

PROPERTIES AND MORPHOLOGY OF LIQUID CHLOROPRENE-METHACRYLIC ACID COPOLYMER MODIFIED EPOXY RESIN/ POLY (BUTYL METHACRYLATE) SEMI-IPN

BIAN Xinsheng (卞新声) HAN Xiaozu (韩孝族) WANG Xinren (汪新仁)

and ZHANG Qingyu (张庆余)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun)

ABSTRACT

A series of liquid chloroprene-methacrylic acid copolymer (CP-co-MAA) modified epoxy resin (ER)/poly (butyl methacrylate) (PBMA) semi-IPN were synthesized. Some physical properties were investigated. DSC diagrams showed two indistinct and inward endothermal transitions corresponding to the transitions of two networks in the semi-IPN system. By observing morphology with SEM technique it shows that there is a multiphase structure, in which CP-co-MAA's domain sizes are about 0.10—0.80 μ . With increasing C/E ratio, the domain sizes are getting smaller, which is due to effect of mixing network of CP-co-MAA promoting entanglement and interpenetrating of PBMA and CP-co-MAA-ER network. In most of the semi-IPN's compositions, ER phase readily maintains its phase continuity while PBMA phase presents a band shape structure. Consequently, crosslinking network keeps in its continuous phase more readily than uncrosslinking one, thus it influences dominantly on the physical properties.

INTRODUCTION

In recent years, interpenetrating polymer network (IPN) has become an important branch of multiphase polymers in the field of polymer science and is growing rapidly towards variety and applicability^[1-6]. The property-morphology relationship of IPN is an important subject which has attracted much interest in IPN's researches. The synergistic effect resulted from the threading and entangling (permanent physical crosslinking) between two networks in IPN systems not only influences compatibility and morphology, but also imparts new combined physical properties.

In this paper, a series of CP-co-MAA-ER/PBMA-semi-IPN's were synthesized by the simultaneous technique in bulk, in which liquid chloroprene-methacrylic acid copolymer (CP-co-MAA) modified epoxy resin (ER) as crosslinking network which can be transferred from toughened resin to reinforced elastomer by readjusting CP-co-MAA/ER ratio, C/E ratio, and poly (butyl methacrylate) (PBMA) as noncrosslinking network which is readily polymerized with the liquid monomer possessing a high boiling temperature. The mechanical properties were studied. The morphology and thermal transition behaviour were examined by SEM and DSC. Through the easily obtained IPN containing changeable properties, three component and

complicated morphology, the relationship between morphology and property have been preliminarily investigated.

EXPERIMENTAL

Materials

CP-co-MAA was prepared by ourselves with average molecular weight of 2000 through the radical cooligomerization with CP/MAA = 4/1 and mercaptanethyl acid used as regulator. ER was the product of Wuxi Resin Factory (618 resin). 2,4,6-tri (dimethylaminomethyl) phenol (DMP-30) made by Shanghai Chemicals Factory. Butyl methacrylate (BMA) was washed with 5% aqueous sodium hydroxide solution, dried with molecular sieves for use.

Synthesis

A given amount of CP-co-MAA and ER were dissolved in a required amount of BMA. AIBN (0.5% W/W) was added to initiate the BMA's polymerization, followed by stirring at room temperature until AIBN dissolved, and then DMP-30 added. The solution was mixed, degassed and poured into mold and maintained at 60°C for 16 h., followed by a further period of 4 h. at 120°C to complete the polymerization.

Measurements

The mechanical properties were measured using a tensile testing machine made in Changchun. The T_g and thermal transition behaviour were determined with a thermal analyser and DSC device (Perkin-Elmer 7 Series). The morphology was observed with scanning electron microscopy (SEM) (Model H-500 made in UK).

RESULTS AND DISCUSSION

Mechanical Properties

Table 1, 2 and 3 show that the tensile strength and T_g of the IPN decrease and the elongation at break increases with increasing C/E ratio and decreasing PBMA content, which indicates that

