

# An Investigation on the Modification of Polypropylene by Grafting of Maleic Anhydride Based on the Aspect of Adhesion

CHI-WEN LIN, WEI-LUN LEE

Department of Chemical Engineering, National Yunlin University of Science and Technology, Yunlin, Taiwan, Republic of China

Received 29 December 1997; accepted 8 February 1998

**ABSTRACT:** Isotactic polypropylene was modified by a chemical grafting of maleic anhydride in a molten state. The degree of grafting, ranged from 0.078–0.368%, was determined by a titration method. Isotactic polypropylene modified by chemical grafting of maleic anhydride was used as an adhesive in bonding the cold-rolled steel sheets for the correlation of its bondability. It was found that the maximum adhesive strength 159 kg/cm<sup>2</sup> was obtained from a degree of grafting 0.217%. A higher degree of grafting was detrimental not only to the initial adhesive strength, but also to the durability aged in a wet environment. Electron spectroscopy for chemical analysis was used to analyze the failure loci, because the joint was separated by shearing. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 383–387, 1998

**Key words:** polypropylene; grafting modification; maleic anhydride; adhesion; failure loci

## INTRODUCTION

The most common free-radical grafting reactions are grafting of unsaturated monomers, such as maleic anhydride (MAH) or acrylic acid to polyolefins, to improve adhesion of polyolefins to polar phases. Some representative patents for these reactions are listed in refs. 1–3. These patents relate to a method for appending carboxyl groups to polymers by reacting a mixture of MAH, a free-radical catalyst, with a polymer above its melting point. The chemical reaction of this grafting modification is not fully clear yet because of its complex characteristics. Some empirical models based on the experience are implemented for a specific process, but they cannot be generalized.

Some semiempirical models based on the theoretical considerations supported by experimental data would be the most interesting way to meet the needs of practical problems. The batch processes in the solution and in the molten state were usually studied in an attempt to know how the physical characteristics of the reaction medium are affecting the modification level of the polyolefins.

Functionalized polyolefins are frequently used as a compatilizer in polyolefin blends, adhesion promoter in polyolefin composites, surface coatings of metals, and core materials of sandwiched structures. For example, some vibration damping laminated steel sheets utilized polypropylene (PP) as core material due to its competitive cost and its satisfied mechanical properties. One of the most important properties of vibration damping steel sheet is the adhesion between the skins and the core during forming. Failure of adhesion not only results in a deterioration of sheet rigidity, but also reduces its damping capacity. From the

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Correspondence to: C.-W. Lin.

Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC86-2221-E-224-022.

*Journal of Applied Polymer Science*, Vol. 70, 383–387 (1998)

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CCC 0021-8995/98/020383-05

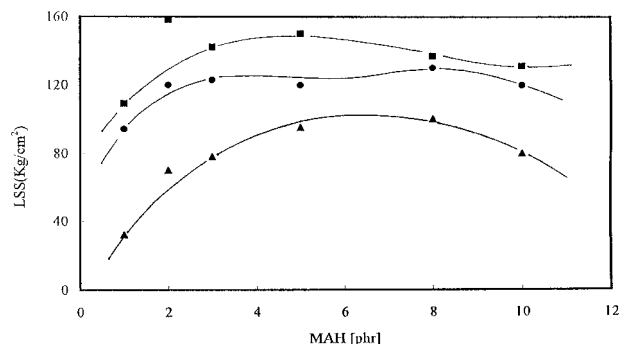
aspect of adhesion, it is the appended polar functional groups that form chemical bonds with metal oxide surfaces. Generally, only a small proportion of polar organic groups is optimum for bonding to oxides, and all that is needed is to occupy the hydroxy groups at the outmost surface. Excess polar groups in the adhesive are detrimental, possibly due to increasing the moisture absorption to the interface or due to the swelling of materials.

Architecture of the modification of polyolefins by a peroxide-catalyzed grafting of MAH has been studied extensively in the past.<sup>4-7</sup> Roover and colleagues<sup>8</sup> endeavored the molecular characterization of MAH-functionalized PP. To the author's best knowledge, MAH grafted-PP (PP-g-MAH) was first studied from a concern of adhesive bonding in 1993 by the author.<sup>9</sup> However, correlation of the adhesive bondability and conditions for grafting reaction is still lack of knowledge. The first purpose of this study is to investigate how the amount of MAH molecules grafted to PP, in terms of the degree of grafting, affects the adhesion to a steel surface, and how the hydrolysis of MAH grafted on isotactic PP (iPP) improves bondability. Second, exploration of the failure loci of the PP-g-MAH/steel adhesive joint is also the interested subject.

