

Grafting of Glycidyl Methacrylate onto Chlorinated Polypropylene and its Bonding to Aluminum Flake

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ABSTRACT: Glycidyl methacrylate (GMA) was grafted onto chlorinated polypropylene (CPP) in the molten state using benzoyl peroxide (BPO) in the presence of styrene (St) as a comonomer. The differential scanning calorimetry (DSC) results indicated that the thermodynamic curve of unpurified grafted CPP was different from the purified, and showed a new broad endothermic peak at 100°C, which may be attributed to the glass transition temperature (T_g) of remained copolymer of GMA and St. Furthermore, transmission electron microscope (TEM) showed that there were two-phase structures in the grafted CPP. Because the grafted CPP was to be

used as a hot melt adhesive, so the influence of initiator concentration, monomer concentration, and reaction temperature on peel strength was investigated. The experiment results showed that a higher degree of grafting was obtained by using two kinds of monomers, such as GMA and St. Increasing the monomer concentration led to an initial rapid increase in the peel strength. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2515–2521, 2007

Key words: chlorinated polypropylene; grafting; glycidyl methacrylate; adhesiveness

INTRODUCTION

Because of its low cost, versatile properties, and growing commercial application, polypropylene (PP) has become one of the fastest growing and more widely used thermoplastic polymers. However, PP is limited in its application in some fields because of its low surface energy, lack of reactive sites, extremely poor hygroscopicity, and poor compatibility with polar polymers. To overcome these drawbacks, chemical modification become a necessary and effective approach, which expands the available market for its application.¹

Chlorinated polypropylene (CPP) is a random polymer with the introduction of the chloride atom into the PP backbone, which improves its polarity. The physical and chemical properties of CPP is different from PP,^{2,3} but its bonding property is still not satisfied for special need as adhesive, especially, as hot melt adhesive for the aluminum/PP. To improve its bonding property, many studies on the introduction of the polar monomer to CPP backbone was carried out.^{4,5} For instance, acrylic acid was grafted onto CPP by free radical process using toluene as solvent.⁶

Glycidyl methacrylate (GMA) is an interesting monomer owing to its epoxy group, which is frequently used as grafting monomer in melt grafting reaction. Recently GMA's grafting yield can be increased greatly

with the assistance of comonomer like styrene.⁷ And this grafting copolymer was successfully used to compatibilize polyolefin and polyester blends.⁸ At the same time, although the research of grafting reaction of GMA is very popular, its using for CPP grafting in the molten condition has hardly been reported.

The aims of this study is by the melt free radical grafting reaction grafted GMA onto CPP in a internal mixer. The structure of grafting product was explored. And considering the purpose of grafted CPP, which was used as a type of adhesive for aluminum flake, the effects of various factors such as monomer, initiator, and reaction temperature on bonding were also studied systematically.

EXPERIMENTAL

Materials

Chlorinated propylene (number-average molecular weight is 343,268 g/mol by ¹³C-NMR, and the unit mole mass of CPP is 76.5 g/mol.), with average chlorinated content of 31%, was purchased from Guangzhou Jinzhuijiang Chemical, Ltd. (Guangzhou, China). Glycidyl methacrylate (the unit mole mass of GMA is 142.5 g/mol), with a purity of 97%, was purchased from Luoyang Hengguang Chemical, Ltd. (Luoyang, China). Styrene, CP grade, Kemio Chemical, Ltd. (Tianjin, China). Benzoyl Peroxide (BPO) was purified by dissolving it in chloroform and reprecipitating with methanol. Trichloroacetic acid (TCA), CP grade, Damao Chemical, Ltd. (Tianjin, China).

