

STUDIES ON THE INTERFACIAL ADHESION BETWEEN FUNCTIONALIZED POLYPROPYLENE AND POLYAMIDE 1010*

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Abstract The interface behavior of polyamide 1010 (PA1010) and polypropylene (PP) was studied. In order to improve their interfacial adhesion, functional PP was prepared by means of grafting glycidyl methacrylate (GMA) on PP main chains and used instead of plain PP. Several technological characterizations were performed here on their interfaces. ESCA was used to confirm that some kind of reaction occurred between end groups of PA1010 and epoxy species of PP-g-GMA. The peel test was adopted to measure interfacial adhesion. It was found that the fracture energy of interfaces between PA1010 and PP-g-GMA was dramatically increased with the content of GMA. Their interfaces were observed as being blurred by using SEM and TEM and a crack that could be seen in the case of the interfaces of the PA1010 and the plain PP disappeared.

Keywords Polyamide 1010, Polypropylene-g-GMA, Interface behavior, Adhesion

INTRODUCTION

Interfaces of polymer blends play an important role in polymer processing through the processes of wetting, absorption and adhesion, which have very dramatic effects on the kinetics of phase separation and their physical and mechanical properties. In a polymeric system the dispersion and morphology of a blending component are controlled by the kinetics of phase separation. And the kinetics depends crucially on the energetic cost of developing concentration gradients (interface)^[1].

For compatible polymer blending system, an adhesive bond is formed by means of inter-diffusion of molecules across the interface^[2, 3]. Good adhesion is generally obtained when the molecules diffuse sufficiently to create entanglements on both sides of the interfaces. However, if two polymers are incompatible, mutual diffusion is limited and bond strength is low. Two common effective ways of increasing the adhesion at incompatible interface are adopted by the addition of graft or block copolymers^[4-10] or forming reactive bonding^[11, 12].

PA1010 is a kind of engineering plastics developed in China. In order to improve its brittleness at low temperature, and its electric properties and also decrease the price, it could be blended with some kind of polyolefins. As is well known, PA1010 and polyolefins are immiscible with each other and their mechanical properties are poor due to their poor interface adhesion. This could be overcome by adopting functional polyolefins to replace the normal one. In this work PP-

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g-GMA was used to blend with PA1010 and good mechanical properties were obtained for this binary blend. Several technologies were used to characterize their interface behavior. The peel test was used to measure the fracture energy of adhesion between PP-g-GAM and PA1010. ESCA was adopted to characterize interfacial chemical reactions of GAM and PA1010. In particular, the effect of concentrations of functional groups, bonding temperature and time on fracture energy and morphologies of interfaces were tentatively studied.

EXPERIMENTAL

PA1010 ($\eta_t = 2.1$) used in this work was supplied by Jilin Shijinggou Union Co. (China). Polypropylene (PP) was provided by Panjin Gas Chemical Co. (China). Containing 10mol% ethylene, its trade name is P340. PP-g-GMA samples and blends of PA1010 and PP-g-GMA were prepared by the reaction extruding method. The preparation methods are described in a previous paper^[13]. The content of GMA in the PP-g-GMA samples used in this work were 0.26%, 0.33%, 0.57%, 0.77% and 1.07%, respectively. Before the test all samples were dried in a vacuum oven for 12 h at 80°C.

The adhesion between two phases was determined by the peel test. The fracture energy of adhesion per unit interfacial area G_a is given by^[14]:

$$G_a = (\lambda - \cos\theta)P \quad (1)$$

where λ is the extension ratio of the flexible member, θ is the peel angle and P is the force per unit width. The peel tests were carried out on an Instron 1121 tester at a peel rate of 0.09 cm/s. The sizes of the strips of PP and PP-g-GMA were 20×4×0.05 cm and 6×4×0.4 cm for PA1010 plates which were prepared by compression molding. Plates of pure PA1010, PP and PP-g-GMA were put on a press under slight pressure. The bonds were peeled at an angle of 180°. Since the extension of strips was very small during peeling, we assumed $\lambda \approx 1$. So the fracture energy of adhesion could be expressed as:

$$G_a = 2P \quad (2)$$

The PA1010 molecular chains grafted to the PP-g-GMA at the interface were characterized by the areal density, Σ . The majority of the bulk PA1010 which did not react with PP-g-GMA was removed by dissolving in the formic acid for three times, and each time took about 8 h. The areal density of PA1010-g-PP copolymer at the interface can be expressed by^[12]:

