

# Properties of Poly(vinyl chloride) Blended with an Emulsion Copolymer of *N*-Cyclohexylmaleimide and Methyl Methacrylate

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**ABSTRACT:** Emulsion-polymerized copolymers of methyl methacrylate and *N*-cyclohexylmaleimide were synthesized and used for blending with poly(vinyl chloride) (PVC) to improve the heat resistance of PVC. The thermal stabilities of the blends with different copolymer contents were characterized by thermogravimetric analysis, torsional braid analysis, and

the Vicat softening temperature. The mechanical properties and rheological behavior of the blends were also determined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 201–205, 2003

**Key words:** poly(vinyl chloride); blends; thermal properties; rheology

## INTRODUCTION

Extensive studies have been carried out on the copolymerization of *N*-substituted maleimides with such vinyl monomers as methyl methacrylate (MMA),<sup>1–6</sup> styrene,<sup>7–9</sup> and vinyl chloride,<sup>10–12</sup> to provide superior thermal stability to the resulting copolymers. It has been experimentally and theoretically<sup>13</sup> proven that the incorporated rigid maleimide structure can effectively improve the thermal properties, such as the Vicat softening temperature ( $T_{\text{Vicat}}$ ), heat-deflection temperature, glass-transition temperature ( $T_g$ ), and thermal-degradation temperature, of these copolymers. In addition to their applications as solitary heat-resistant materials, these copolymers are used in blends with other polymers as heat-resistant agents<sup>14</sup> because of the high cost of producing *N*-substituted maleimides.

In this study, copolymers of *N*-cyclohexylmaleimide (ChMI) and MMA were synthesized by the emulsion-polymerization method and were blended with poly(vinyl chloride) (PVC) for the purpose of improving the heat resistance of PVC. The dependence of the thermal properties, mechanical properties, and rheological behavior of the blends on the copolymer contents was studied.

## EXPERIMENTAL

### Materials

ChMI, provided by Zhuozhou Haihui Chemicals Co., Ltd. (China), as a commercial product, was recrystallized from a mixture of alcohol and water and stored in the absence of light before it was used. MMA was washed first with aqueous sodium hydroxide for the removal of the inhibitor and then with water, to neutrality, before it was used. Sodium lauryl sulfate (SLS),  $\text{K}_2\text{S}_2\text{O}_8$ , and  $\text{Al}_2(\text{SO}_4)_3$  were all analytically pure and were supplied by Beijing Chemical Regent Co. (China). The water used in all the experiments was distilled and deionized water (DDW). PVC ( $K = 66–68$  and  $P = 1000–1150$ ), tribasic lead sulfate (TLS), and dibasic lead phosphate (DLP) were supplied by Tianjin Chemical Reagent Co. (China).

### Synthesis of the copolymers

A given amount of SLS was dissolved in DDW in a 1000-mL, four-necked flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen duct. The contents were effectively stirred, and pure nitrogen was passed for 15 min. The temperature was increased to 80°C, and the monomer mixture was added gradually to the flask together with a prepared solution of  $\text{K}_2\text{S}_2\text{O}_8$  with vigorous stirring at 80°C for 1 h. After that, the reaction vessel was maintained at that temperature for 0.5 h and then at 90–95°C for another 1 h. The reaction was stopped and precipitated by being poured into a 3%  $\text{Al}_2(\text{SO}_4)_3$  solution. The precipitated polymer was filtered, washed with methyl alcohol for about 24 h for the removal of the residual ChMI mono-

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**TABLE I**  
Recipe of Emulsion Copolymerization

	Sample		
	1	2	3
MMA (g)	100.0	90.0	70.0
ChMI (g)	0.0	10.0	30.0
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g)	0.4	0.4	0.4
SLS (g)	1.0	1.0	1.0
DDW (mL)	300	300	300

mer and SLS, and then dried in a vacuum oven at 80°C before analysis. The conversion was measured gravimetrically and was always over 96%. The copolymerization procedures followed the recipe given in Table I. The number-average molecular weight and weight-average molecular weight of the copolymer (70:30 MMA/ChMI) detected by gel permeation chromatography were 53,800 and 153,000, respectively.  $T_g$  of the copolymer, as measured by torsional braid analysis (TBA), was 128.0°C.

