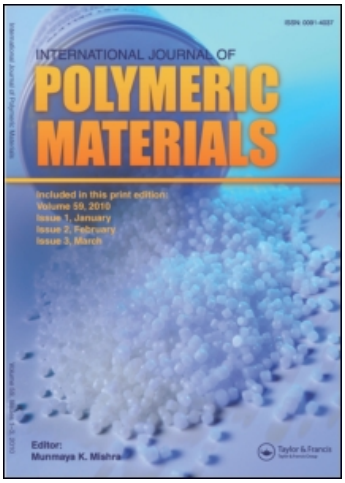

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Study on thermal stability, mechanical properties and rheological behavior of poly(St-PhMI-MMA) blended with PVC

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STUDY ON THERMAL STABILITY, MECHANICAL PROPERTIES AND RHEOLOGICAL BEHAVIOR OF POLY(St-PhMI-MMA) BLENDED WITH PVC

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Terpolymers of N-phenylmaleimide (PhMI), styrene (St) and methyl methacrylate (MMA) were synthesized by emulsion polymerization. The thermal properties of PVC blended with the terpolymer had been investigated by TGA, Torsional Braid Analysis (TBA) and Vicat softening point tester. The results show that the glass transition temperature (Tg) and Vicat softening point of the blends increase with increasing terpolymer content. The mechanical properties and rheological behavior were also determined. The results show that the mechanical properties of the blends improve with increasing terpolymer content, and the apparent melt viscosity of the blends decreases with increasing terpolymer content. The compatibility of the blend system was also investigated by TBA and SEM.

Keywords: PhMI, PVC, blends, thermal stability, mechanical properties, rheological behavior

INTRODUCTION

Materials are the foundation of the development of science and industry. Theoretical and applied researches of high strength or special properties materials play an important role in material science.

There has been a considerable interest in the synthesis of copolymers that contain maleimide moieties, especially of PhMI [1–5]. Such copolymers contain five-member planar rings in the chain, which hinder chain rotation, resulting in greater structural stiffness and higher thermal stability. Solution copolymerization of PhMI with other vinyl monomers such as styrene, methyl methacrylate and vinyl acetate have been studied [5–7], focusing

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on the copolymerization behavior. These copolymers tend to form an alternating structure when PhMI reacts with electron-donor commoners, such as styrene at low conversions, regardless of the monomers feed composition. In such a case the desired copolymer structure and properties are difficult to control by simply adjusting the monomers' composition. Emulsion copolymerization of these monomers may produce structure-controlled copolymers under the studied condition [4].

Because of the higher thermal stability, these copolymers were used as heat-resistant modifiers blended with PVC, aimed at increasing the thermal properties of PVC [8–10], such as Vicat softening point. Studies on mechanical properties, glass transition temperature, rheological behavior and morphology of these blends are rather limited until now. In this work, the thermal properties, mechanical properties, rheological behavior and morphology of blends of PVC and PhMI-containing emulsion terpolymers have been investigated. The results show that the Vicat softening point (T_{Vicat}) and glass transition temperatures (Tg) of the blends increase with increasing content of PhMI-containing terpolymer. Tensile strength and notch impact strength of the blends also increase with increasing content of PhMI-containing terpolymer, while hardness does not change. The TBA graph and SEM results suggested that the blended system has some compatibility.

EXPERIMENTAL

Materials

N-phenylmaleimide (PhMI) was synthesized from maleic anhydride and aniline according to reference [11]. Methyl methacrylate (MMA) and styrene (St) were twice washed with 5% NaOH aqueous solution before use. Sodium lauryl sulfate (SLS), $K_2S_2O_8$, $Al_2(SO_4)_3 \cdot 18H_2O$ were AR grade and supplied by Beijing Chemical Reagent Co.. Water used in all experiments were distilled water (DDW). PVC, tribasic lead sulfate (TLS), dibasic lead phosphate (DLP) were all chemical grade, supplied by Tianjin Chemical Reagent Co..