## EXPERIMENTAL

The reaction of MAH with iPP was conducted by loading PP pellets into the mixing chamber of a Brabender Plasticorder at 160°C while maintaining the speed of the screws at 30 rpm. After 3 min, the PP was molten and dicumyl peroxide (DCP) was added for another 4 min. Finally, MAH was added for a further 3 min mixing. Determination of the degree of grafting was conducted by a method of acid-base titration suggested by Gaylord and associates.<sup>5</sup> Modified PP (mPP) was dissolved completely in the boiling xylene, followed by adding ~ 5 mL thymol blue (1% in DMF) as an indicator. The titration agent was using 0.05N KOH/ethylene alcohol solution to titrate the mPP/xylene solution. The acid number and degree of grafting were calculated according to Gaylord and associates.<sup>5</sup>

The laminate of steel/mPP/steel with 2 cm in width and 1.0 cm in overlap length was prepared for single lap shear testing. The thicknesses of the steel sheet and the core adhesive were 0.5 and 0.1 mm, respectively. The dumbbell-shaped polymer specimens with a thickness of ~ 1.0 mm were precut and used for the measurement of tensile rupture strength. An average strength was taken



**Figure 1** LSS vs. MAH loading with DCP at 0.1 (▲), 1.0 (■), and 5.0 (●) phr.

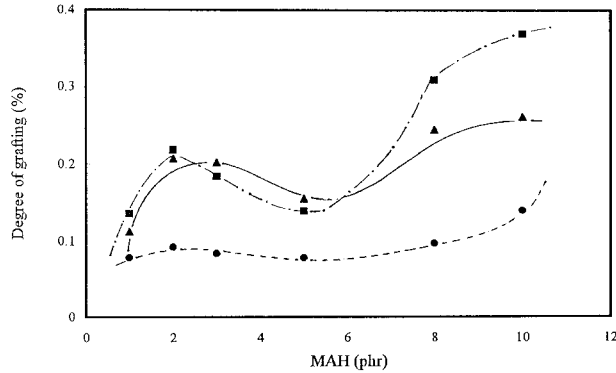
from three measurements. The testing was performed in an Instron machine, model 4467. A measurement of water absorption for mPP was performed by immersing the mPP film (0.1 mm in thickness) into the water bath at 50°C for 24 h. The durability of the adhesive joint was evaluated by measuring the residual lap shear strength (LSS) after it was aged in the same condition as the measurement of water absorption of the mPP.

Hydrolysis of the mPP film was conducted in an environmental chamber at 90°C and 90% relative humidity for 30 min. The contact angles of mPP were measured with a horizontal low-power microscope equipped with a protractor eyepiece and rotatable cross-hairs. A drop of ethylene glycol ~ 2 mL in size was placed on the horizontal surface of the sample, and the contact angles at both sides of the projected silhouette of the drop were measured. Average values for three drops were taken as representative of the PP or mPP film surface. All measurements were taken after 2 min contact time.

Electron spectroscopy for chemical analysis (ESCA) was used to identify the chemical states at the film surface and the failure loci of shearing the bond of PP-g-MAH/steel. The spectrometer used was magnesium  $K_{\alpha}$ X-ray source operated at a constant power of 330 W (110 kV and 30 mA). The vacuum in the analyzer chamber of the instrument was maintained at  $6.7 \times 10^{-8}$  Pa throughout the experiment.

## RESULTS AND DISCUSSION

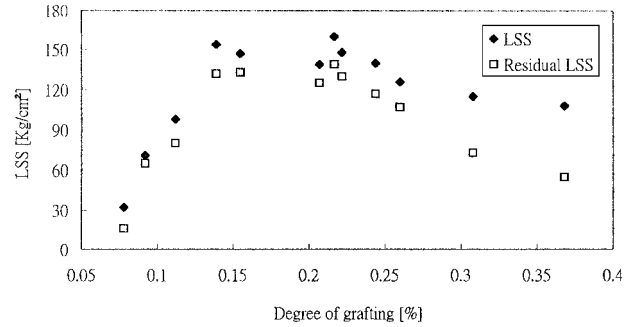
The LSSs of the mPP to steel sheets were shown in Figure 1. Generally, a moderate amount of DCP, such as 1.0 part per hundred of rubber (phr), resulted in the most significant improvement in adhesion. Among the various compound-