### Preparation and characterization of the blends

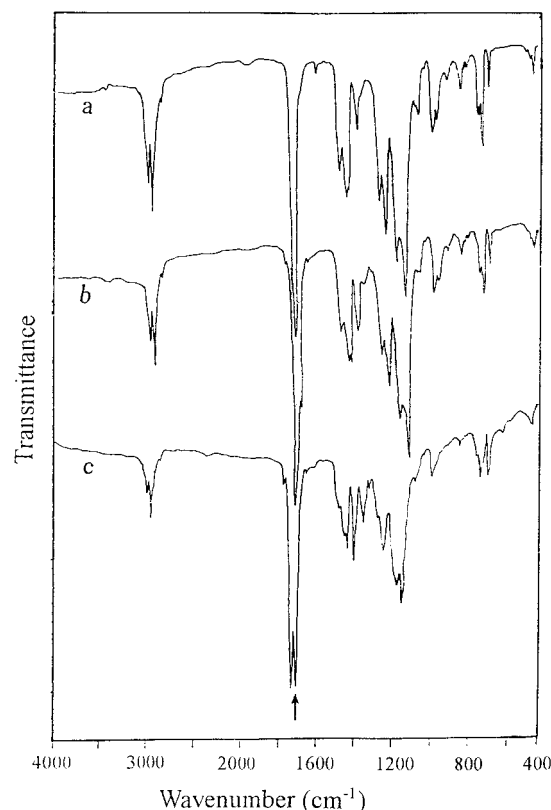
A predetermined amount of PVC, poly(MMA-co-ChMI) (70:30 MMA/ChMI), and additives, according to Table II, were mixed thoroughly, and the mixture was milled on a library two-roll mill for 10 min at 190°C. Sheets were prepared from the blends in the melt through compression molding at 180–190°C. The sheets were kept at 80°C for 6 h for the release of any inner stress. Samples of suitable dimensions for mechanical testing were cut from the sheets with a saw.

The tensile tests were performed with an electronic tensile tester at room temperature. The extension rate was 10 mm/min. Four samples of each were subjected to the tests. The notch impact tests were carried out on an X CJ-40 impact tester under the same conditions with flat specimens 12 mm wide and 5 mm thick. The number of samples of each was 6. The fractured surfaces of the tensile and impact specimens were observed with scanning electron microscopy (SEM) with the method of Zelinger.<sup>15</sup>

Thermogravimetric analysis (TGA) was carried out on a Shimadzu DT-40 thermogravimetric analyzer at a heating rate of 10°C/min under an air atmosphere.

**TABLE II**  
Recipe of Blends

	Sample					
	1	2	3	4	5	6
Copolymer (part)	0	5	10	15	20	25
PVC (part)	100	100	100	100	100	100
TLS (part)	1.5	1.5	1.5	1.5	1.5	1.5
DLP (part)	3	3	3	3	3	3



**Figure 1** FTIR spectra of the copolymers: (a) PMMA, (b) 90:10 MMA/ChMI, and (c) 70:30 MMA/ChMI.

The  $T_g$  values of the blends were determined with a GDP-3 torsional braid analyzer at a heating rate of 2°C/min.  $T_g$  was taken from the maximum of the logarithmic decrement in amplitude per cycle.

The rheological behavior of the blends was investigated with a Shimadzu Koka flow tester. The fixed-temperature method was used. The nozzle diameter was 1 mm, and the nozzle length was 10 mm. The weight of the test specimen was 1.2 g.

The  $T_{Vicat}$  values of the blends were determined at a heating rate of 2°C/min. The temperature at which the needle, with a load of 1 kg, pushed into the sample 1 mm was taken as  $T_{Vicat}$ .