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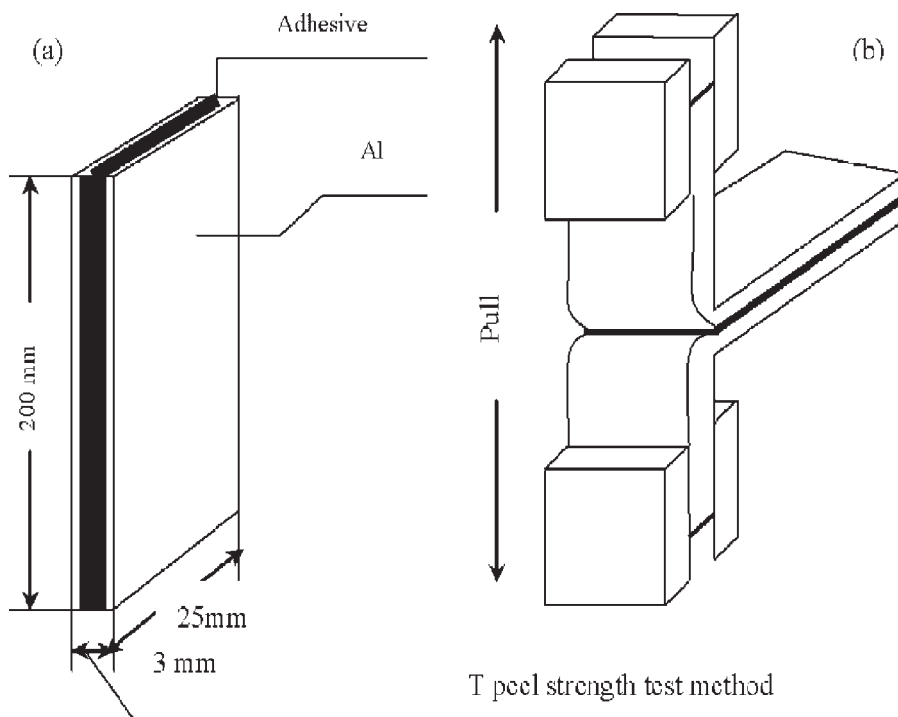


Figure 1 Schematic diagram of T peel strength test: (a) the size of specimen; (b) scheme of T peel strength testing method.

Experimental procedure

The grafting of GMA onto CPP pellets was conducted on internal mixer (Haake Rheomix 600) equipped with sigma blades, and mixing speed was 100 rpm. In the typical grafting process, the CPP pellets was moistened with the mixture of GMA, St, and BPO at room temperature for about 9 min in order that the mixture would be absorbed by the CPP pellets. Actually, in this procedure, it was found that CPP was capable of absorbing liquid monomers completely, thus facilitating material feeding and reducing monomer loss. Then the mixture

was fed into a preheated Haake mixer and allowed to react for 10 min. After the reaction had completed, the samples were discharged from the mixing chamber and cooled to the room temperature.

The modified CPP samples were purified in this way: The samples were dissolved in toluene with the concentration of 6% (wt/vol) at 60°C, then precipitated in 10 volumes of acetone at room temperature, and conducted the process above again, to remove residual and polymerized GMA or St. Finally, the purified samples were dried in a vacuum oven for 24 h at 60°C.

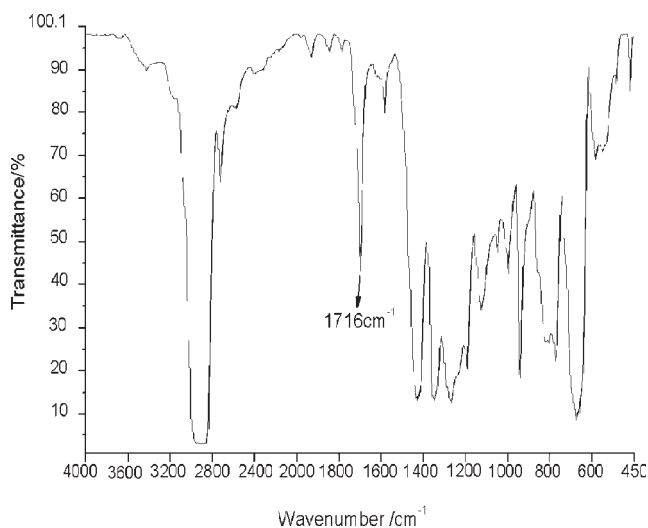


Figure 2 FTIR spectrum of purified gCPP.

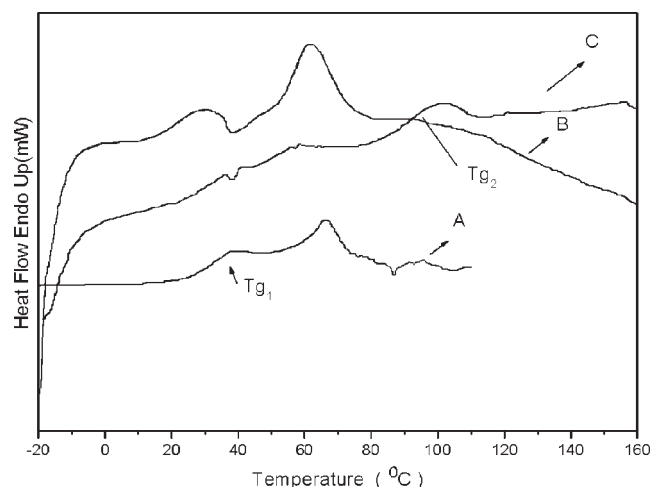


Figure 3 DSC curves of (A) CPP, (B) purified gCPP, and (C) unpurified gCPP.

