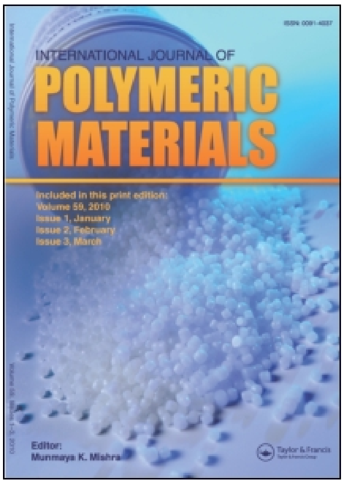

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THERMOANALYSIS AND MECHANICAL PROPERTIES OF EMULSION COPOLYMER POLY(MMA-PMI-ST)

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Terpolymers of methyl methacrylate (MMA), N-phenylmaleimide (PMI) and styrene (St) were synthesized by emulsion copolymerization. The glass transition temperatures (T_g) and the thermostability of copolymers were determined by differential scanning calorimetry (DSC) and programmed thermogravimetric analysis (TGA), respectively. The terpolymers show a considerable increase in decomposition temperature, activation energy of decomposition and T_g with increasing content of PMI. Furthermore, the Vicat softening points of the terpolymers rise with PMI content. The mechanical properties (tensile strength and impact strength) of the terpolymers decrease with increasing PMI content and increase insignificantly with increasing St content.

Keywords: MMA, PMI, emulsion polymerization, thermalanalysis, mechanical property

INTRODUCTION

PMMA is a widely used polymer in modern plastic technology but liable to decompose at high temperature. The thermostability of homopolymer of PMMA had already been determined by N. Grassie et al. [1].

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N-phenylmaleimide (PMI) is a 1,2-ethylenic type monomer with a five-member planar ring structure, so its incorporation into PMMA's backbone will lead to copolymers with a great structural stiffness as well as a higher thermal stability [2–3]. Solution copolymerization of MMA with PMI has been already studied, and it has been found that the copolymer's thermal stability will increase furthermore by the incorporation of styrene to the system [4].

Emulsion terpolymers of MMA-PMI-St could act as thermostable plastic materials and modifiers for PVC to improve PVC's thermal stability [5–8]. But the systematic research on the thermal and mechanical properties of poly (MMA-PMI-St) has been lacking until now. In this paper, thermostability, activation energy of degradation and T_g of these copolymers were investigated by thermal analysis and the results are discussed. At the same time, the mechanical properties of the copolymers are studied here.

EXPERIMENTAL

Materials

PMI was synthesized in one stage according to the method by Matsunaga Fujinao [9]. After recrystallization twice from ethyl alcohol-water (volume ratio: 1:2), PMI gives yellow needles, mp 89°C. MMA, St were washed twice with 5% solution of sodium hydroxide to eliminate inhibitor, and a few times with distilled water, then dried over anhydrous sodium sulfate. The MMA, St, emulsifying agent sodium lauryl sulfate (SLS), initiator $K_2S_2O_8$ and $Al_2(SO_4)_3$ were all analytically pure and supplied by Beijing Chemical Regent Corporation.

Emulsion Copolymerization

The copolymerization was carried out in a dried, clean 100–ml four–necked flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen duct. The solution of SLS was stirred over 15 minutes under nitrogen in the flask before part of the $K_2S_2O_8$ solution was added. The system was heated to 80°C before the monomer solution was gradually added to the system for about 1 hour. Then the residual $K_2S_2O_8$ solution was added to the system 0.5 hour after the reaction. The total monomer/water ratio is fixed at 30% and $K_2S_2O_8$ is 5% by weight of total monomer. The copolymerization proceeded under nitrogen atmosphere at 80–85°C for another hour, then was stopped and precipitated by 2% $Al_2(SO_4)_3$ solution. The copolymer was isolated by filtration, and washed a few times with hot water, and dried.