**Figure 2** Degree of grafting vs. MAH loading with DCP at 0.1 (▲), 1.0 (■), and 5.0 (●).

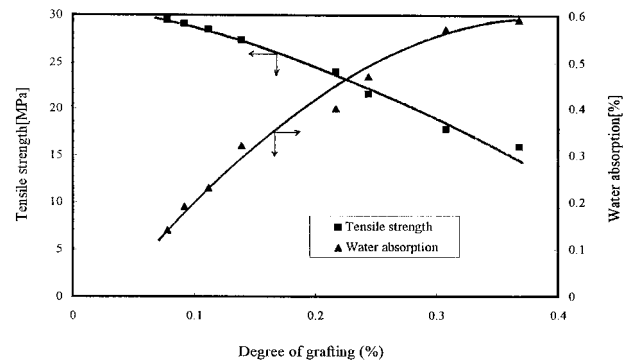
ing conditions, the maximum adhesive strength of 159 kg/cm<sup>2</sup> was obtained at 1.0 phr DCP and 2.0 phr MAH. However, too large or too small a proportion of DCP was less advantageous to the bondability of grafted PP. It was reported in ref. 4 that serious chain scission occurred in the system of peroxide-catalyzed grafting PP. A higher amount of DCP was thought to induce more chain scissions and thus result in a decline in the stiffness that usually was an important factor for an adhesion to decide the shear strength of a joint. On the other hand, the proportion of MAH has less significance to the bondability of the mPP film once the MAH/PP weight ratio was > 0.02 (i.e., one molecule of anhydride per 50 C<sub>3</sub>H<sub>6</sub> units). It shows that a small amount of MAH, no more than 2 phr, is sufficient to achieve a strong chemical bonding between PP-g-MAH and the steel substrate. More amount of MAH is unable to promote adhesion further.

Figure 2 shows the dependence of the degree of grafting on the MAH loading with DCP at 0.1, 1.0, and 5.0 phr, respectively. It can be seen that a higher degree of grafting usually is obtained at higher MAH loading. The loading of DCP at 5.0% resulted in a lowest grafting efficiency. On the other hand, the amount of DCP at 0.1% and 1.0% resulted in a higher grafting and showed peak values with MAH at a moderate loading (i.e., 2 phr) and a higher loading (i.e., 10 phr). It was therefore thought that the reaction of grafting favored a lower peroxide loading. Figure 3 demonstrates the dependence of LSS on the degree of grafting. LSS became higher as the degree of grafting increased. The maximum LSS (159 kg/cm<sup>2</sup>) is obtained at a degree of 0.217%. After that, the adhesive joint deteriorated. On the same figure, a comparison of the residual adhesive strength of the joint, soaking in a water bath at

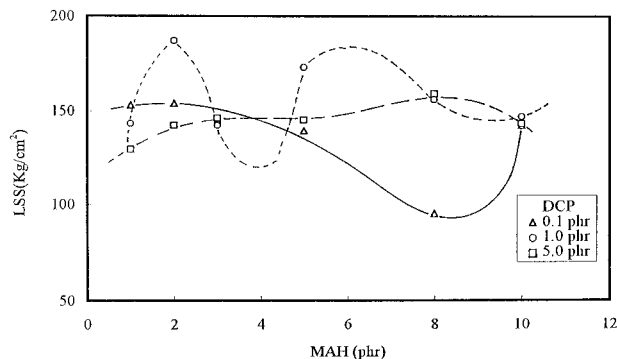


**Figure 3** Initial LSS and residual LSS plotted against degree of grafting.

50°C for 24 h, was made. All the joints deteriorated after aging and all, observed by the naked eyes, fractured cohesively. It is worth noting that the sample with a higher degree of grafting deteriorates more pronouncedly. For example, the joint with a 0.368% grafting deteriorates from 109 kg/cm<sup>2</sup> to 54 kg/cm<sup>2</sup>. Although all other samples with lower and moderate degrees of grafting showed a decrease in adhesive strength, their decreases were not as pronounced as those with a higher degree of grafting. A study on the water absorption of the PP-g-MAH film with a thickness of 1 mm was performed in a water bath at 50°C for 24 hr, and the results were shown in Figure 4. The higher degree of grafting the higher level of water absorption was found. It could be that the excessive carboxyl groups catch more water molecules and resulted in a higher degree of water absorption. This explains well that the joints with higher graftings exhibit lower durability as aged in a warm water bath. In the same figure, the tensile strengths are plotted against the degree of grafting. It was found that the tensile rupture strength decreased as the degree of grafting increased. The possible reason responsible for the