$$\Sigma = N_a \rho / M_n = -(N_a \rho / M_n) \lambda \ln[1 - (N/C)/(N/C)_\infty] \quad (3)$$

where (N/C) and $(N/C)_\infty$ are the normalized N_{1s} counts for studied samples and pure PA1010 respectively. λ is the escape length of N_{1s} electrons including the take off angle of the instrument and is 1.9 nm^[12]. N_a is the Avogadro's number, ρ is the mass density of PA1010 and M_n is the number average molecular weight of PA1010. From the intensity of the measured XPS, we could calculate the areal density of copolymer at the interface. The XPS measurement was carried out on ESCA CAB MK- II electron spectrometer (VG Co.).

Morphologies of interfaces were observed on a JXA-840 scanning electron microscope. The joined samples were sectioned under cryogenic conditions. Phase contrast between PA1010 and polypropylene was achieved by staining the PA1010 phase with an alcohol solution (1% by weight) of iodine for a period of 12 h.

A Philips 400T transmission electron microscope was also used to observe the interfacial morphology. The samples were cut from the welded sheets which include the PA1010/PP-g-GMA joint. The cubical sample was pretrimmed with a glass knife and then microtomed with a 35 Diatome diamond knife using a Reichert Ultracut S microtom. Sections were stained with phosphotungstic acid, which can selectively stain PA1010.

RESULTS AND DISCUSSION

The Formation of Copolymer at the Interface

In our previous paper^[15], FTIR was used to characterize the formation of PA1010-g-PP copolymer in the reactive blends. Here, XPS was used to calculate the amount of PA1010 grafted onto PP-g-GMA. Figure 1 shows XPS spectra in the nitrogen region for samples with various values of GMA contents in PP-g-GMA. From this figure, it is important to notice that there is only one peak for nitrogen at 399.8 eV, which is in good agreement with the literature value for amides^[16]. For the plain PA1010, two peaks for nitrogen are observed: one belongs to an amide (399.8 eV), the other to an amino group (400.7 eV). This implies that $-NH_2$ end groups in PA 1010 have reacted with PP-g-GMA. Figure 1 also clearly shows that the intensity of the bonding energy of N_{1s} increases with the amount of GMA contents in PP-g-GMA, indicating that PA1010 grafted on PP-g-GMA increases with the content of GMA in PP-g-GMA.

Effect of Concentrations of Functional Group on Adhesion Bond Strength

The increase of the functional group would increase the adhesion bond strength.. The relationship between adhesive bond strength and concentration of the functional group can be expressed by a Langmuir adsorption isotherm^[14]:

$$\sigma_f = \sigma_{f,m} \theta = \sigma_{f,m} [b C / (1 + b C)] \quad (4)$$

where $\sigma_{f,m}$ is the interfacial strength at complete surface coverage, θ is the fractional coverage, C is the concentration of the functional groups in bulk, and b is a constant. Figure 2 shows the peel strength as a function of concentration of GMA in PP-g-GMA. The joint strength increases significantly with GMA contents and levels off to a plateau. It fits a Langmuir adsorption isotherm well. In some cases as little as 0.26% (mole fraction) of the functional groups can dramatically increase the adhesive strength. The effectiveness of functional groups in adhesion promoting is quite specific with respect to the surface chemical composition. The interfacial strength is dependent on the amount of *in situ* formed copolymer and corresponding reaction kinetics.

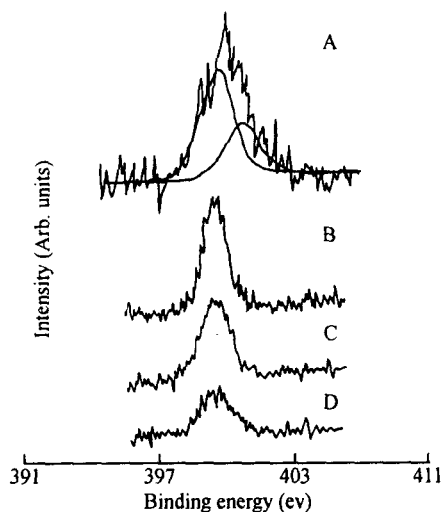


Fig. 1 XPS spectra of N_{1s} of PA1010 and blends of PA1010/PP-g-GMA with different GMA contents