## RESULTS AND DISCUSSION

### Compositions of the copolymers

IR spectra of poly(MMA-co-ChMI) with different monomer mixture proportions are shown in Figure 1. With the incorporation of ChMI units, the most significant feature is the appearance of the absorption peak at 1710 cm<sup>-1</sup>, which is the peak of the stretching vibration absorption of carbonyl groups in ChMI units in the backbones of the copolymers.<sup>6</sup> The peak at 1710 cm<sup>-1</sup> gradually increases with an increasing ChMI feed content. When no ChMI is fed, there is no absorption at 1710 cm<sup>-1</sup> on the Fourier transform infrared

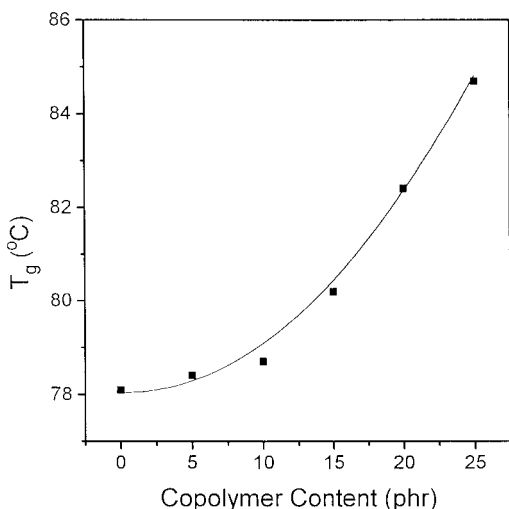
**TABLE III**  
**Elemental Analysis Results of Copolymers**

Sample	MMA/CHMI in feed monomers	N content in copolymers	MMA/CHMI in copolymers
1	100:0	0.000	100:0
2	90:10	0.746	90.5:9.5
3	70:30	2.220	71.6:28.4

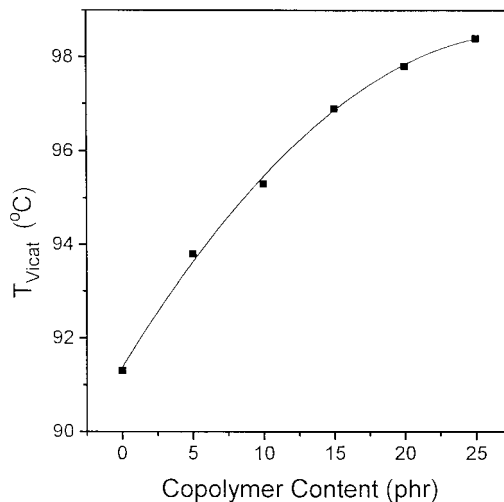
(FTIR) spectrum. This indicates that the ChMI content in the copolymer increases with an increasing ChMI feed content. The conclusion is supported by the elemental analysis results (Table III). The data show that the composition of the copolymers is similar to the recipe of the monomer feed.

**$T_g$  and  $T_{Vicat}$  of the blends**

The relationships between the copolymer content and the values of  $T_g$  and  $T_{Vicat}$  of the blends are shown in Figures 2 and 3. As shown in Figure 2,  $T_g$  of the blends increases with an increasing amount of the copolymer in the blends. The  $T_{Vicat}$  value of PVC that we obtained in this article is 91.3°C. When 20 parts of the copolymer are blended with 100 parts of PVC,  $T_{Vicat}$  of the blend is 6.5°C higher than that of PVC. The same tendency is also illustrated in Figure 3. Both the  $T_g$  and  $T_{Vicat}$  values reflect the ability of the chain segments to move. The more difficult it is for the chain segments to move, the higher  $T_g$  and  $T_{Vicat}$  are. The carbonyl group and the rigid bulky maleimide units in the backbone of poly(MMA-co-ChMI) result in a chain with higher polarity and stiffness than the chain of PVC. When blended with PVC, the copolymer increases the interaction between the macromolecular chains and reduces the ability of the chain segments to rotate. The



