sci., A-2*, **5**, 929 (1967).
14. L. Manderkern, *Crystallization of Polymer*, Kagaku Dojin, 1966, p. 109.
15. T. Hata, *Kobunshi*, **22**, 58 (1973).
16. B. Wunderlich, *Macromolecular Physics*, Academic, New York, 1976, pp. 12-13.

ACHMAD SJUKUR BRATAWIDJAJA
ISMINGSIH GITOPADMOYO

Institute for Research and Development of Textile Industries
Jl. Jend A. Yani No. 390
Bandung, Indonesia

YASUSHI WATANABE
TATSUKO HATAKEYAMA

Research Institute for Polymers and Textiles
1-1-4, Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan

Received August 14, 1987
Accepted February 16, 1988