A) 0%, B) 0.26%, C) 0.57%, D) 0.77%

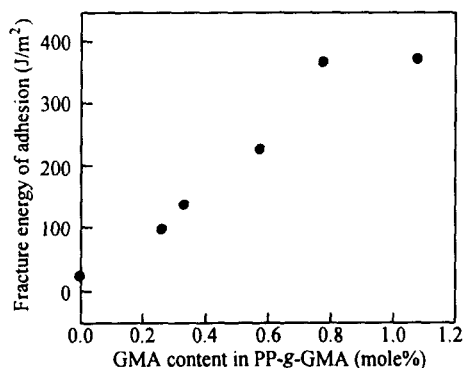


Fig. 2 Peel strength in the interfaces of PA1010/PP-g-GMA blends as a function of concentrations of GMA

The areal density of PA1010-g-PP copolymer at the interface can be obtained from Eq. (3), the GMA contents in PP-g-GMA versus the areal density of copolymer (Σ) is given in Fig. 3.

It was found that Σ increased significantly with GMA contents, eventually achieving a constant value at 0.7~0.8% GMA content. This result indicates that the reinforcement effect is due to the interfacial chemical bonding between PA1010 end groups and epoxy species in PP-g-GMA , the interfacial adhesion is proportional to the *in situ* formed copolymer amount at the interface. Within the scope of GMA content in PP-g-GMA used in this work, G_a increases with the amount of copolymer at the interface, the constant of G_a at higher GMA contents seems to correspond to the saturation of *in situ* formed PA-g-PP-g-GMA copolymer. So, excess amounts of the functional groups are not necessary and they may degrade the bulk properties and thus adversely affect the bonding strength.

Two reactive kinetics models were built up to explain the situation of the *in situ* formed copolymer at the interfaces with different GMA contents in PP-g-GMA (Fig. 4). One model is for low GMA contents, and the other is for higher GMA contents. For the PP-g-GMA with high functional contents, it is possible that the interfacial reaction occurs in one PP- g -GMA molecule at several reaction sites, and reacted PP-g-GMA distributed along the interface, as shown in Fig. 4A. In this case, it is difficult for other reactive molecules to diffuse through the interface to react with PA1010 and further increase in GMA contents cannot produce a reaction. But for the low content GMA in PP-g-GMA, the reacted PP-g-GMA did not distribute along the interface due to the relatively few functional sites in this case and the interfacial reaction can go on if the reactive groups are available from other PP-g-GMA molecules.

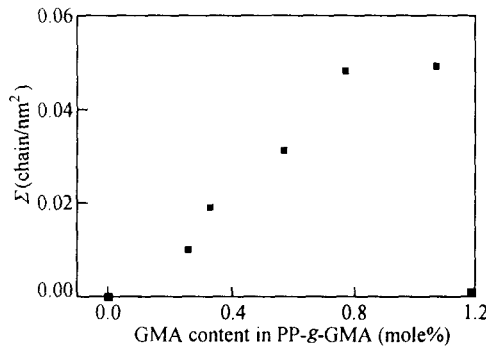


Fig. 3 The dependence of areal density of *in situ* formed PA1010-g-PP-g-GMA at interfaces on the contents of GMA in PP-g-GMA

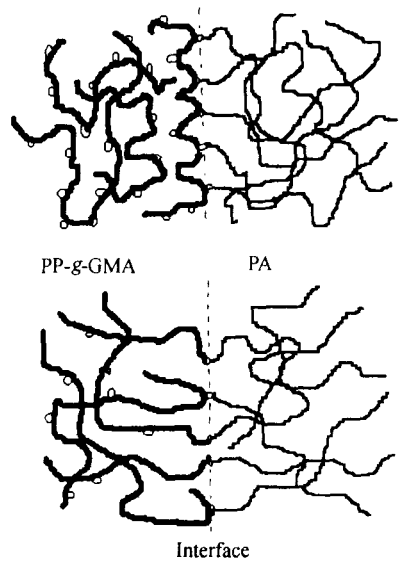


Fig. 4 Reaction models of PA1010 and PP-g-GMA
A) for high GMA content in PP-g- GMA
B) for low GMA content in PP-g-GMA