Copolymer Analysis

The samples used for thermal analysis were washed with methyl alcohol in a flask with a rotating magnet in it for about 12 hours to remove the residual PMI monomer and SLS. The copolymer was then dried in a high vacuum drying oven at 60°C for 24 hr. The conversion was measured gravimetrically and was always more than 90%. The composition of copolymer was measured by elemental analysis using a PE-240 elemental analyzer. The analysis results are shown in Table 1. The results show that the copolymer's compositions were very close to the monomer feed proportions.

The molecular masses of the copolymers were determined by gel permeation chromatography (GPC). $\overline{M}_w$ are always between 11×10^4 and 27×10^4, and the molecular mass distribution parameters vary from 3.8 to 13.2, usually less than 7. As shown in Tables 2–3, both $\overline{M}_w$ and $\overline{M}_n$ increase with the increase of PMI and St feed content at low PMI(St) content but reach a peak and lower $\overline{M}_w/\overline{M}_n$ under proper feed content of PMI and St. This is because of the mechanism of emulsion polymerization.

Structure changes in the copolymer were investigated by using a FTS-40 IR spectrophotometer. Two IR spectra of MMA-PMI-St copolymers at different monomer feed proportions are shown in Figure 1. With the incorporation of PMI, the most significant feature is the increase of the singly substituted benzene group absorption (marked

TABLE 1 Elemental Analysis of Terpolymer of MMA-PMI-St

MMA:PMI:St (feed ratio)	MMA:PMI:St (test value)
95:0:5	95.3:0:4.7
85:10:5	86.9:9.0:4.1
75:20:5	76.2:19.2:4.6
95:5:0	96.5:3.5:0
85:5:10	85.6:4.7:9.7
75:5:20	74.1:4.6:21.3

TABLE 2 Copolymer Molecular Weight at Different PMI Feed Content (St 5 wt%)

PMI feed content, wt%	0	5	10	15	20
$\overline{M}_w, 10^4$	19.56	25.86	25.82	27.10	24.08
$\overline{M}_n, 10^4$	1.48	3.79	6.74	7.06	5.74
$\overline{M}_w/\overline{M}_n$	13.2	6.83	3.83	3.84	4.20

TABLE 3 Copolymer Molecular Weight at Different St Feed Content (PMI 5 wt%)

St feed content, wt%	0	5	10	15	20
$\overline{M}_w, 10^4$	11.33	25.86	26.73	21.11	18.27
$\overline{M}_n, 10^4$	1.21	3.79	3.71	3.60	3.56
$\overline{M}_w/\overline{M}_n$	9.36	6.83	7.21	5.86	5.13