Synthesis and Characterization of Terpolymer

The terpolymer of PhMI, MMA and St was synthesized by emulsion polymerization. A solution of SLS was placed in a 100 ml four necked flask equipped with a stirrer, a thermometer, a condenser and a nitrogen inlet, and stirred for 30 min under nitrogen. $K_2S_2O_8$ was used as initiator. The monomer ratio of PhMI/MMA/St is 20 : 75 : 5. The monomers mixture was added to the reaction vessel at 80°C over the course of 1.5 hour under nitrogen atmosphere. The reaction was then held at 85°C for additional 2 hours. The terpolymer was precipitated by $Al_2(SO_4)_3$ solution and purified by washing with warm DDW. After drying, it was extracted with methanol

TABLE 1 Recipes of blended PVC

No.	0	1	2	3	4	5
PVC Parts	100	100	100	100	100	100
Terpolymer Parts	0	5	10	15	20	25
TLS	1.5	1.5	1.5	1.5	1.5	1.5
DLP	3	3	3	3	3	3

for 24 hours, and then dried in vacuum. The molar mass was determined by gel permeation chromatography (GPC) [12], $\bar{M}_w$ is usually 24×10^4, and $\bar{M}_n$ is usually 5.74×10^4. The composition of the terpolymer was detected using a PE-240 elemental analyzer, and the IR analysis was performed using a Matlson 1000 Fourier transform infrared (FTIR) [4].

Preparation of Blends

PVC was mixed with a predetermined weight of terpolymer and stabilizers (TLS, DLP) were then added to this mixture. All components (as shown in Tab. 1) were first mixed in a mixer and then milled on a laboratory two-roll mill at a temperature of 180°C for 10 min. Five millimeter-thick plates were pressed at temperature of 180 – 190°C.

Equipment and Characterization Procedures

The mechanical properties of the blends were measured using TJ-5000N tensile strength tester and XCJ-40 notch impact strength tester at 25°C. The rheological behavior was investigated by a Shimudzu Koka flow tester [13]. The fixed temperature method was used, and the weight of the specimen was 1.5 g. The morphology of the blends was studied by scanning electron microscopy (SEM) using the method of Zelinger [14]. Dynamic mechanical measurements were carried out by torsional braid analysis (TBA) at a heating rate of 2°C/min. The thermal stability was tested using a Shimudzu DT-40 thermogravimetric analysis (TGA) in a static air atmosphere. About 3.0 mg of the sample were placed in a platinum cell which was positioned on the detector plate, then the furnace was heated at 10°C/min. The Vicat softening point was measured using Vicat softening point tester at a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Composition of the Terpolymer

The IR spectra of MMA-PhMI-St at different monomer feed proportion are shown in Figure 1. With the incorporation of PhMI, the most significant feature is the increase of the singly substituted benzene group absorption at