Figure 5 shows SEM micrographs of PA1010/PP, PA/1010/PP-g-GMA interfaces. The lighter region on the left side of the micrograph is PP or PP-g-GMA and the darker region on the right is PA1010, which has been stained with iodine. The interface of PA1010 and pure PP shows a crack between two phases and almost no mutual adhesion. Compared with the interface of PA1010 and PP, it is clearly seen that the interfaces containing PP-g-GMA have an improved adhesion between two polymers. As the GMA contents in PP-g-GMA increase, the interface becomes blurred. When the PP-g-GMA sample with 1.07% GMA content was used, it formed a diffusion boundary because of the reaction occurring at the interface.

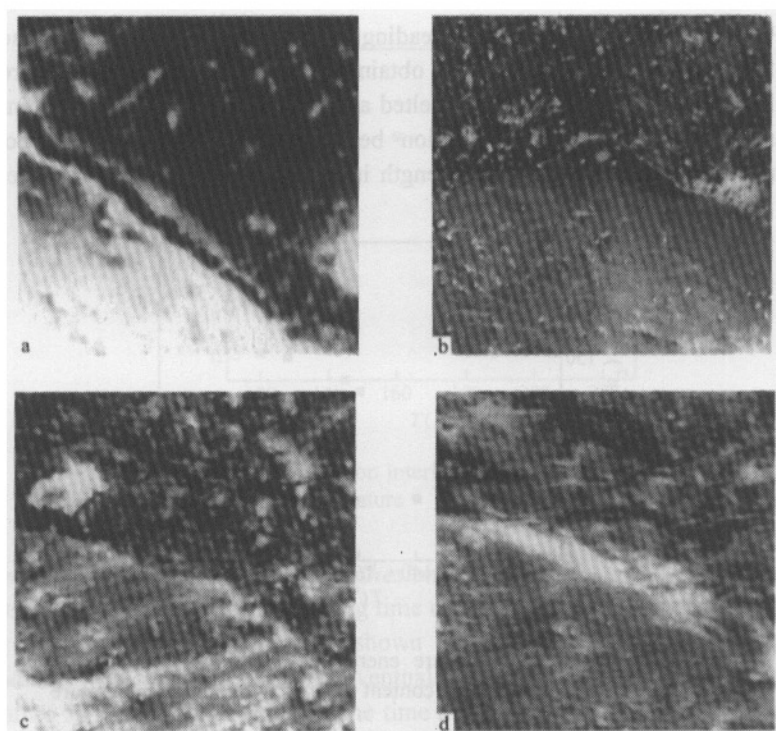


Fig. 5 SEM pictures of interfaces of couples consisting of PA1010 (on upper side) and PP-g-GMA (on lower sides) ($\times 3500$)

Contents of GMA in PP-g-GMA: a) 0%, b) 0.26%, c) 0.33%, d) 1.07%

TEM pictures were also obtained in this work by using phosphotungstic acid as the staining agent, as shown in Fig. 6. Unfortunately, it is difficult to distinguish the interfacial region and impossible to determine the change of interfacial thickness.

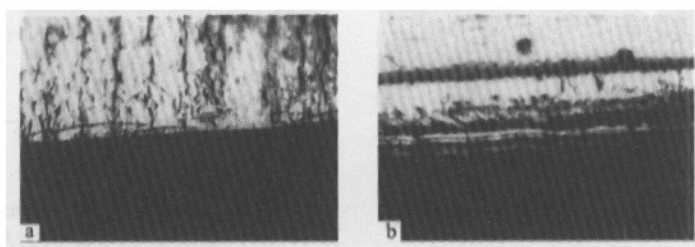


Fig. 6 TEM pictures of sample C and sample D in Fig. 5
The black part is PA1010. a) Sample C, b) Sample D

Effect of Temperature on the Fracture Energy of Adhesion

The interfacial adhesion intensity as a function of temperature is shown in Fig. 7. The overall trend is that with increasing bonding temperature the fracture energy increased. But, the dependence of interfacial strength on temperature shows different behaviors for non-reactive and reactive systems. For the reactive interface, the increase of interfacial adhesion with bonding temperature occurs in different patterns at three distinct regions. First, PP-g-GMA adheres weakly to PA1010 with apparent interfacial failure when the bonded temperature is lower than the melting temperature of PP. When the bonding temperature is higher than T_m of PP and lower than T_m of PA1010 G_a increases with temperature. The molecular mobility of PP increases significantly and results in the

diffusion of PP-g-GMA into PA1010, thus leading to the increase of coupling amount between PA1010 and PP-g-GMA. The highest G_a is obtained near the melting temperature of PA1010 because both PP-g-GMA and PA 1010 are melted and the mobility of PA1010 amino end groups increases dramatically, and chemical reaction between GMA and PA1010 becomes highly possible. It should be noted that the peel strength increases sharply near their respective melting points.