**Figure 2** Relationship between  $T_g$  and the copolymer content.

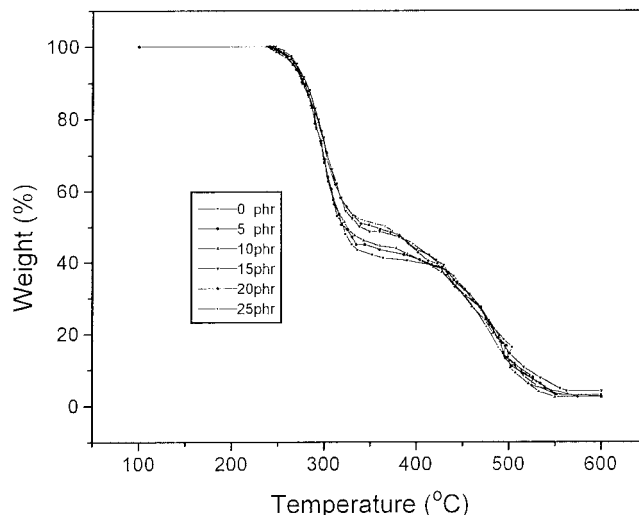


**Figure 3** Relationship between  $T_{Vicat}$  and the copolymer content.

increase in  $T_g$  and  $T_{Vicat}$  means that the copolymer of MMA and ChMI enhances the heat resistance of PVC.

**TGA**

The TGA curves of the polymers are presented in Figure 4. All the polymers show the same initial degradation temperature, and, like PVC, all the blends undergo a two-step degradation process. The result is reasonable because a small amount of the blended copolymers would not affect the degradation behavior of PVC much. The increasing amount of residual mass at the plateau and the second step is attributable to the thermal stability of poly(MMA-co-ChMI), which is higher than that of PVC. The initial degradation temperature of the copolymer of MMA and ChMI (70:30) is 288.4°C, and that of PVC is 243.0°C.



**Figure 4** TGA curves of the blends with different copolymer contents.

**TABLE IV**  
**Mechanical Properties of the Blends with Different Copolymer Contents**

Property	Copolymer content (phr)					
	0	5	10	15	20	25
Tensile strength (MPa)	$66.8 \pm 1.08$	$66.0 \pm 0.6$	$68.0 \pm 0.55$	$68.6 \pm 0.89$	$68.8 \pm 0.7$	$71.0 \pm 0.76$
Impact strength ( $\text{kJ}/\text{cm}^2$ )	$2.57 \pm 0.14$	$2.86 \pm 0.2$	$2.90 \pm 0.18$	$2.82 \pm 0.02$	$2.72 \pm 0.06$	$2.23 \pm 0.2$