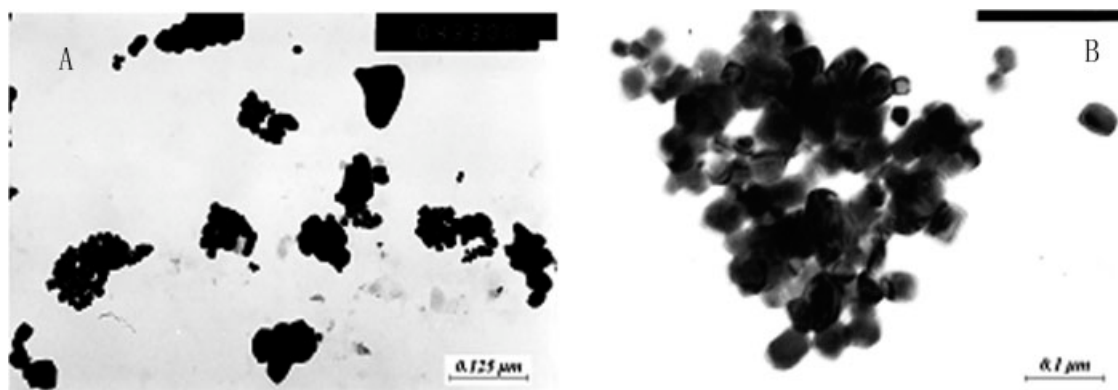


Figure 4 TEM micrograph of grafted CPP (A) ($\times 80,000$) and (B) grafted CPP ($\times 10,000$).

Determination of the grafting yield of GMA by means of a nonaqueous back-titration procedure and $^1\text{H-NMR}$

Nonaqueous back-titration

The grafting degree was determined by a nonaqueous back-titration procedure.⁹ About 1 g of the purified sample was dissolved in 100 mL of hot toluene, followed by the addition of an excess amount of 0.3N trichloroacetic acid (TCA) solution to toluene. The mixture was stirred and maintained at 130°C for 90 min to drive the ring opening reaction of the epoxy group (with the acid) to completion. The residual TCA was titrated with 0.1N ethanolic KOH using isotacphenolphthalein as indicator.

$^1\text{H-NMR}$

The spectra of the GMA-grafted chlorinated polypropylene were performed at 600 MHz on an INOVA 600 spectrometer. The samples were finely cut and were measured in CDCl_3 at room temperature. In all cases, tetramethylsilane (TMS) was used as internal standard.

Determination of the bonding strength of the grafted CPP to aluminum flake

Peel strength tests were conducted using an AG-10KNA apparatus at room temperature according to GB/T 2791-1995, China. Aluminum flake was abraded by sand paper, then washed with acetone, and dried naturally. The gCPP film (0.01 cm thick) was clamped by two aluminum flakes and placed in the hydraulic machine, pressed at 120°C for 3 min, then took out and cooled at room temperature. Appropriate test specimens were cut and used (Fig. 1).

RESULTS AND DISCUSSION

Samples of the purified copolymer were pressed into thin films ($\approx 100 \mu\text{m}$) between two Teflon sheets at 90°C for 3 min under a pressure of 3 MPa. Transmittance spectra of all films were acquired by a Perkin-

Elmer (Spectrum one) FTIR spectrometer after 50 scans at a resolution of 4 cm^{-1} . The FTIR spectra of purified sample shows a peak at 1716 cm^{-1} (Fig. 2), which corresponds to the carbonyl group of GMA. And the peaks of weak intensity, typical of deformation vibrations of the epoxy group, located at 839, and 816 cm^{-1} respectively, which confirms that grafting of GMA onto CPP has occurred.