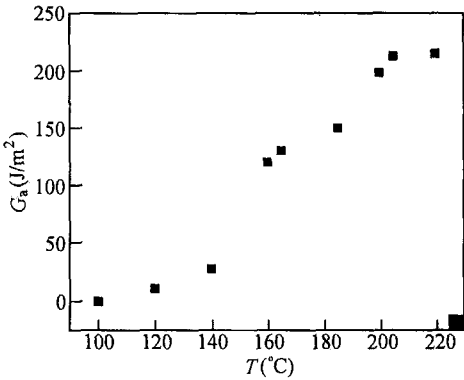


Fig. 7 Dependence of fracture energy of adhesion G_a of plaques PA1010 and PP-g-GMA (GMA content 0.57%) on bonding temperature

SEM pictures could also provide some evidence. As shown in Fig. 8A, the plaques of PA1010 and PP-g-GMA stuck together at 125°C did not show any bonding to occur. But when the temperature was raised to 165°C, PP-g-GMA started to melt and its chains were able to diffuse. The polar GMA groups may diffuse into the interface region and react with the amino or carboxyl groups of PA1010. When the temperature was increased further, both PP-g-GMA and PA1010 melted, and the highest reactivity was obtained.

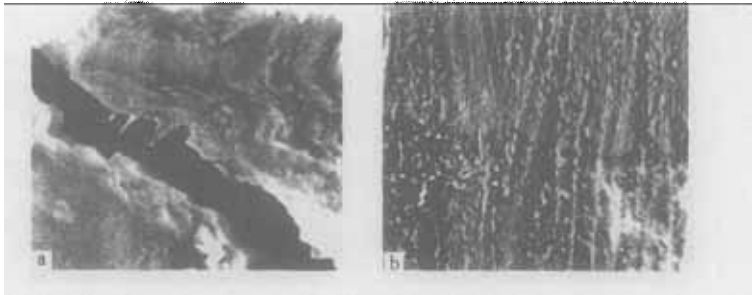


Fig. 8 SEM pictures of interfaces of plaques of PA1010 and PP-g-GMA (content of GMA, 0.57%) at bonding temperatures: a) 125°C, b) 165°C

Dependence of G_a of interfaces of plaques of PA1010 and PP on bonding temperature is shown in Fig. 9. The adhesion between plain PP and PA1010 was very weak and in some cases, PP and PA1010 would separate from each other during sample preparation. But, their interfacial adhesion still increased with temperature. It could be noted that at a temperature over 160°C, a sudden increase in adhesion happened. This behavior can be explained as follows: at this temperature range, PA1010 could crystallize, while PP was in the molten state. The crystallization of PA1010 in the vicinity of the interface might result in a breakup of the original interface plane with a subsequent influx of PP melt across the interface. The later crystallization of the PP influxes could induce a mechanically interlocked interface and cause an increase in interfacial adhesion^[17].

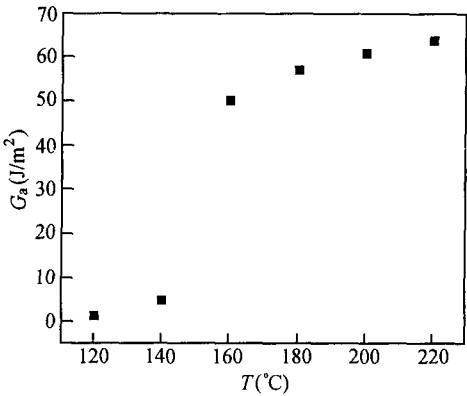


Fig. 9 Dependence of G_a on interfaces of plaques of PA1010 and PP on bonding temperature

Effect of Bonding Time on the Interfacial Adhesion

In order to determine the effect of the bonding time on the fracture energy of adhesion, a relatively low bonding temperature was chosen. As shown in Fig. 10, the fracture energy of adhesion increases gradually with bonding time and eventually levels off to a constant value at about 150 min. This feature suggested that the longer the time available for diffusion, the higher the amount of reaction between PP-g-GMA and PA1010.