**Figure 4** Dependence of tensile strength and moisture absorption on the degree of grafting.



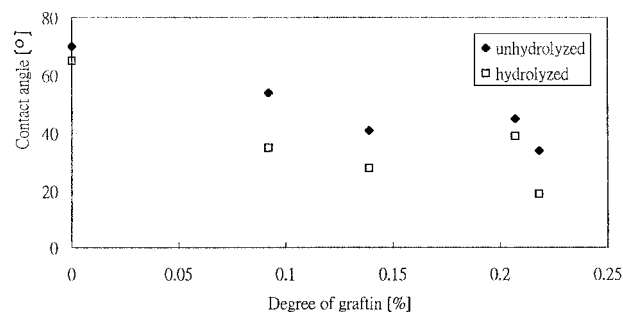
**Figure 5** LSS of hydrolyzed PP-g-MAH film bonded to steel sheets.

decrease of the tensile strength was chain scissions accompanied in an extensive grafting reaction as reported in refs. 4–6. This explains well that the initial adhesive strength becomes poorer as the grafting increases extensively. Therefore, the author believed that a proper amount of the functional groups (i.e., the carboxyl groups in this case) is necessary to offer sufficient sites for chemical reaction and bonding. A further functionalization not only induced a decline of rupture resistance leading to a cohesive failure of the adhesive, but also caused more water absorption and resulted in a deterioration of the interface and the poor durability.

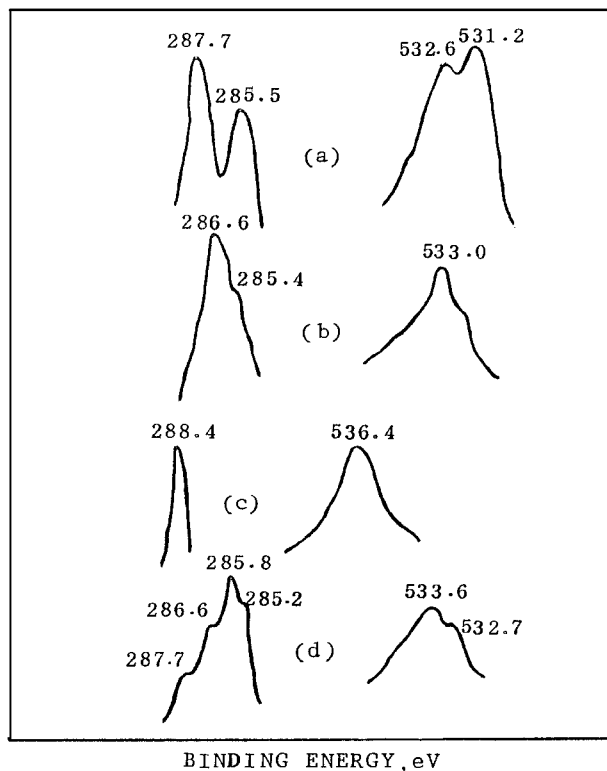
The effect of hydrolysis of mPP was studied. The LSS increased tremendously if the mPP adhesive was hydrolyzed before bonding (as shown in Fig. 5). In particular, for those lower graftings formulated with 0.1 phr DCP, the hydrolyzed films resulted in much higher LSS values than the unhydrolyzed films, increasing up to 3.6 times. For optimum grafting, formulated with 1.0 phr DCP and 2.0 phr MAH, the specimen exhibited an even higher LSS value up to  $187 \text{ kg cm}^{-2}$ , ~18% higher. It was also worth noting that most of the readily hydrolyzed film with 0.1 and 5.0 phr DCP resulted in a ceiling joint strength, ~150  $\text{kg/cm}^2$ . These results raised the hypothesis that an extensive hydrolysis treatment would be able to create much more active sites for bonding by driving the surface transformation of  $-(\text{CO})_2\text{O}-$  to  $(\text{COOH})_2$  to occur more readily, and the latter is more efficient for adhesive bonding. The measurements of contact angles are reported herein for several samples, including the unmodified PP. As can be seen in Figure 6, the contact angle of unmodified PP changed little after 30 min treatment for 90% relative humidity absorption. On the other hand, all of the contact angles of the

mPP samples obviously changed. This was probably attributed to the surface transformation of anhydride from  $-(\text{CO})_2\text{O}-$  to  $(\text{COOH})_2$  due to hydrolysis. It is worth noting that the samples with 0.092% and 0.207% grafting, reacted with 0.1 and 5.0 phr DCP, respectively, showed the final contact angles as  $36^\circ$  and  $39^\circ$ . Such close values of contact angle indicated that the two specimens had very similar wettability after they were readily hydrolyzed. This is in accord with the result of LSS (i.e., most of the specimens came to a ceiling strength of  $150 \text{ kg/cm}^2$  after they were readily hydrolyzed before bondings).