Table 1 Different types of the samples

Samples	Compositions	Types
PBMA	Uncrosslinked PBMA	Homopolymer
ER	Epoxy resin thermoset	Homopolymer
O	C/E ratio 0.5, modified ER	Copolymer
A	C/E ratio 0, PBMA 50%	ER/PBMA—semi—IPN
B	C/E ratio 0.4, PBMA 43%	ER/PBMA—semi—IPN
C	C/E ratio 0.5, PBMA 40%	ER/PBMA—semi—IPN
D	C/E ratio 1.0, PBMA 33%	ER/PBMA—semi—IPN
E	C/E ratio 1.5, PBMA 29%	ER/PBMA—semi—IPN
F	C/E ratio 2.0, PBMA 25%	ER/PBMA—semi—IPN
G	C/E ratio 1.0, PBMA 17%	ER/PBMA—semi—IPN
H	C/E ratio 1.0, PBMA 43%	ER/PBMA—semi—IPN
I	C/E ratio 1.0, PBMA 50%	ER/PBMA—semi—IPN
J	C/E ratio 1.0, PBMA 57%	ER/PBMA—semi—IPN

Table 2 The mechanical properties of CP-co-MAA-ER/PBMA-semi-IPN system

Samples	PBMA	A	B	C	D	E	G
Tensile strength (Kg/cm ²)	183	Brittle	206	170	150	116	146
Elongation (%)	10	0	30	40	50	110	55

Table 3 The thermal transition temperatures of PBMA, ER and semi-IPN

Samples	T_1 (DSC)	T_2 (DSC)	T_g (TDA)	Physical appearance
PBMA	41	—	36	White, transparent
ER	—	105	97	Yellowish, translucent
A	43	100	64	Opaque
O	45	75	62	Yellow, translucent
C	47	70	51	Opaque
D	44	67	48	Opaque
E	42	68	40	Yellowish, translucent
F	—	59	20	Yellowish, translucent
G	—	—	48	Opaque
H	—	—	50	Opaque

by adjusting the C/E ratio it will directly influence the IPN's properties and can change the crosslinking network in the IPN from toughened resin to elastomer. Also the PBMA content can effect the physical properties at constant C/E ratio.

Thermal Transition Behavior

The glass transition temperatures of the samples are listed in Table 3. The T_1 corresponds to the endothermal transition temperatures of PBMA (41°C) and CP-co-MAA (45°C, sample O) of CP-co-MAA-ER network and the T_2 corresponds to the temperature of ER of CP-co-MAA-ER network. As compared with correspondent homopolymers, the sample A has two distinct but inwardly shifted endothermal transitions in absence of CP-co-MAA. In CP-co-MAA-ER/PBMA-semi-IPN system, the T_1 and T_2 inwardly shift with increase of C/E ratio in comparison with sample PBMA, ER, A and O. The results mentioned above also can be observed in DSC diagram (see Fig. 1). The drop of T_1 is due to the decrease of CP-co-MAA's transition temperature for the CP-co-MAA-ER network being an elastomer. On the other hand, T_1 can be effected by both transitions of PBMA and CP-co-MAA, and the two close transitions are merged into one transition. The data of the T_g showed in Table 3 decrease and are in the intermediate between T_1 and T_2 with increasing C/E ratio, which is a result of mixing PBMA network with CP-co-MAA-ER network. The T_g does not belong to any pure network. Changing PBMA content at constant C/E ratio influences the T_g little (see sample D, G and H), which exhibits that crosslinking network in a semi-IPN system is dominant in the effect on T_g , particularly in a system possessing two neighboring T_g 's.