Thermal behavior of the gCPP

Figure 3 shows DSC curves of CPP (A), purified gCPP (B), and unpurified gCPP (C). It can be seen that the DSC curve of CPP shows a broad baseline transition at 35–39°C. This can be attributed to glass transition temperature (T_g) of CPP. A sharp endothermic peak appeared at 66°C, which corresponds to the fusion of CPP. As can be seen from Figure 3, DSC curve of CPP appears the zigzag when the temperature is above 90°C. It may be that the

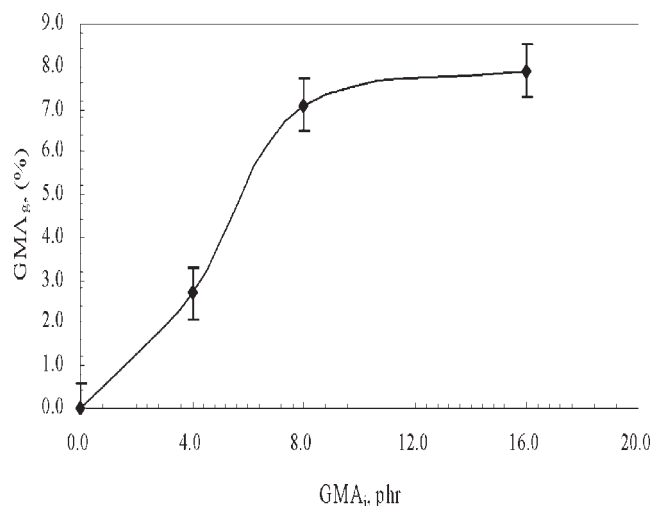


Figure 5 Effect of GMA on the grafting CPP; $[\text{St}]_i/[\text{GMA}]_i = 1$ (mol/mol), $[\text{BPO}]_i = 0.4$ phr, temperature = 140°C, i = initial; g = graft.

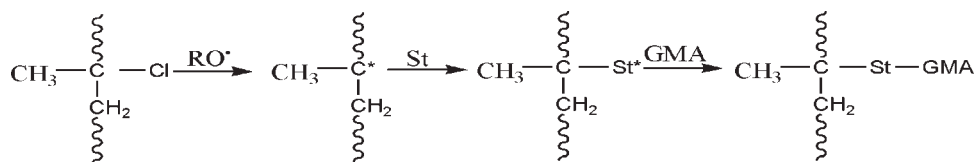


Figure 6 Schematic description of styrene-assisted free radical grafting of GMA onto CPP.

chain degradation reaction happened when CPP is exposed in a high temperature environment. Compared with CPP, purified grafted CPP has a similar thermodynamic curve. However, different from the purified one, the unpurified grafted CPP shows a more complex thermodynamic curve, there is no apparent fusion peak. Furthermore, a new broad endothermic peak begins to appear at 100°C, which may be formed by the T_g of remained copolymer of GMA-*co*-St.

Microscope examination (TEM)

To confirm the existence of GMA-*co*-St, gCPP was dissolved in toluene and formed solution. A drop of solution was placed into container containing distilled water. When the oil-membrane formed by solution extended completely, oil-membrane was adhered onto the Cu-net and dried overnight at room temperature. Transmission electron microscopy (TEM) measurement was carried out with a Japan100SX transmission electron microscope applying an accelerated voltage of 120 KeV.

TEM gives further evidence, which helps to show the morphology of gCPP. Figure 4(A) shows TEM micrographs of the gCPP membrane, which appears that grafted CPP was composed of two phases: a white CPP phase and a dark GMA-*co*-St phase and GMA-*co*-St phase was distributed in the CPP phase. In a higher resolution, as can be seen in Figure 4(B), the dispersed phase was formed by some smaller copolymer particles. Dispersed copolymer particles tend to aggregate in the process of the forming membrane of grafted CPP. The TEM results indicated that the side reaction of monomer copolymerization is existed in melt grafting reaction.

The grafting yield of GMA

Nonaqueous back-titration procedure

In the case of a free-radical-initiated reaction, the use of a comonomer of St cause a more noticeable improvement of grafting yield of GMA (Fig. 5). This is ascribed to the role of such reactive comonomer as St that was acted as a reactive linker between the GMA and CPP. Figure 5 illustrated that GMA's grafting yield tends to level off at high initial GMA concentrations. Although, the GMA's grafting yield is increased as the increase of initial GMA concentrations. This result indicated that, besides grafting reaction, more side reactions, such as degradation, and crosslinking, happen in melt grafting condition.