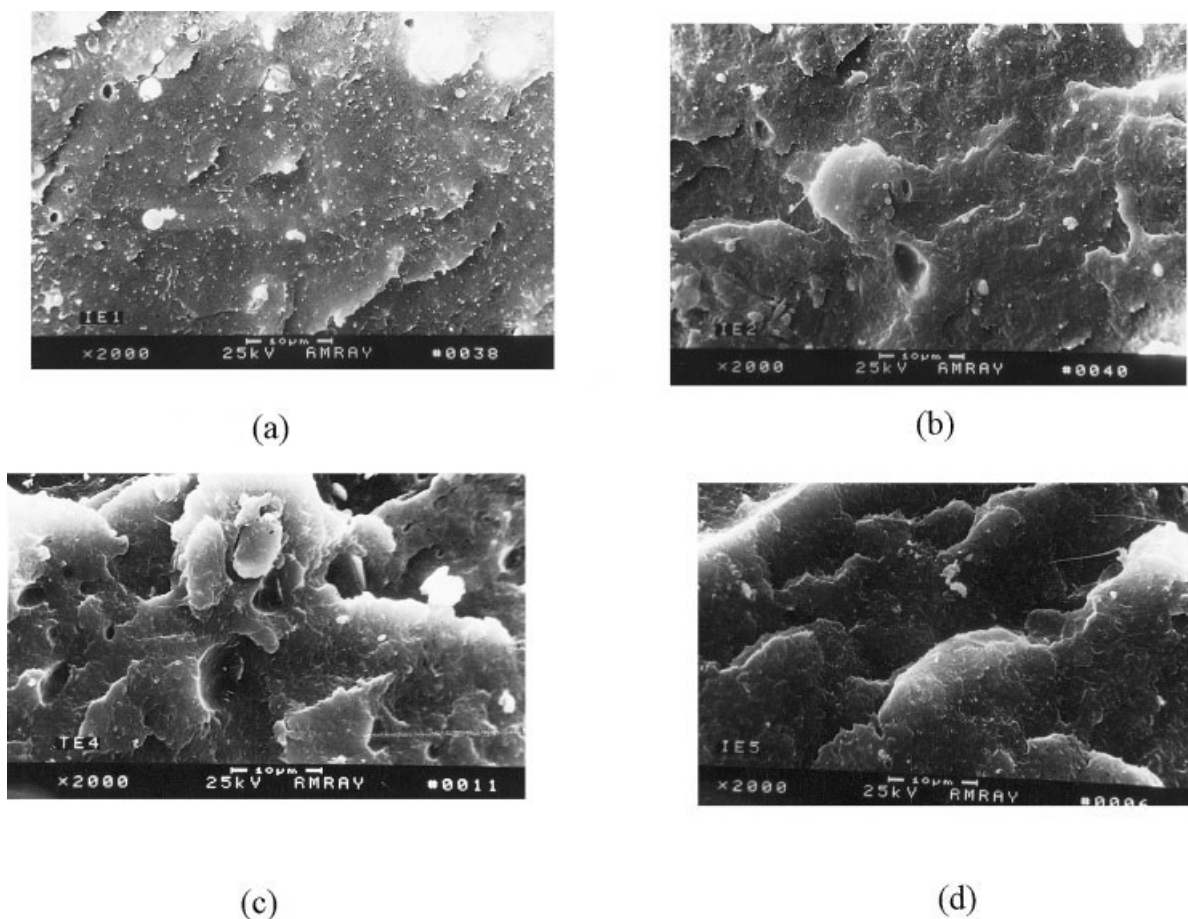
### Mechanical properties and morphology of the blends

The values of the tensile strength and impact strength of the blends are listed in Table IV. The results indicate that the tensile strength increases with the copolymer content. This is because the copolymers in the blends increase the interactions between macromolecular chains.

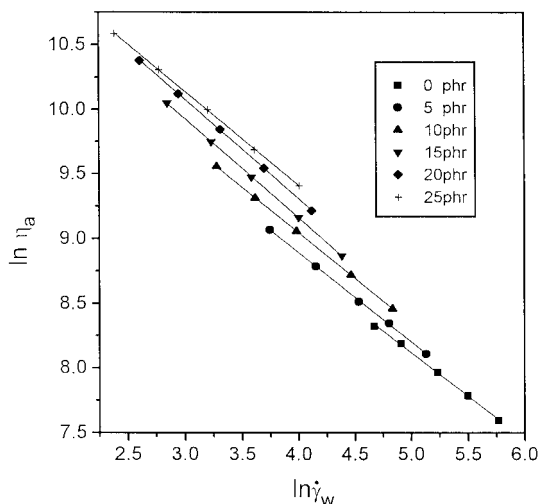
The impact strength of the blends increases somewhat with the copolymer when the ratio of the copolymer to PVC is lower than 10/100, and it decreases with the further addition of the copolymer. This comes from the close relationship between the properties of the blends and their morphology.

The SEM micrographs (Fig. 5) show the impact-

fractured surfaces of the blends. All the blends exhibit a heterogeneous surface morphology, and the domain size of the discrete phase increases with the content of the copolymer and becomes continuous when the copolymer content reaches 25 phr. The irregular shape of the boundary between the two phases indicates that there is strong adhesion between the phases and that severe phase separation does not occur. This conclusion is supported by the TBA results: a single peak is observed in TBA curves, whereas the transition becomes increasingly broader with increasing copolymer content. It can be concluded from the change in the impact strength that, when the content of the copolymer is increased to 10 phr, the rigid copolymer phase reaches an appropriate size and the material is



**Figure 5** SEM micrographs of the impact-fractured surfaces of the blends: (a) copolymer content = 5 phr, (b) copolymer content = 10 phr, (c) copolymer content = 20 phr, and (d) copolymer content = 25 phr.