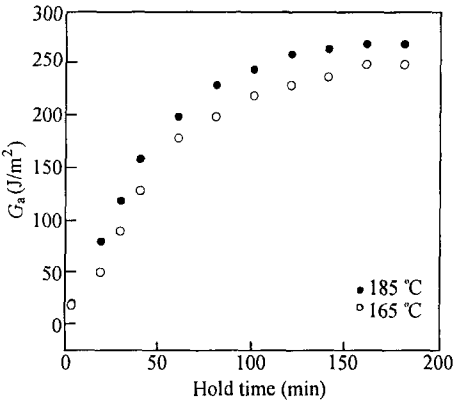


Fig. 10 Dependence of fracture energy of adhesion of plaques of PA1010 and PP-g-GMA (0.57% of content of GMA) on bonding time

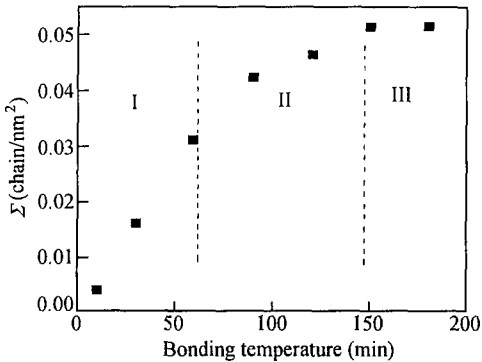


Fig. 11 The amount of PA1010-g-PP-g-GMA copolymer formed by the interfacial reaction as a function of bonding time
Bonding temperature fixed at 185 °C

The reaction kinetics was analyzed by plotting of the areal density of *in situ* formed copolymer versus time, based on the Fredrickson's reaction kinetics theory^[18]. As shown in Fig. 11, in the early stage of the reaction (regime I), corresponding to the times $\tau \ll t \ll \tau_p$ (where τ_p is the terminal relaxation time; τ corresponds to the longest Rouse time for the chains below the entanglement threshold), both the depletion of reactive groups at the interface and the copolymer saturation effects are negligible. The interfacial concentration of reactive chains is approximately fixed at the initial concentration, the number of copolymer chains formed at interface in the time interval t can be expressed as:

$$\Sigma(t) = K C_A C_B t \tag{5}$$

where C_A and C_B are the concentrations of type A and type B reactive groups in the interfacial

region, respectively. From Fig. 11, can be seen that there is a good relation between Σ and bonding time at the initial stage.

At the intermediate regime (regime II), i.e. $\tau_p \ll t \ll \tau_o$, where τ_o is the time for the build-up of the copolymer coverage, the reactive concentration at the interface $C(t) = C_o [\pi t / \tau_p]^{-1/4}$ is reduced below the bulk concentration C_o , and copolymer coverage grows as:

$$\Sigma(t) = (2 / \pi^{1/2}) C_o (D_o t)^{1/2} \quad (6)$$

the amount of the copolymer is controlled by center-of-mass polymer diffusion and independent of the reaction kinetics constant, i.e. K . In the third stage (regime III), a saturation of Σ is observed, corresponding to $t \gg \tau_o$. In this regime, the coverage at the interface has built up to the extent that a significant chemical potential barrier appeared for reactive chains near the interface. The reactant depletion effect could be negligible, but the copolymer saturation effect should be critical.

CONCLUSION

The interfacial adhesion between PA1010 and PP-g-GMA or PP could be determined by a peel test. It was found that the fracture energy between two phases was related to GMA contents in PP-g-GMA, which determined the amount *in situ* formed copolymer at the interface. The formation of PA1010-g-PP-g-GMA copolymer was an important factor for controlling the final interfacial strength. Within the scope of GMA content used in this work, the interfacial adhesion increases with the content of GMA in PP-g-GMA. The fracture energy of adhesion changes significantly near the melting temperatures of PP and PA1010. The plot of G_a versus bonding time could be divided into three different regions. This feature could be attributed to different reaction kinetics behavior at the interfaces.

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