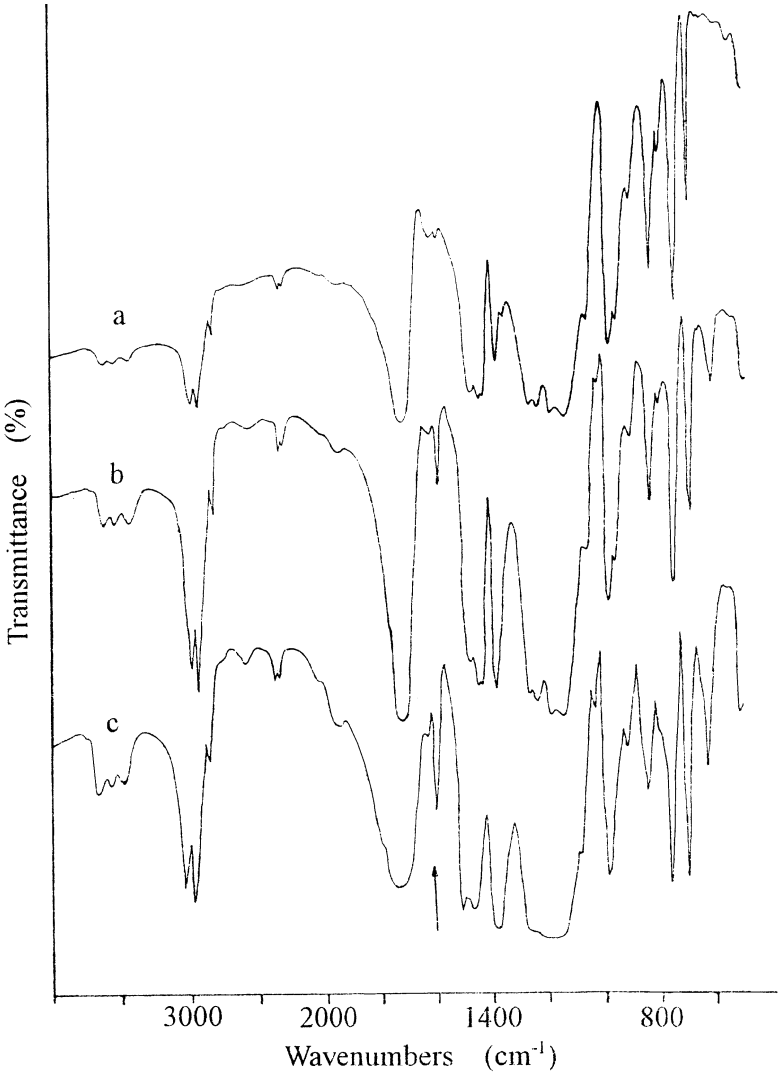

FIGURE 1 FTIR spectrum of copolymers. (a) MMA-St (95 : 5); (b) MMA-PMI-St (75 : 20 : 5); and (c) MMA-PMI-St (65 : 30 : 5).

1600 cm^{-1} (marked by an arrow). It is observed that the absorption peak of the singly substituted benzene group gradually increases with increasing PhMI feed content. When there has no PhMI in the feed, the absorption shows a little peak because of the existence of styrene segments. This indicates that the PhMI content in the copolymer increased with increasing

PhMI feed content. The composition of terpolymer was measured by elemental analysis using a PE-240 elemental analyzer. The monomer feed proportions and analyzed results were summarized in Table 2.

The results show that the copolymers' compositions were directly related to the monomer feed proportions. This result should be noted that the measured terpolymer coposition are actually determined by the initally charged monomer copositions, since the monomers are almost fully consumed and the formed coagula are always negligible. Thus, this expression can be used to estimate the high-conversion terpolymers' composition.

Mechanical Properties

The mechanical properties of blended PVC at different contents of terpolymer are shown in Table 3. As seen from Table 3, the tensile strength and notch impact strength increase with increasing terpolymer content up to 15% terpolymer, while the hardness keeps stable. Above 15% terpolymer, all these properties remain constant. The results show that terpolymer can increase the mechanical properties of PVC. This may be due to the strong interaction between PVC and terpolymer molecular chain moieties.

Thermal Properties of Blended PVC

The glass transition temperature (Tg) and Vicat softening point (T_{Vicat}) of blended PVC at different terpolymer content are shown in Table 4. As seen from Table 4, Vicat softening point increases linearly with increasing terpolymer content. The linear relationship between T_{Vicat} and terpolymer

TABLE 2 Emulsion copolymerization of MMA, St and PMI[a]

$MMA:PMI:St$[b]	*Ingredients* SLS, g	$K_2S_2O_8, g$	*Copolymer's composition* $(MMA:PMI:St)$
95:0:5	0.45	0.045	95.3:0:4.7
75:20:5	0.45	0.045	76.2:19.2:4.6
65:30:5	0.45	0.045	64.3:30.6:5.1

[a] Solid content is 30 wt%.
[b] Total monomer content is 15 g.