**Figure 6** Rheological behavior of the blends with different copolymer contents.

toughened, exhibiting the highest value of the impact strength.

#### Rheological behavior of the blends

The rheological behavior of the blends was measured at 180°C. A plot of  $\ln \eta_a$  (where  $\eta_a$  is the apparent viscosity) versus  $\ln \dot{\gamma}_w$  (where  $\dot{\gamma}_w$  is the apparent shear rate) is depicted in Figure 6.  $\eta_a$  decreases with  $\dot{\gamma}_w$  and increases with the copolymer content. According to the Oswald–Dewal power law,  $\tau_w = \kappa \dot{\gamma}_w^n$ , and the rheological equation of state<sup>16</sup> is  $\eta_a = K \dot{\gamma}^{n-1}$ , The non-Newtonian parameter flow power  $n$  can be obtained. When the copolymer content is 0, 5, 10, 15, 20, or 25 phr,  $n$  of the blends is 0.33, 0.31, 0.30, 0.23, 0.23, or 0.27, respectively. The decrease in the value of  $n$  shows that the non-Newtonian property in the melt decreases with the copolymer added. The increase in  $\eta_a$  is due to the copolymer chains enhancing the inter-

action between the chain units and the high average molecular weight of the copolymers.

#### CONCLUSIONS

Used as a heat-resistant agent, poly(MMA-*co*-ChMI) has been blended with PVC and has improved the heat resistance of blends, as characterized by  $T_{Vicat}$  and  $T_g$ . The tensile strength increases with the increase in the content of the copolymer in the blends. The impact strength of the blends has a maximum value when the copolymer content is 15 phr. The blends show a two-phase morphology detected by SEM micrographs, but severe phase separation does not occur. The added copolymer results in an increase in  $\eta_a$  and a decrease in  $n$ .

#### References

- Bharel, R.; Choudhary, V.; Varma, I. K. *J Appl Polym Sci* 1993, 49, 31.
- Yuichi, K.; Kazuo, K.; Koichi, N. *J Appl Polym Sci* 1997, 63, 363.
- Xulin, J.; Hongyun, T.; Ping, X.; Deyue, Y. *J Appl Polym Sci* 1999, 74, 1293.
- Xulin, J.; Hongyun, T.; Ping, X.; Deyue, Y. *J Appl Polym Sci* 1999, 74, 1417.
- Shaosheng, D.; Yuezheng, W. *J Appl Polym Sci* 1999, 72, 1335.
- Shaosheng, D.; Yuezheng, W. *J Appl Polym Sci* 1999, 74, 516.
- Barrals-Rienda, I. M.; De la Campa, J. I. G.; Ramos, I. G. *J Macromol Sci Chem* 1977, 11, 267.
- Yuan, Y.; Siegmund, A.; Narkis, M.; Bell, J. P. *J Appl Polym Sci* 1996, 61, 1049.
- Yuan, Y.; Siegmund, A.; Narkis, M.; Bell, J. P. *Polym Adv Technol* 1995, 6, 675.
- Shan, G.; Weng, Z.; Huang, Z.; Pan, Z. *J Appl Polym Sci* 1997, 63, 1535.
- Horing, S.; Jakowlew, S.; Ulbricht, J. *Plast Kautsch* 1982, 29, 622.
- Otsuka, M.; Matsuoka, K. *Kogyo Kagaku Zasshi* 1970, 73, 1062.
- Guilin, Z.; Baiqing, D.; Yongde, W.; Shaosheng, D. *Chem J Chin Univ* 2001, 22, 249.
- Shen, J.-S. *J. U.S. Pat.* 5,073,615 (1991).
- Zelinger, J. *J Polym Mater* 1976, 5, 99.
- Arai, T. *A Guide to the Testing of Rheological Properties with Koka Flow Tester*; Maruzen: Tokyo, 1958; p 16.