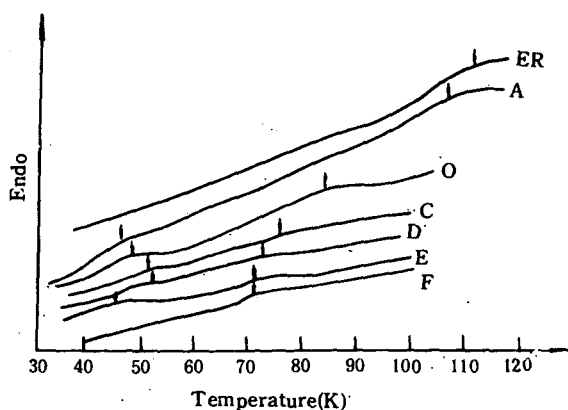


Fig. 1. The DSC diagram of the samples

Morphology

The morphology of CP-co-MAA-ER/PBMA-semi-IPN is more complicated than those of other IPN's because there are two phase structure of the CP-co-MAA-ER network and the domain sizes of CP-co-MAA are about $0.08\text{--}0.30\mu$ (see micrograph 1 in Fig.2). The ranges of the domain sizes are listed in Table 4. It can be observed from micrograph 2 in Fig. 2 that the degree of the phase separation of sample A is relatively large and its domain size is about $0.5\text{--}2.0\mu$. The domain distribution of sample G is relatively uniform and the boundaries of the phase are also distinct. The domain sizes are about $0.17\text{--}1.0\mu$ which is in the intermediate between the two ranges mentioned above, the large of which attributes to PBMA and the small one belongs to CP-co-MAA of the modified resin network. With increase of PBMA content, the phase boundaries are no longer distinct and a white band shape structure with partial continuity appears (see micrograph 4—7). A domain structure with a range of domain sizes ($0.10\text{--}0.76\mu$) disperses within the white band shape structure and the resin phase (black structure). With increasing C/E ratio the miscibility of the two incompatible polymer networks will be promoted. Therefore the distribution of the domain sizes is going to be uniform. From micrograph 9 in Fig.2, it shows that the domain densely disperse in the continuous phases, mainly in the band shape structure. The effect of the C/E ratio to adjust compatibility can be observed by physical appearance.

Table 4 The ranges of the domain sizes of the samples

Samples	O	A	G	D	H	I	J	C	F
Sizes (μ)	0.08— 0.30	0.05— 2.00	0.13— 1.00	0.10— 0.80	0.10— 0.85	0.10— 0.76	0.10— 0.60	0.13— 0.76	0.08— 0.30
Micrograph	1	2	3	4	5	6	7	8	9

To sum up, a multiphase morphology is existed in the CP-co-MAA-ER/PBMA-semi-IPN system. The particles of CP-co-MAA in the crosslinking network mainly disperse in the band shape structure (PBMA) deposited on the ER continuous phase. According to the ranges of the domain sizes, these particles are CP-co-MAA rather than PBMA. In the formation of networks, the PBMA part readily mixes with the CP-co-MAA part of the crosslinking network because of the similar molecular chain structure, so the CP-co-MAA plays a role of "mixing network

