

**THE THERMAL ANALYSIS OF POLYMER BLENDS OF
POLY(ETHYLENE OXIDE)/POLY(METHYL METHACRYLATE)**

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Thermal analysis of the PEO/PMMA system show for the blends with higher molecular weight PMMA two glass transition temperatures in the 75-80 w/w% PMMA range. Thermal treatment is accompanied by a shift of this composition range of two Tg to lower PMMA contents. On the other hand observed melting point depression in the 0-60 w/w% PMMA range indicate compatibility of the blend components. Small negative interaction parameters approaching zero with increasing PMMA content of the blend, support the possible incompatibility in the observed composition range of two Tg.

Starting with the paper of Cortazar et al.[1], in the last decade were published a series of contributions concerning the compatibility of poly(ethylene oxide) - PEO- and poly(methyl methacrylate) -PMMA. Based on melting point depression measurement the authors concluded on the miscibility of the polymer pair in the molten state. But the glass transition temperature (Tg) change of only 15° in the composition range of 0-40 w/w% PMMA was very small compared with the difference of about 170° between the Tg of the blend components [2].

The miscibility in the molten state of PEO and PMMA is confirmed by Martuscelli and al. by melting point depression [3], ¹³C n.m.r. [4] and wide angle X-ray scattering [5]. The authors showed that the Tg of the blends obey the Fox equation in both the composition ranges of 0-40 w/w% PMMA (Tg increase of about 45°) and 70-100 w/w% PMMA [3]. Similar Tg data were reported by Min et al. [7] (composition range 75-100 w/w% PMMA) and Liberman et al. [8] (80-100 w/w% PMMA). Li and Hsü [9] observed also a single Tg for the 0-25 and 50-100 w/w% PMMA composition ranges. The miscibility is proved by IR measurements, but melting point depression was not observed by these authors.

Using small-angle neutron scattering, Ito et al. [10] found a concentration dependence of the Flory-Huggins interaction parameter, χ_{AB} . The parameter is slight negative for low PMMA content and approaches zero for a PMMA monomer fraction of the blend of 0.75.

Taking into account these contradictory data concerning the compatibility of PEO/PMMA blends, in the present study are analysed the influences of molecular weight, solvent and blend preparation and thermal treatment on the Tg of the blends.

Experimental

Materials

PEO samples (Aldrich) were purified by repeated precipitation from chloroform solution, first with diethylether and then twice with hexane. The samples were dried for 5 days in vacuum at 130°C. The PMMA samples were synthesized by group-transfer polymerization in THF at room temperature [11] in the presence of tris-(diethylamino)-sulfonium-bifluoride as catalysator and 1-methoxy-1(trimethylsiloxy)-2-methyl-propene as initiator. The polymers were purified by multiple precipitation of the THF solution with methanol and then dried for one week in vacuum at room temperature. The main characteristics of the polymers used for blend preparation are shown in Table 1.

Table 1. Polymers used for Blend Preparation

Polymer	M_n	M_w/M_n ^{a)}	T_g (°C) ^{b)}	T_m (°C)
PEO	1,000 ^{c)}	1.03	- 71.6	45.0
	8,000 ^{c)}	1.08	- 62.6	67.0
	100,000 ^{e)}	-	- 62.2	66.0
PMMA	1,700 ^{c)}	1.09	48.0	-
	16,000 ^{c)}	1.09	114.0	-

a) by GPC; b) by DSC; c) by vapour pressure osmosis and
e) by membrane osmosis, M_w by light scattering, $M_w=110,000$

Polymer Blends

The following series of blends were prepared by casting from $CHCl_3$ solution:

I - PEO 100,000/PMMA 16,000; II - PEO 8,000/PMMA 16,000; III - PEO 1,000/PMMA 16,000; IV - PEO 100,000/PMMA 1,700 and V - PEO 8,000/PMMA 1,700. (Numerals indicate the M_n of the polymers.)

The used composition ratio PEO:PMMA (w/w%) were of: 10:90, 25:75, 40:60, 50:50, 60:40, 75:25 and 10:90. For series I were analysed supplementary the blends of 15:85, 20:80, 80:20, 85:15 and 95:15.

To study the influence of the solvent and blend preparation, blends of series I were also obtained by freeze drying from benzene solution.