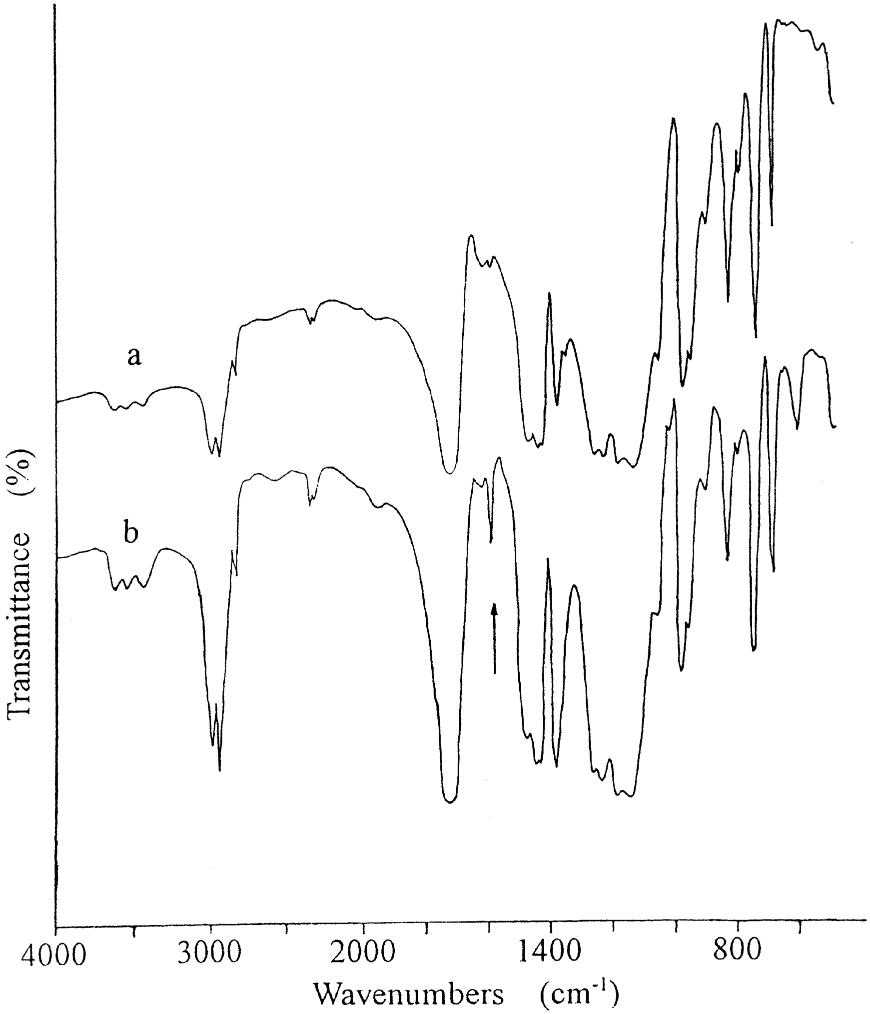

FIGURE 1 FTIR spectra of copolymers. (a) MMA-St(95:5); (b) MMA-PMI-St(80:15:5).

by an arrow). It is observed that the absorption peak of the singly substituted benzene group gradually increases with increasing PMI feed content. When no PMI's fed, the absorption shows a little peak because of the existence of styrene segments. This also indicates that the PMI content in the copolymer increased with increasing PMI feed content.

Thermogravimetric analysis was carried out by means of a Shimadzu DT-40 thermogravimeter (TG). Half-loss weight temperature T_{d50} was obtained when the weight loss of the copolymer reached 50% at a heating rate of 10°C/min in air atmosphere.

Copolymer's glass transition temperature, T_g, was measured by using a Shimadzu DT-40 differential scanning calorimetry (DSC) with α-Al_2O_3 as reference material at a heating rate of 20°C/min under nitrogen. The sample was scanned once in the DSC before the test. T_g value was taken from the midpoint of the temperatures of the initial and final tangents in the DSC traces in the second scan [10].

The copolymers used for mechanical property test were milled on a laboratory two-roll mill at temperatures of 180–190°C for 10 min and five–millimeter-thick plates were pressed at temperature of 190°C. The mechanical properties of the copolymers were measured using a TJ-5000N tensile strength tester and a XCJ-40 impact strength tester at 25°C. The Vicat softening point values were measured by using a Vicat softening point tester at a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

The thermal stability of the copolymer has been arbitrarily defined as a function of the initial thermal decomposition temperature (T_{di}) and the half weight loss temperature (T_{d50}) at particular environmental conditions described previously. Experimental results are given in Tables 4–5. For the purpose of comparison, some thermograms on the studied series of copolymers are shown in Figure 2.