$^1\text{H-NMR}$

The proposed mechanism of the St-assisted free radical grafting was that St reacted with CPP tertiary macroradicals and the resulting styryl macroradicals then copolymerized with GMA. In this way, instead of grafting GMA directly on CPP chains, the comonomer served as a mediator to bridge the gap between the CPP and GMA monomer, this is depicted in Figure 6.

When GMA was grafted on CPP, the epoxy ring in GMA molecule was opened. In the process of GMA grafted onto CPP, there can be a side reaction, which can produce hydrogen chloride, which can react with epoxy group in GMA molecule (Fig. 7). Owing to the low grafting yield of GMA grafted onto CPP, epoxy groups in GMA molecules reacted with hydrogen chloride produced by side reaction completely. The aforementioned results can be verified by $^1\text{H-NMR}$ spectra. The corresponding $^1\text{H-NMR}$ spectra of GMA-grafted chlorinated polypropylene are shown in Figure 8. In $^1\text{H-NMR}$ spectra of copolymer, the secondary hydrogen resonance of the epoxy ring should lie in between 2.6–2.9 ppm range if epoxy ring was not opened. There was, however, no peak between 2.6–2.9 ppm range in $^1\text{H-NMR}$ spectra of copolymer, which proves that the conclusion above is correct.

The grafting yields of GMA in the copolymer were determined by quantitative $^1\text{H-NMR}$ analysis from the relative areas of the following signals shown in Table I. In the structure of GMA-grafted chlorinated polypropylene copolymer, there is a single aromatic group that contains five hydrogen atoms. The number of hydrogen atoms on the remainder of the graft is 15. Thus the signal from these hydrogen atoms adds up to 3 times than the aromatic signal intensity. So, take the aromatic peak intensity (a), multiply by 3 and subtract that value from the sum of the two big integrals

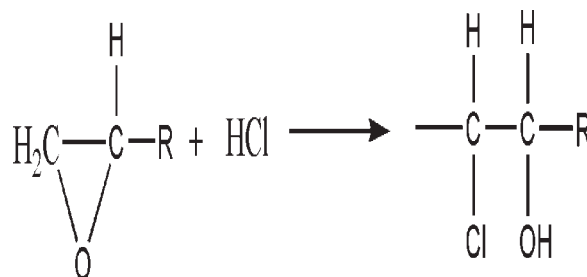


Figure 7 Epoxy group side reactions in melt-reaction procession.