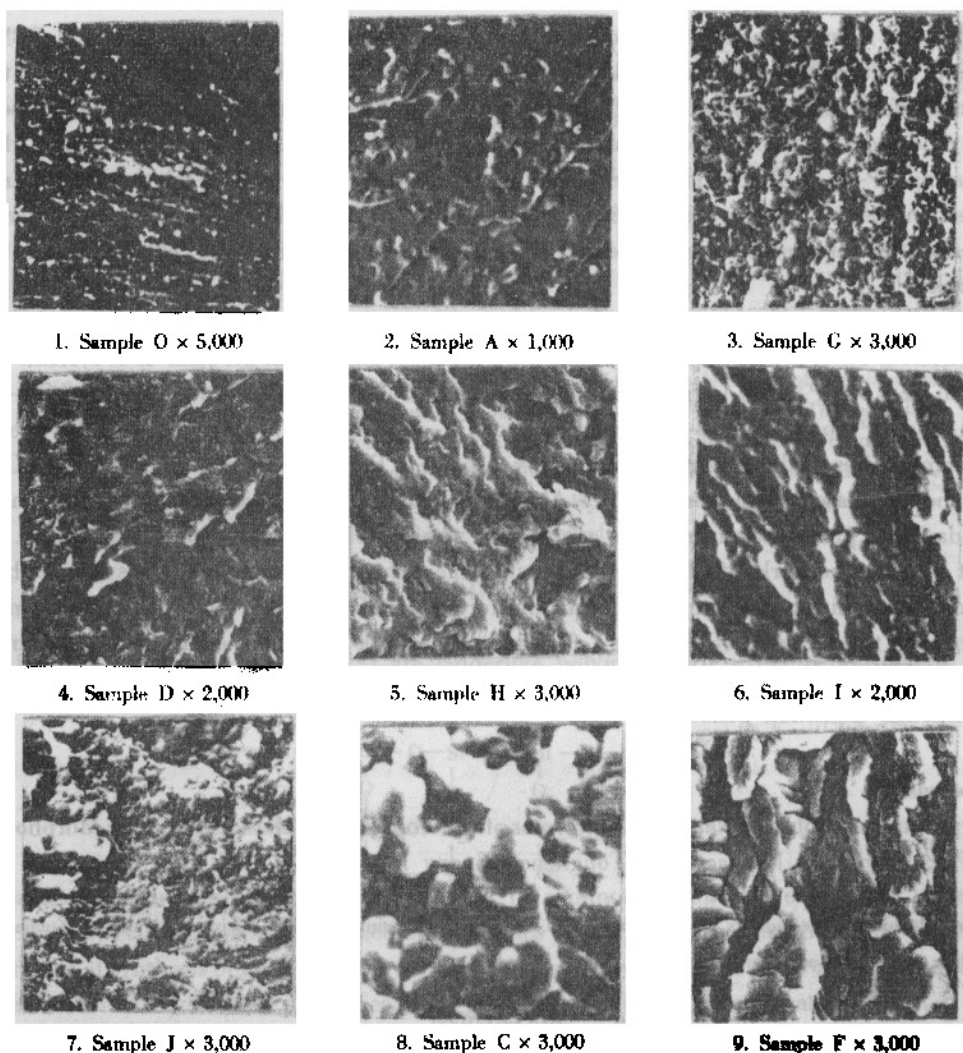


Fig.2. The SEM micrographs of the samples

reagent" in the semi-IPN system. The ER phase still remains continuity although the PBMA content equals or even surpasses the ER content, which is due to the ER part being frame of the crosslinking network in the semi-IPN system. This shows that a crosslinking network more readily maintains phase continuity than an uncrosslinking one in a semi-IPN system. In many cases, the band shape structure is no longer a pure phase but a mixing one with CP-co-MAA because of the effect of mixing network. The CP-co-MAA's mixing effect provides more chances to interentanglement between the two networks, as a result, the domain size is getting smaller with increase of C/E ratio.

CONCLUSION

Tensile strength and T_g decrease and elongation increases with increasing C/E ratio in CP-co-MAA-ER/PBMA-semi-IPN system. The physical properties of the semi-IPN can be

transformed from toughened resin to reinforced elastomer by changing C/E ratio and PBMA content. There are two indistinct and inward endothermal transition peaks corresponding to two networks of the semi-IPN system in DSC diagrams. T_1 and T_2 tend to drop down with increase of C/E ratio and T_1 is a combined transition of PBMA and CP-co-MAA. Therefore, T_1 drops while increasing CP-co-MAA content. The data of T_g show the further evidence for the DSC results. Transition behavior appearing between that of two networks has been considered as a partial evidence for interpenetrating in semi-IPN resulted from mixing and entangling of two networks^[7].

The two phase structure of CP-co-MAA-ER network make the IPN's morphology complicated. There are three phases, CP-co-MAA, PBMA and ER, in the semi-IPN system. The domain sizes of CP-co-MAA are about 0.08—0.30 μ , PBMA 0.50—2.00 μ in absence of CP-co-MAA, and CP-co-MAA 0.10—0.80 μ in most of CP-co-MAA-ER/PBMA-semi-IPN systems. The domain sizes tend to be smaller and mainly disperse in PBMA phase while increasing the C/E ratio and ER phase remains continuously. Although ER and PBMA partially mix each other on the boundaries of phase their own phase continuities remain. These observations indicate that the effect of mixing networks of CP-co-MAA provides more chances for the semi-IPN system to have two networks mixed and interthreaded in the formation of networks. At this point, it can be approached that in semi-IPN system, crosslinking network is to be a continuous phase more preferable than uncrosslinking one and the effects of crosslinking network on physical properties and thermal transition behavior are more prominent.

Keywords:

Interpenetrating Polymer Network; Copolymer of Chloroprene and Methacrylic Acid; Morphology of IPN; Poly(Butyl Methacrylate); Toughened Epoxy Resin

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REFERENCES

- [1] Hourston D. J., Zia Y., *J. Appl. Polym. Sci.*, **1984**, 29, 629.
- [2] Skinner E., Emeott M. and Jevne A., *U. S. Pat.*, 4,247,578, **1981**.
- [3] School R., *Rubber and Plastics News*, **1982**, March 15, p. 2.
- [4] Elsabee M. Z., Dror M. and Berry G. C., *J. Appl. Polym. Sci.*, **1983**, 28, 2151.
- [5] Cassidy E. F., Xiao H. X., Frisch K. C. and Frisch H. L., *J. Polym. Sci., Polym. Chem. Ed.*, **1984**, 22, 2667.
- [6] Sperling L. H. *Polym. Eng. Sci.*, **1985**, 25, 517.
- [7] Kim S. C., Klempner D., Frisch K. C. and Frisch H. L., *Macromolecules*, **1976**, 9, 263.