TABLE 3 Mechanical properties of blended PVC at different terpolymer contents

Terpolymer content (w/w)	0	5	10	15	20	25
Tensile Strength (MPa)	57.23	58.63	61.23	65.73	62.52	65.5
Impact Strength (KJ/m^2)	2.25	2.10	2.63	2.74	2.73	2.74
Hardness (MPa)	113.2	110.6	113.8	111.0	110.1	110.7

TABLE 4 Vicat softening point and glass transition temperature

Terpolymer content (*g*/100 *g PVC*)	0	5	10	15	20	25
Vicat softening point (°C)	91.5	93.5	96.0	97.2	98.6	100.6
Tg (°C, TBA)	78.5	81.4	84.8	87.9	89.9	91.4

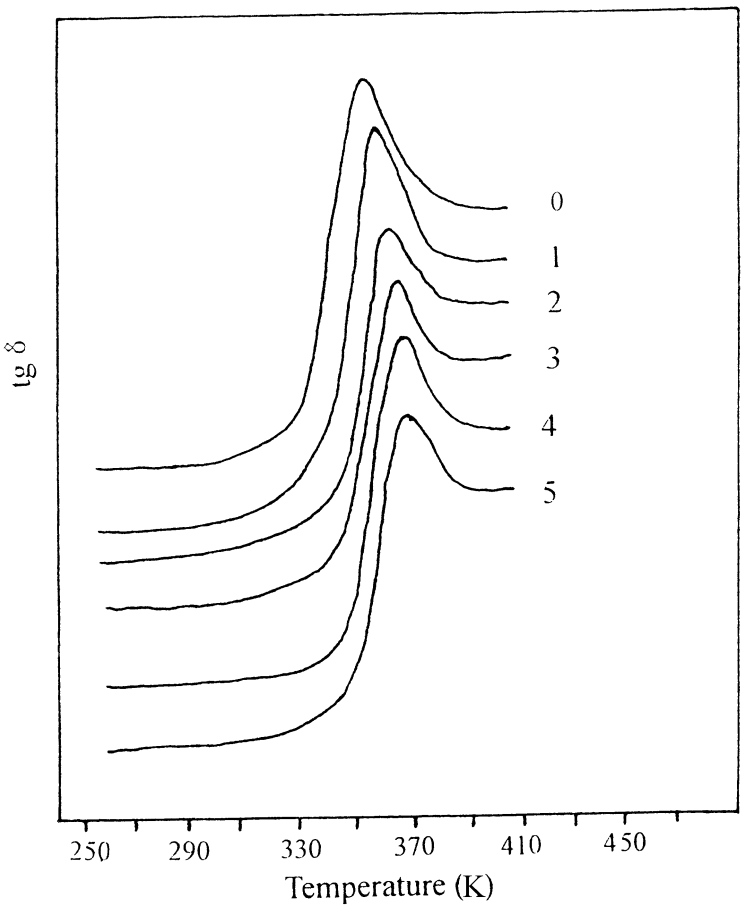

FIGURE 2 TBA curves of the blends at different terpolymer levels.

content within the composition range studied is expressed as follows:

$$T_{\text{Vicat}} = 91.8(\pm 0.28) + 0.354X$$

where X represents the part of terpolymer in 100 part PVC (phr). This result shows that PhMI containing terpolymer can increase the service temperature of PVC.

The single *Tg* of the blended PVC (as seen from Tab. 4 and Fig. 2) increases with increasing the content of PhMI containing terpolymer. According to Utracki [15], the relationship between *Tg* of blended system and *Tg*s of the components is as follows:

$$W_1 \ln(Tg/Tg_1) + kW_2 \ln(Tg/Tg_2) = 0$$

The glass transition temperature of PVC (Tg_1) and PhMI containing terpolymer (Tg_2) used in this work are 78.5°C and 107.8°C respectively. According to the data in Table 4, the obtained k value is 3.18. k represents the compatibility of the blended system. When $k \gg 1$ or $k \ll 1$ the blended system has no compatibility [15]. In this work, the value of k is 3.18, which suggests the blended system is somewhat compatible. The SEM photography (as shown in Fig. 5) also shows the same result.

Figure 3 is the TGA graph of the blended system. As seen from Figure 3, PhMI containing terpolymer can decrease the decomposition rate. The weight loss of PVC is due to the expulsion of HCI. The weight loss rate increases with increasing of $[H^+]$ or $[H\cdot]$. PhMI moieties in the terpolymer, which contain N atom, will absorb H^+ or $H\cdot$ and make the $[H^+]$ or $[H\cdot]$ in the blended system decrease. Therefore the decomposition rate decreases with increasing PhMI-containing terpolymer.