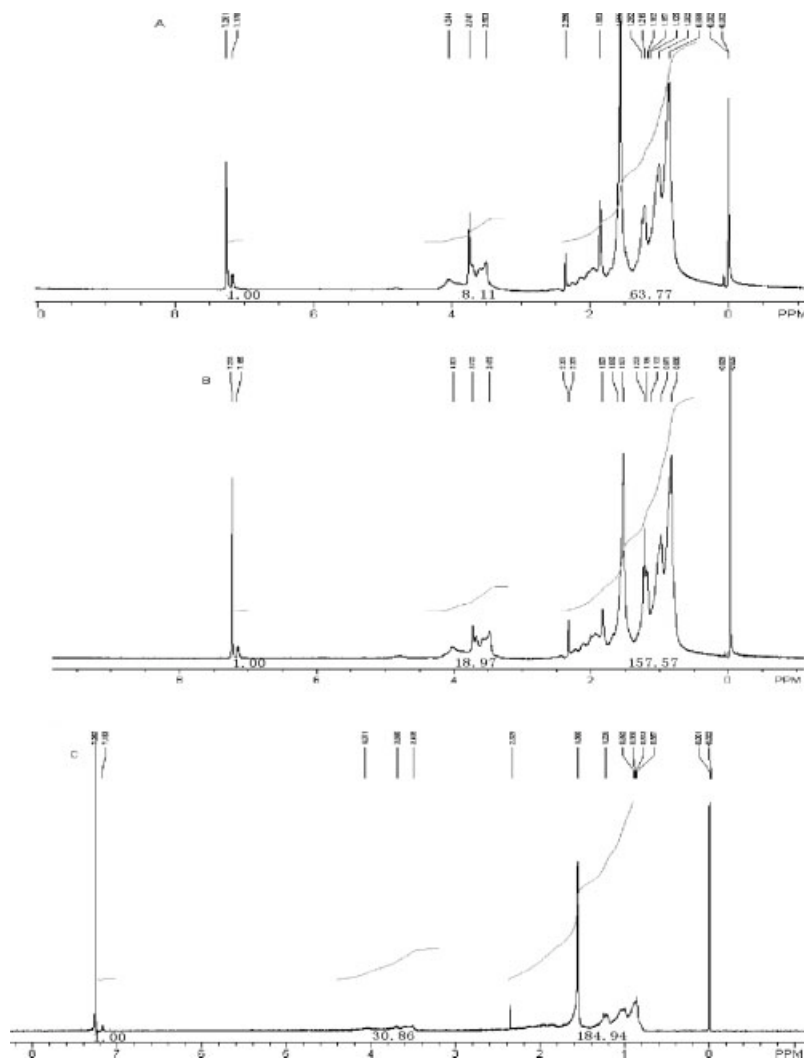


Figure 8 $^1\text{H-NMR}$ spectra of GMA-grafted chlorinated polypropylene; $[\text{St}]_i/[\text{GMA}]_i = 1$ (mol/mol), $[\text{BPO}]_i = 0.4$ phr, temperature = 140°C , i = initial; g = graft. $[\text{GMA}] = 4.0, 8.0,$ and 16.0 phr (A, B, and C), respectively.

is $(A_{0.5-2.4} + A_{3.2-4.4} - 3A_{7.0-7.2})$. CPP mole content is $(A_{0.5-2.4} + A_{3.2-4.4} - 3A_{7.0-7.2})/5$, GMA is $A_{7.0-7.2}/5$, so the mole ratio of CPP to GMA is $(A_{0.5-2.4} + A_{3.2-4.4} - 3A_{7.0-7.2}/A_{7.0-7.2})$. The mole ratio (x) and percentage of the grafting yield mass of GMA in the grafting copolymer is calculated as follows:

$$\text{NMR grafting yield mole ratio } (x) = \frac{A_{0.5-2.4} + A_{3.2-4.4} - 3A_{7.0-7.2}}{A_{7.0-7.2}} \times \frac{M_{\text{CPP}}}{\overline{M}_n(\text{CPP})}$$

$$\text{NMR\% grafting yield mass} = \frac{xM_{\text{GMA}}}{xM_{\text{GMA}} + M_{\text{CPP}}} \times 100$$

where $\overline{M}_n(\text{CPP})$ is number-average molecular weight of CPP, M_{CPP} is the unit mole mass of CPP, and M_{GMA} is the unit mole mass of GMA.

Percentage of the grafting yield mass of GMA in the grafting copolymer is shown in Table II. The GMA's grafting yields are increased with the increasing of initial

GMA concentrations. Table II illustrated that GMA's grafting yields tend to level off at high initial GMA concentrations. In the Figure 5 and Table II, the obtained percentages of the grafting yield mass of GMA in the copolymer have been compared. Data are in good agreement.

Peel strength of GMA-grafted CPP

Effect of reaction temperature

Figure 9 shows the evolution of peel strength as a function of temperature. the peel strength of speci-

TABLE I
Assignment of the Characteristic Signals in the $^1\text{H-NMR}$ Spectra for GMA-grafted Chlorinated Polypropylene Copolymers

$A_{7.0-7.2}$	[5H]	C_6H_6
$A_{3.2-4.4}$	[5H]	GMA
$A_{0.5-2.4}$	[6H]	GMA
	[3H]	C_6H_6
	[5H]	CPP

TABLE II
Effect of GMA on the Grafting of CPP

Sample	[GMA] _i (phr)	Integral areas of hydrogen atoms			Grafting yield mass of GMA by ¹ H-NMR method (%)
		A _{7.0-7.2}	A _{0.5-2.4}	A _{3.2-4.4}	
CPP	0.0	0.00	–	0.00	0.0
A	6.0	1.00	63.77	8.11	2.8
B	9.0	1.00	157.57	18.97	7.0
C	12.0	1.00	184.94	30.86	8.5

[St]_i/[GMA]_i = 1 (mol/mol), [BPO]_i = 0.3 phr, temperature = 140°C, *i* = initial, and *g* = graft.

mens decreased gradually with increasing reaction temperature. Yu et al. reported that CPP and gCPP tended to decompose, and gCPP was more stable than CPP at higher temperature.¹⁰ Because samples preparing lasted for 10 min in a internal mixer at 120, 130, 140, and 160°C respectively. At aforementioned temperatures gCPP will in part decompose, especially at higher temperature, which led to decrease of the bulk strength of gCPP. gCPP broke easily when specimens were carried out in tensile experiment, which result in decrease of the peel strength of gCPP acted as adhesive. Although higher temperature is beneficial to the decomposition of peroxide, but owing to the poor stability of CPP, a lower reactive temperature should be chosen in the melting grafting.