Figure 7 illustrates the  $\text{C}_{1s}$  and  $\text{O}_{1s}$  core-level photoemission spectra from electron spectroscopy for chemical analysis by analyzing the PP-g-MAH surface and fractured surface from lap shearing of the joints using hydrolyzed and unhydrolyzed films. The PP-g-MAH surface in spectrum (a) shows two major peaks for carbon atoms at 285.5 and 287.7 eV, respectively. The peak at 285.5 eV corresponds to the hydrocarbons in the main chain, and 287.7 eV is ascribed to the carbon originating from the carboxyl groups in anhydride. Spectra (b) and (c) represent a pair of fractured surfaces of PP-g-MAH and steel substrate. The hypothesis of weak boundary layer<sup>10</sup> was presumed herein that a very thin layer of residual adhesive remained on the steel surface, although the adherend sides seemed clean when examined by the naked eyes. The spectrum for the adhesive side showed a pronounced peak at 286.6 eV, a carbon–oxygen single bond, and a tiny peak at 285.4 eV. On the other hand, the spectrum for the adherend side showed a shift of the peak to a higher binding energy at 288.4 eV, which is ascribed to a carbonyl carbon (C=O). Spectra (d) correspond to the fractured surface at the adherend side for the hydrolyzed PP-g-MAH debonding from the steel surface. It showed four peaks at 285.2, 285.8, 286.6, and 287.7 eV, respectively,



**Figure 6** Contact angles of ethylene glycol on various PP and mPP samples.



**Figure 7**  $C_{1s}$  (left) and  $O_{1s}$  (right) spectra for unhydrolyzed PP-g-MAH (a) and the fractured surface for unhydrolyzed adhesive at adhesive side (b) and adherend side (c), and the fractured surface for hydrolyzed adhesive at adherend side (d).

and looked like a spectrum combining spectra (a) and (b). Accordingly, the  $C_{1s}$  core level photoemission spectra suggested that the failure loci for shearing the bonds of the unhydrolyzed PP-g-MAH to steel is through the MAH itself. On the other hand, the failure loci for shearing the bond of the readily hydrolyzed PP-g-MAH to steel is between the MAH and PP (i.e., degrafting). For the  $O_{1s}$  core-level photoemission spectra, spectrum (a) represents the PP-g-MAH surface. There are two main peaks located at 531.2 and 532.6 eV, respectively. The oxygen of the carbonyl bond has a lower binding energy than the single-bonded oxygen. Spectra (b) and (c) correspond to a pair of fractured surfaces for shearing the joint of the unhydrolyzed PP-g-MAH to steel. The spectrum for the adhesive side retained a sharp peak at 533.0 eV, possibly shifted from the carbon—oxygen single bond, and a tiny peak corresponding to the C=O groups. This result is in accord with the results from the  $C_{1s}$  spectra that the failure loci for the unhydrolyzed PP-g-MAH detached from the steel surface is through the cleav-

age of the MAH molecule itself that exists on the mPP surface and orients to bond the steel. On the other hand, the spectra of the adhesive side for the hydrolyzed PP-g-MAH debonding from the steel surface shows no observable  $O_{1s}$  peak. This may be ascribed so that the failure loci is through the bonds between MAH and PP.

## CONCLUSIONS

Only a small amount of DCP and MAH in the system of DCP-catalyzed grafting of MAH to PP was sufficient to achieve a strong adhesive bonding to steel substrate. The maximum adhesive strength was obtained at a degree of grafting 0.217%, which was formulated with 1.0 phr DCP and 2.0 phr MAH. Lower grafting offers insufficient sites for bonding and exhibits lower adhesive strength. On the other hand, higher grafting may weaken the cohesive strength of mPP and exhibits a decline of adhesive strength again. Higher graftings also led to a poorer durability of the adhesive joint, probably due to absorbing water more extensively. Hydrolysis of the grafted anhydride [i.e., the surface transformation of  $(CO)_2O$ — to  $(COOH)_2$ ] has a significant effect on the promotion of the adhesive strength. The ESCA study showed that the failure loci for the unhydrolyzed PP-g-MAH debonding from the steel surface was through the cleavage of the MAH itself. On the other hand, degrafting between MAH molecules and PP dominated when the readily hydrolyzed PP-g-MAH was applied.

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