The following kinetic equation was assumed to hold for these thermal degradation reactions [11].

$$\ln\frac{1-C^{1-n}}{T^2(1-n)} = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{1}$$

When the reaction order $n = 1$,

$$\ln\left(\frac{-\ln C}{T^2}\right) = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{2}$$

TABLE 4 Thermogravimetric Analysis Results of Copolymers at Different PMI Feed Content (St 5 wt%)

PMI feed content, wt%	PMMA	0	5	10	15	20
T_{di},°C	262.4	266.8	280.9	291.3	301.3	301.8
T_{d50},°C	316.6	334.6	337.9	342.5	348.1	355.9
E_a,KJ/mol	49.08	74.03	88.10	99.73	113.29	121.06
R^2	0.9922	0.9979	0.9989	0.9997	0.9993	0.9996

TABLE 5 Thermogravimetric Analysis Results of Copolymers at Different St Feed Content (PMI 5 wt%)

St feed content, wt%	0	5	10	15	20
T_{di},°C	283.4	280.9	282.6	280.8	280.6
T_{d50},°C	327.0	337.9	338.1	339.6	339.1
E_a,KJ/mol	79.77	88.03	86.64	91.90	92.75
R^2	0.9983	0.9988	0.9998	0.9999	0.9918

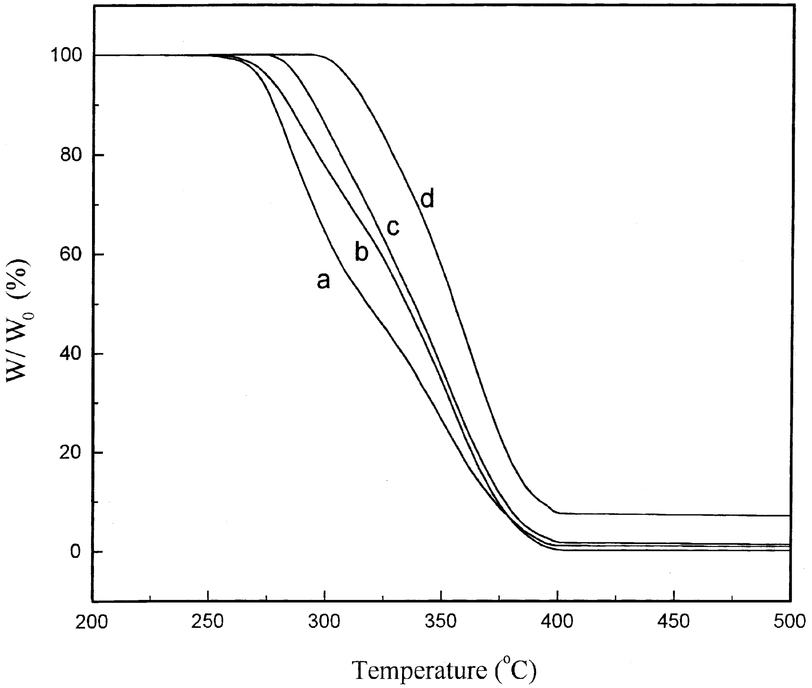

FIGURE 2 Thermogravimetric analysis diagrams (10°C/min). (a) PMMA; (b) MMA-St(95:5); (c) MMA-PMI-St (90:5:5); (d) MMA-PMI-St (75:20:5).

where $C = \frac{W}{W_0}$, W = remaining weight, W_0 = initial weight, A = frequency actor, ϕ = heating rate, R = ideal gas constant and E = activation energy. It was found that when $n = 1$ the linear correlation of coefficients have maximum values for almost all the samples. According to equation(2), a plot of $-\ln(\frac{-\ln C}{T^2})$ against $\frac{1}{T}$, is shown in Figure 3.

Many studies showed that PMMA is liable to decompose at high temperature. T_{d50} of PMMA was found to be 316.6°C in our study. The results in Table 4-5 indicate that the thermal stability tends to increase as both the PMI and St feed contents increase. Copolymers' T_{di}, T_{d50} and E_a all increase with increasing PMI feed content. But with increasing feed content of St, copolymer's T_{di} has not been improved. At the same time, T_{d50} and activation energy E_a have no significant improvement when the feed content of St was more than 5 wt%. T_{d50} increased 18°C when PMMA copolymerized with 5 wt% St, but T_{di} only increased 4.4°C. With 5 wt% PMI incorporated,