The Rheological Behavior of Blended System

The blended PVC was prepared according to the recipes in Table 1. The rheological behavior was studied using a Shimudzu Koka flow tester. The

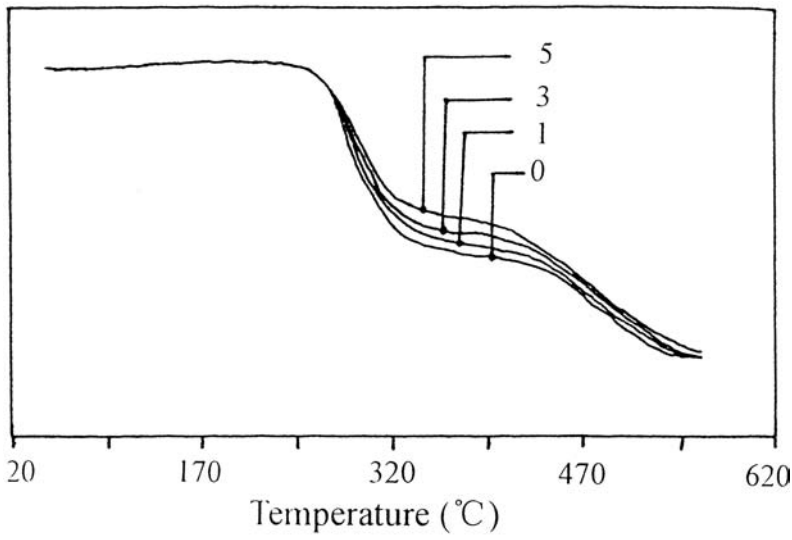

FIGURE 3 Thermogravimetric analysis diagrams (10°C/min).

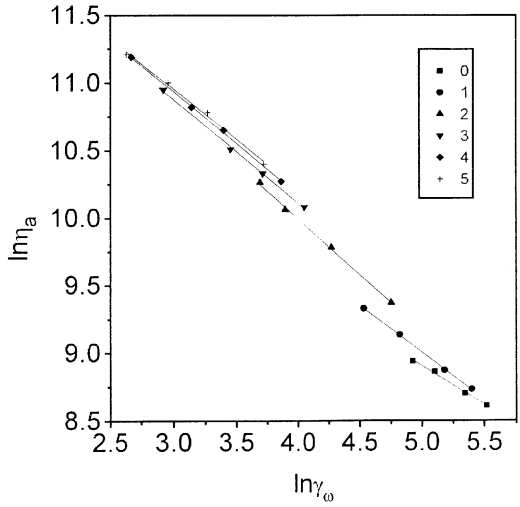

FIGURE 4 Plots of $\ln\eta_a$ *versus* $\ln\gamma_\omega$ of the blends.

experimental temperature was fixed at 180°C, with experimental stresses of 90, 100, 110, 120 and 130 Kg/cm^2, respectively. The plots of $\ln\eta_a$ *versus* $\ln\gamma_\omega$ are given in Figure 4. As shown from Figure 4, the apparent viscosity η_a decreases with increasing shear rate. It is shown that the flow behavior of the blended PVC in the melt is a pseudoplastic or shear thinning liquid behavior. The apparent viscosity of the blended PVC in the melt increases with increasing the content of PhMI containing terpolymer. When the composition of PhMI-containing terpolymer is 0, 5, 10, 15, 20 and 25 parts, the flow index n is 0.432, 0.303, 0.231, 0.171, 0.232 and 0.255 respectively, with a lowest value 0.171 at 15 part PhMI containing terpolymer.

PhMI-containing terpolymer is a polar molecule. The interaction between PVC and terpolymer molecules increases with increased content of the PhMI-containing terpolymer. This will raise the flow energy of PVC, resulting in an apparent increase in the viscosity of the blends system in the melt. Furthermore, the glass transition temperature of PhMI-containing terpolymer, which contains five member ring in the chain and have large pendant groups, is higher than PVC. The higher flow energy of the terpolymer will result in the increase of the apparent viscosity of the blends system.