All blends were dried for 3 weeks in vacuum at 80°C.

Thermal Analysis

The thermal behaviour of the blends was studied using PERKIN-ELMER DSC 7. For the T_g measurements were investigated samples of 10-15 mg in the temperature range between -110° and 140°C, using cooling and heating rates of 30°/min, respectively. Some of the samples were quenched directly in liquid nitrogen to improve the T_g measurements. The T_g data were measured in the second heating cycle by the inflection point of the DSC traces. For blends of series I were used different heating rates and the T_g have been extrapolated for zero heating rate.

The depression of the melting temperature, T_m , was studied using the blends of series I only. The samples were first annealed for 5 min at 90°C to assure melting of all crystallites, then they were quenched to the desired temperature of crystallization, T_c , and maintained for 15 min for complete crystallisation. T_m represents the peak maximum of the DSC traces obtained using a heating rate of 15°/min.

Results and Discussion

Glass Transition

Typical thermograms are shown in Fig. 1. Glass transition and melting temperatures were recorded using different sensibilities (ratio of 8:1). The thermograms are jointed together at 0°C.

Blends with PMMA 16,000 show two T_g for the 75-80 w/w% PMMA content. Blends with PMMA 1,700 show for the same composition an enlarged glass transition of about 100°C. Because of this excessive spreading an exact determination of T_g was not possible mainly for some of the blends of series V.

The composition dependence of the glass transition is illustrated in Fig. 2. Are included literature data (open signs). Blends showing two T_g are marked by arrows and brackets. The dashed line represents the Fox equation [12] for the T_g vs. composition dependence of compatible polymer blends.

Except of the data published by Li and Hsu [9] (open horizontal squares) the observed single T_g in the range of lower PMMA content are nearly composition independent, suggesting on the existence of similar amorphous phases. T_g temperatures predicted by the Fox equation, however, should be situated in the range of the observed depressed melting temperatures. As it was not possible to suppress crystallization even by direct quenching in liquid nitrogen, it is not possible to verify if a second T_g is hidden by the T_m peak and thus to decide on the compatibility of the blend components in that composition range.

A second series of T_g measurements was carried out using both the solution casted and freeze dried blends of series I. Annealing for different times at 150°C was performed to study the influence of thermal treatment. The data are presented in Table 2. Are included the corresponding melting temperatures. It is remarkable that mainly for longer annealing times a shift of the range of two T_g to lower PMMA contents is observed (Fig. 3). T_m is less affected by this thermal treatment.

Melting behaviour

According to Nishi and Wang [13] the melting point depression is characteristic for miscible blends and can be used for evaluation of the Flory-Huggins interaction parameter, χ_{12} . Assuming the linear relationship between the melting temperature, T_m, of the crystalline phase (subscript 2) and the temperature of crystallisation, T_c, of the semicrystalline/amorphous polymer system