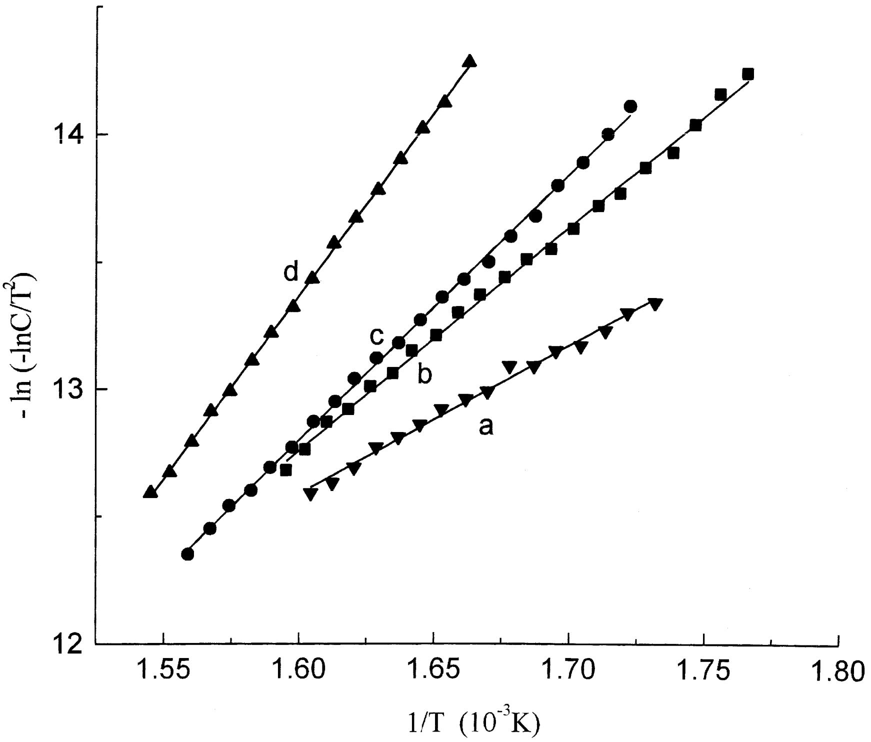

FIGURE 3 Thermogravimetric analysis plot of $-\ln(\frac{-\ln C}{T^2})$ against $\frac{1}{T}$ (a) PMMA; (b) MMA-St(95:5); (c) MMA-PMI-St (90:5:5); (d) MMA-PMI-St (75:20:5).

PMMA's T_{d50} increased 10.4°C and T_{di} increased 21°C. T_{d50} of temperature of MMA-PMI-St (75:20:5) is 39.3°C higher than neat PMMA, and T_{di} is 39.4°C higher than PMMA. This is probably because of the presence of 1,2-ethylenic units directly linked to styrene units [2].

Thus, the incorporation of PMI and St with MMA in emulsion copolymerization does restrain the decomposition reaction of PMMA, which is related to the previous studies of solution copolymerization of MMA-PMI-St[4]. And at the same time, the incorporation of PMI will highly increase copolymer's T_{di}, T_{d50} and activation energy E_a of degradation but incorporation of St only has significant effect when its feed content was lower than 5 wt%.

Glass Transition Temperature and Vicat Softening Temperature

Copolymer's T_g and Vicat softening temperature (T_{Vicat}) are other important thermal properties. Copolymers' T_g and T_{Vicat} are shown in Tables 6–7. The results show that coploymers' T_g and T_{Vicat} increase with increasing PMI feed content while decrease with increasing St feed content. And it was found that T_{Vicat} is usually several degrees lower than T_g for the same sample.