The Morphology and Compatibility of Blend System

The SEM graphs of impact fractured surface and tensile breaking surfaces of the blended system are shown in Figure 5. As seen from Figure 5, the blended system has not very significant phase separation. When the content

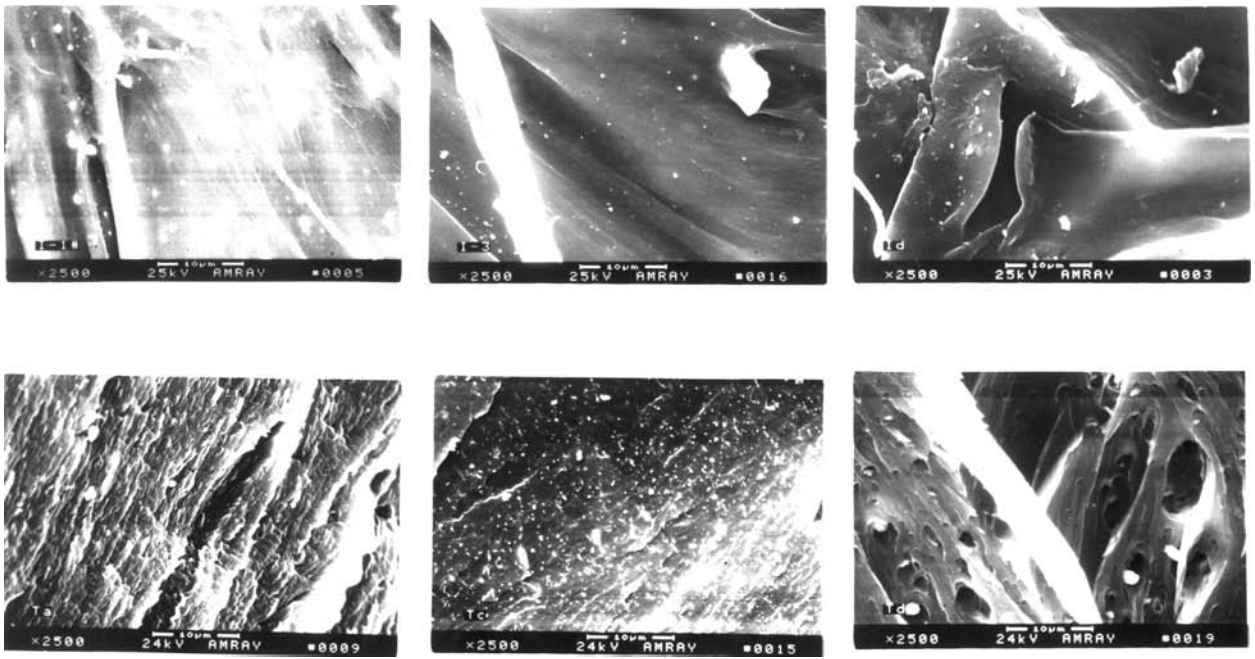

FIGURE 5 SEM photographs of the blends. *I*: Impact breaking surface, *T*: Tensile breaking surface, Terpolymer content: I-1, *Ta*: 5 part; I-3, *Tc*: 15 part; and I-4, *Td*: 20 part.

of PhMI-containing terpolymer is 15 parts the compatibility of the blended system is the best. This result explains why this recipe posseses good mechanical properties and the lowest flow index *n*.

CONCLUSIONS

1. The mechanical properties of blended PVC increase with increasing the content of PhMI-containing terpolymer.
2. The Vicat softening point and glass transition temperature of blended PVC increase with increasing content of PhMI-containing terpolymer. So the terpolymer can increase the service temperature of PVC.
3. The apparent viscosity of the blended system in the melt increases with increasing fraction of PhMI-containing terpolymer. Therefore the content of terpolymer should not be too high in order for it to be useful in processing.
4. Below 15% loading, the blended system has a good compatibility, the PhMI-containing terpolymer can enhance the mechanical properties of blended PVC, and the thermal stability of the blended system increases with increasing content of the terpolymer.

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