$$T_m^0 - T_m = \lambda (T_m^0 - T_c) \quad (1)$$

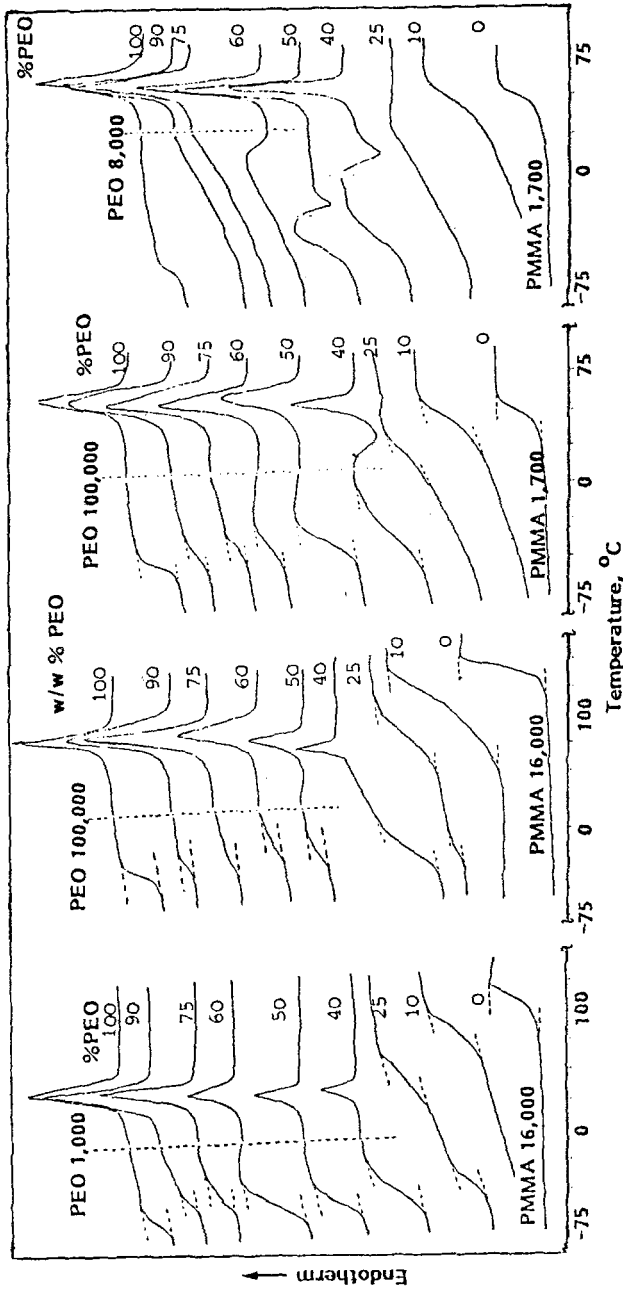


Fig. 1. DSC Thermograms of PEO / PMMA Blends
 (The numerals behind the polymer abbreviation represent the number average molecular weights; the numerals on the curves show the w/w% PEO content)

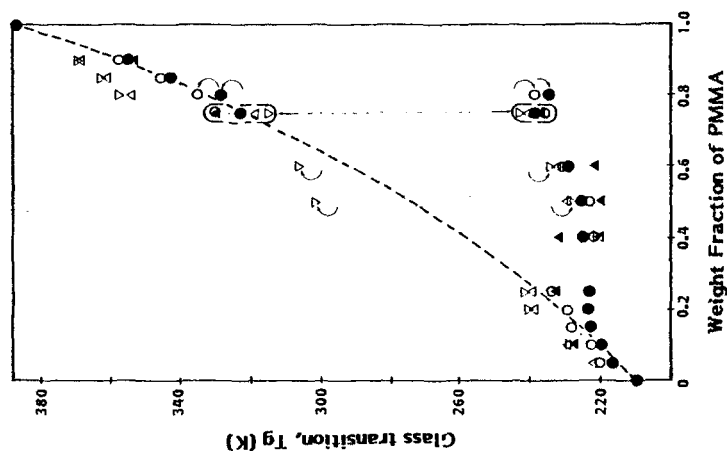


Fig. 3 Tg vs. Composition of PEO, 100,000/ PMMA 16,000 Blends
 Full signs: solution casted blends
 ● - initial; ▲ - annealed 3 days (150°C)
 Open signs: freeze dried from benzene
 ○ - initial; annealed at 150°C
 △ - 20 days and ▽ - 40 days