The linear relationship between T_g of poly(MMA-PMI-St) and PMI feed content with the composition range studied is expressed as follows:

$$T_g = 119.3(\pm 0.91) + 0.79 \times \mathrm{PMI(wt\,\%)}.$$

TABLE 6 T_g and T_{Vicat} of Copolymers at Different PMI Feed Content (St 5 wt%)

PMI feed content, wt%	PMMA	0	5	10	15	20
T_g,°C	115.0	119.0	124.0	126.2	132.6	134.5
T_{Vicat},°C	111.9	114.1	119.1	121.7	124.5	134.4

TABLE 7 T_g and T_{Vicat} of Copolymers at Different St Feed Content (PMI 5 wt%)

St feed content, wt%	0	5	10	15	20
T_g,°C	126.2	124.0	121.6	119.9	118.2
T_{Vicat},°C	122.5	119.1	115.8	115.4	112.9

The value in the brackets is standard deviation. The T_g value is thus enhanced by about 0.79°C per 1 wt% of PMI. But the glass transition temperature of terpolymer, as seen from Table 7, decreases with increasing St content.

The glass transition temperature and Vicat softening temperature reflect the stiffness and the mobility of molecular chain segments. PMI containing terpolymer contains five-member planar rings in the chain, which hinder chain rotation, resulting in greater structural stiffness. So, the T_g and T_{Vicat} of terpolymer increase with increasing PMI content.

With the incorporation of St, the structural stiffness of the molecular chain will decrease because of the decreasing molecular interaction. So T_g and T_{Vicat} decrease with increasing content of St.

Mechanical Property

The mechanical properties of the terpolymers at different feed proportion are summarized in Tables 8–9. As seen from Table 8, the tensile strength decreases 43.4 Mpa and the impact strength drops about 60% as the PMI feed content increases from zero to 20 percent (wt). PMI containing terpolymer contains five-member rings in the chain, and this ring contains a big side-group (phenyl group). So the interaction of molecular chain will decrease with increasing PMI content, resulting in lower tensile strength. The stiffness of molecular chain increases with increasing PMI feed content. This is a reason of impact strength decrease with increasing PMI feed content.

TABLE 8 Mechanical Properties of Copolymers at Different PMI Feed Content

PMI feed content, wt%	0	5	10	15	20
Tensile Strength, Mpa	61.1 (7.9)	52.8 (4.8)	44.7 (4.8)	33.5 (3.6)	17.7 (2.4)
Impact Strength, KJ/m^2	2.12 (0.06)	2.4 (0.43)	2.08 (0.12)	1.62 (0.09)	0.82 (0.27)

The values in the brackets are standard deviations.

TABLE 9 Mechanical Properties of Copolymers at Different St Feed Content

St feed content, wt%	0	5	10	15	20
Tensile Strength, Mpa	42.4 (2.9)	52.8 (4.8)	53.4(8.7)	56.3 (10.6)	57.0 (9.9)
Impact Strength, KJ/m^2	2.1 (0.23)	2.4 (0.43)	2.25 (0.05)	2.3 (0.17)	2.0 (0.2)

The values in the brackets are standard deviations.

The tensile strength and the impact strength of the terpolymer, as seen from Table 9, increase with increasing St feed content. The tensile strength of poly (MMA-co-PMI), in which the monomer feed composition is 95:5, is 42.4 MPa. It will rise to 57 MPa when the feed ratio of MMA:PMI:St is 75:5:20. The impact strength does not change significantly as St feed content increases. When the St feed content is 5 wt%, there is a minimal maximum, indicated that 5 wt% is an optimal feed content for St monomer.

CONCLUSIONS

1. The incorporation of PMI and St to PMMA in emulsion polymerization will highly restrain the thermal decomposition reaction of PMMA. PMI is an effective monomer for improving the thermal properties of materials, especially for glass transition temperature and decomposition temperature.
2. The tensile strength decreases and the impact strength drops as the PMI feed content increases. But the tensile strength and the impact strength of the terpolymers increase with increasing St feed content. 5 wt% is an optimal feed content for St monomer.

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