Effect of the peroxide concentration

Figure 10 illustrates the effect of the BPO concentration on peel strength of grafted CPP. The peel strength increases accordingly from 1600 to 2500 N/m when BPO's initial concentration was increased from 0.0 to

0.4 phr. However, when BPO's initial concentration keep on increasing, the evolution of peel strength turns to decrease from 2500 to 900 N/m. the reason might be that great deals of BPO decompose, which generate excessive primary radicals, can facilitate the degradation reaction of CPP's molecular chain. Then the decrease of molecular weight deteriorated the mechanics property of grafted CPP.

Effect of amount of GMA

The effect of initial quantity of GMA on peel strength is also illustrated in Figure 11. It is the commonly accepted fact that the increase of monomers can promote to obtaining a high grafting yield in the melt grafting. But the peel strength that relates to the grafting yield doesn't seem to be proportional to the amount of GMA. In initial process, the peel strength tends to level off at low initial GMA concentrations. For example, at the low amount (GMA) of 0.3, the grafted CPP's peel strength was found to be only 393 N/m. When the amount of GMA is over 6%; however, the peel strength tends to increase rapidly. This

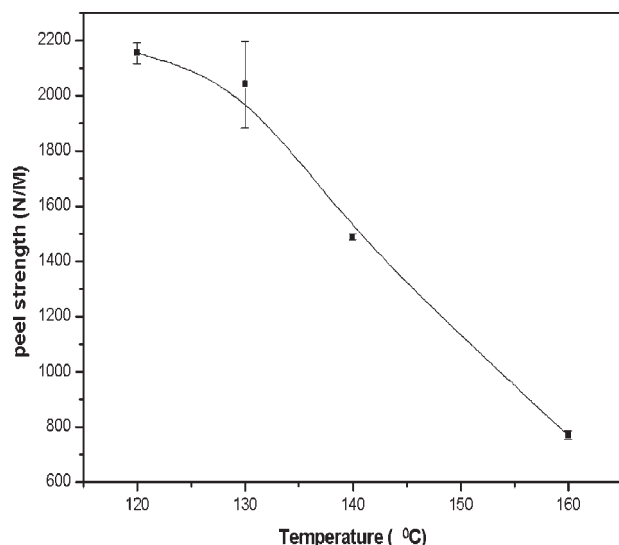


Figure 9 Effect of reaction temperature on the peel strength. [GMA]_i = 10 phr; [BPO]_i = 0.4 phr; [St]_i/[GMA]_i = 1 (mol/mol). Mixing speed = 100 rpm (revolution/min).

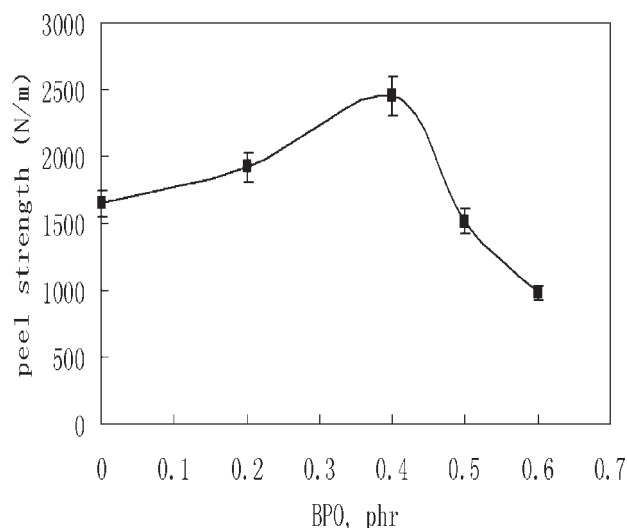


Figure 10 Effect of BPO amount on peel strength [GMA]_i = 10 phr; [St]_i/[GMA]_i = 1 (mol/mol). Mixing speed = 100 rpm, temperature = 140°C.