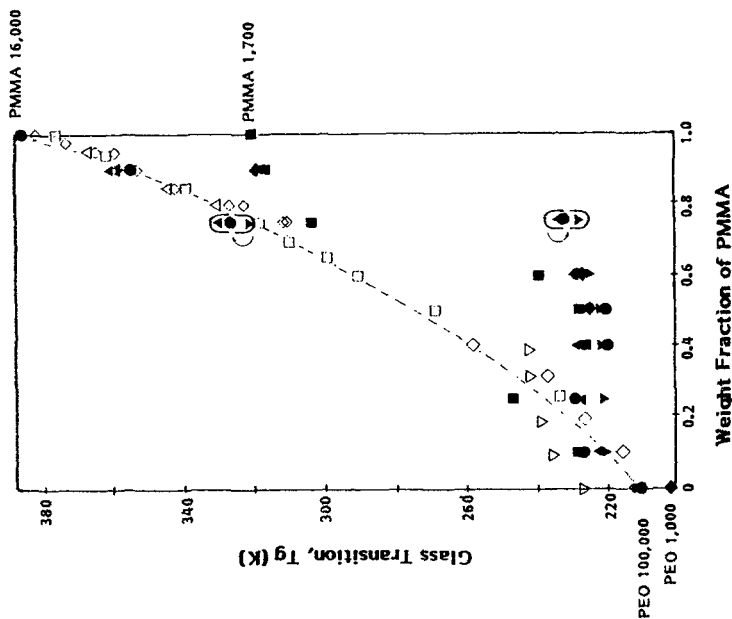


Fig. 2 Tg vs. Composition of PEO/PMMA Blends
 Full signs: this work, solution casted blends
 ● - 100,000/16,000; ▲ - 8,000/16,000; ▼ - 1,000/16,000
 ■ - 100,000/1,700 and ◆ - 8,000/1,700 (M_n values)
 Open signs: literature data: ▽ - 4,000,000/93,600 /2/;
 small ◇ - 20,000/116,000 (M_{visc}) /3/; ◇ - /6/ and
 □ - /9/ 100,000/106,000 and △ - 18,500/600,000 (M_w)

Table 2. Thermal Characteristics of the PEO, $M_n=100,000$ / PMMA, $M_n=16,000$ Blends

Composition w/w % PEO/PMMA	Blends casted from CHCl_3 -solution ^{a)}		Blends by freeze drying of benzene solution ^{b)}			
	Tg (°C) After thermal treatment at 80°	T _m (°C)	Tg (°C) After thermal treatment at 80°	T _m (°C)	Tg (°C) Annealed 20 days at 150°C	T _m (°C) Annealed 40 days at 150°C
100/0	-62.0	66.0	-	-	-	-
95/5	-55.6	64.8	-	63.3	-49.3	65.2
90/10	-52.6	64.9	-44.0	62.9	-43.0	64.1
85/15	-49.5	63.3	-	62.2	-	-
80/20	-48.5	63.2	-	61.4	-33.6	63.5
75/25	-49.3	62.8	-39.0	61.0	-32.9	63.3
60/40	-47.1	58.1	-40.9	57.7	-51.6	59.4
50/50	-46.4	55.6	-52.4	54.3	-42.9	55.0
40/60	-42.2	53.2	-50.6	53.8	-39.8	54.4
25/75	{ -34.0 49.5	-	{ -34.7 57.1	-	{ -31.6 45.6	-
20/80	{ -37.7 55.5	-	{ -33.4 62.5	-	{ 80.4 -	-
15/85	65.0	-	72.7	-	87.5	-
10/90	81.2	-	84.2	-	84.4	-
0/100	114.0	-	-	-	95.2	-
					{ -36.5 29.0	{ -37.5 33.1
					{ -29.0 41.2	{ 84.4 -
					89.8	-
					96.1	-

All blends were dried for 3 weeks under vacuum at 80°C. After thermal treatment the blends were quenched to liquid nitrogen temperature using a cooling rate of 30°C/min.

a) Tg values extrapolated for zero heating rate, b) Tg values for h.r. 30°C/min

which supposes a constant stability parameter, λ , the equilibrium melting temperature, T_m^0 , can be evaluated by extrapolation of the T_m vs. T_c data for $T_m=T_c$.

Knowing T_m^0 , the interaction parameter, χ_{12} , can be computed by using the expression:

$$[(T_m)^{-1} - (T_m^0)^{-1}] = -[(RV_{2u})/(\Delta H_{2u}V_{1u})] \chi_{12}(1 - \phi_2)^2 \quad (2)$$

Neglecting the effects of entropy, χ_{12} can be related to the respective interaction energy density, B , of the polymer pair:

$$\chi_{12} = BV_{1u}/RT \quad (3)$$

Substitution in equ. (2) gives finally:

$$[1 - (T_m/T_m^0)] = -[(BV_{2u})/(\Delta H_{2u})] \phi_1^2 \quad (4)$$

The expression can be used for the evaluation of B using literature data for ΔH_{2u} , the enthalpy of fusion per mole repeating unit, V_{2u} , the molar volume of the repeating unit and the densities of the components [13,14]. The latter are necessary for calculation of the volume fractions, ϕ , starting with the weight fractions of the crystalline and amorphous components.