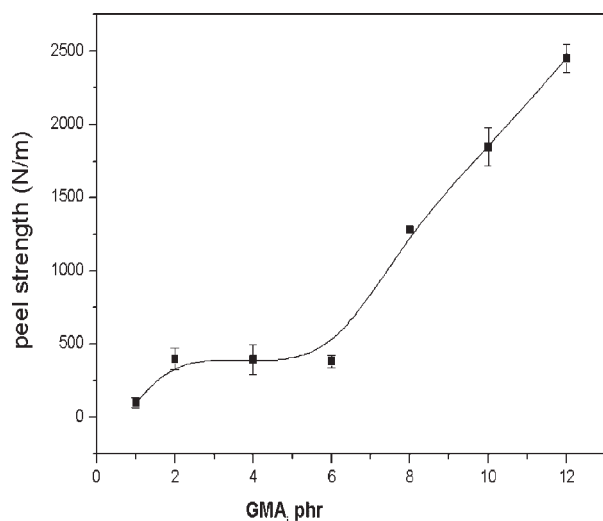


Figure 11 Effect of amount of GMA on peel strength. $[St]_i/[GMA]_i = 1$ (mol/mol), $[BPO]_i = 0.4$ phr, Mixing speed = 100 rpm, temperature = 140°C.

is especially true for high initial GMA concentrations. The reason is that, in the case of CPP, the main side reaction is dyhydrichloride, which lead to a reduction in the molecular weight. Furthermore, the production of HCl wastes certain amount of GMA. Combination of two reasons results in poor peels strength at low initial GMA concentrations.

Effect of different ratios of $[St]_i/[GMA]_i$ on peel strength

Besides acting as a bridge between macromolecular radical and GMA monomer, a second important contribution of St as comonomer lies in its ability to facili-

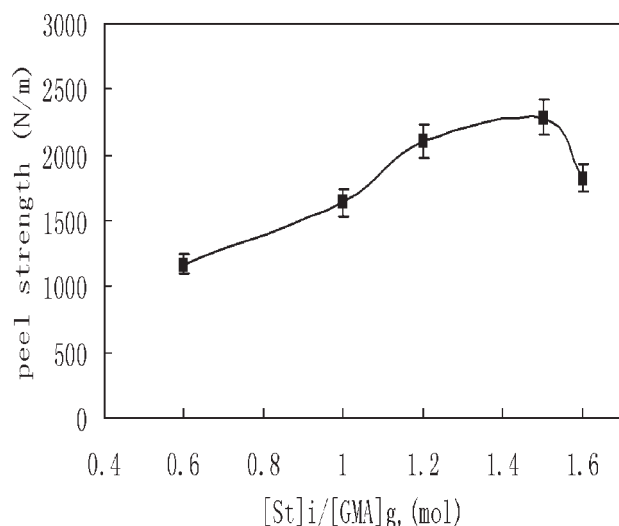


Figure 12 Effect of different ratios of $[St]_i/[GMA]_i$ (mol/mol) on peel strength. $[GMA]_i = 10$ phr; $[BPO]_i = 0.4$ phr Mixing Speed = 100 rpm, temperature = 140°C.

tate the mixing of reactor, which benefits to react completely. Figure 12 showed the peel strength of grafted CPP as a function of the molar ratio of $[St]_i/[GMA]_i$ for a given initial amount of GMA (10%) at 140°C. The more St is added, the higher of the peel strength of grafted CPP can be achieved. It is also clear that the peel strength of grafted CPP is not proportional to the amount of St; and the curve shows a maximum value at concentration ratio of $[St]_i/[GMA]_i$ is 1.3, then followed by a drop at higher ratios of $[St]_i/[GMA]_i$. The presence of a maximum in the peel strength curve must, therefore, be because of the greater propensity of the copolymerization of side reaction at higher ratios of $[St]_i/[GMA]_i$. In fact, instead of grafting reaction, a great deal of monomers happened self-copolymerization in such reactive system. Moreover, the side produce was distributed in the CPP phase, which facilitates further decrease of mechanic property of grafted CPP appeared to act as a plasticizer.

CONCLUSIONS

The bonding property of CPP is not satisfied for special need in adhesive, especially, as hot melt adhesive for the aluminum/PP. in the past study, the researches focused on the introducing the polar monomer on CPP backbone by free radical process using toluene as solvent. However, this method is not friendly to environment because of a great deal of noxious solvents.

Incorporation of the St to the grafting reaction of GMA onto CPP gives rise to an increase of the grafting yield and peel strength with aluminum associated with a significant reduction of the degradation of CPP. As we have shown, it can be seen that some copolymer of GMA and St (GMA-co-St) were dispersed in the phase of grafted CPP, which change the thermal and mechanic properties of CPP. This work has shown that, through the optimizing of parameters, grafted CPP has an high bonding strength for aluminum flake.

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