In Fig. 4a are presented the T_m vs. T_c data according to equ. (1). Are shown data of both solution casted (full signs) and freeze dried blends (open signs). The observed change of the slope of the T_m vs. T_c data indicate a change of the stability parameter in the composition range 75-100 w/w% PEO. This change suggests that melting point depression is governed not only by thermodynamic factors, but also by the kinetic dependant morphology of the blends. The blends in the composition range 40-75 w/w% PEO show straight lines nearly parallel with the flater straight lines in the 75-80 w/w% PEO range.

Correspondingly two mean values of the stability factor and of the interaction parameter (Fig. 4b) are obtained. The values are compared with literature data in Table 3.

It is interesting to note that by T_m depression are obtained similar values of the interaction parameters for similar composition ranges of the blend. These values are, however, larger negative than the data raported by other methods of investigation.

Conclusion

The miscibility of PEO/PMMA blends could not be confirmed for the whole range of composition by the thermal analysis data obtained in the conditions used in this work. T_g measurements show for blends with the higher molecular weight PMMA

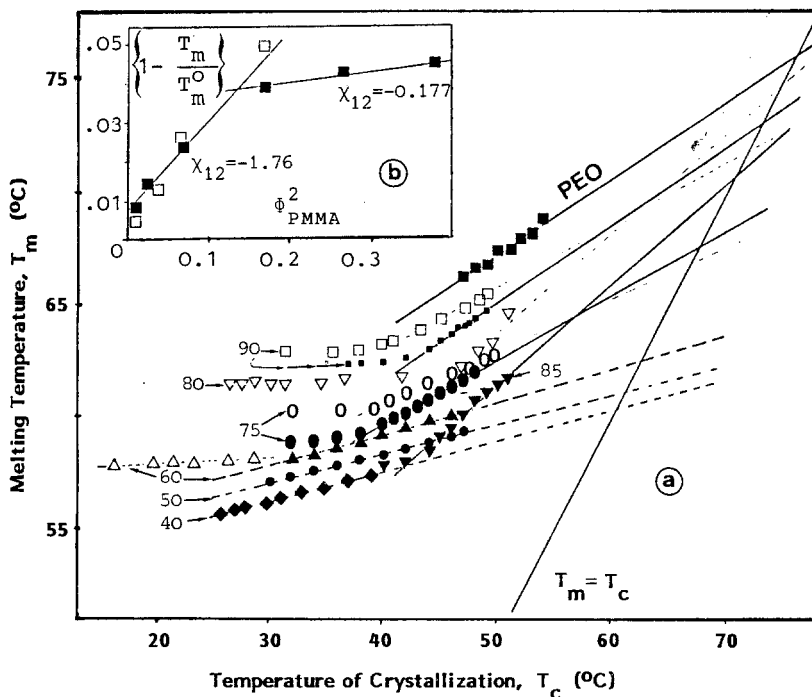


Fig. 4 Melting Temperature vs. Crystallization Temperature

Table 3. Interaction Parameters of the PEO/PMMA Blends

Authors	Molecular Weights PEO/PMMA	Composition w/w % PEO	B cal/cm ³	χ_{12}
This work	100,000/ 16,000	75-95 ^{a)}	-12.42 ^{c)}	-1.76
		40-95 ^{b)}	- 1.25 ^{c)}	-0.177
Cortazar /1/	4,000,000/ 93,600	60-90	- 1.07 ^{c)}	-0.139
Martuscelli /3/	20,000/116,000	80-95	-15.6 ^{c)}	-1.93
Martuscelli /6/	100,000/110,000	60-90	- 2.85 ^{c)}	-0.35
Lieberman /8/	various/600,000	40-90	- 1.22 ^{c)}	-0.157
Min /7/	700,000/120,000	-	- 0.94 ^{d)}	-
Ito /10/	145,000/129,000	70	-	-5×10^{-3} e)
		25	-	-1×10^{-3} e)

a) T_m measured for blends with 75-95 w/w% PEO obtained at higher T_c

b) T_m for blends with 75-95 w/w% PEO obtained at lower T_c and all other blends in the 40-75 w/w% PEO range

c) by T_m -depression, d) calorimetric and e) by neutron scattering

two T_g for the composition range 75–80 w/w% PMMA. By annealing the composition range of two T_g is shifted to lower PMMA contents of the blends. For all blends in the composition range up to 60 w/w% PMMA is observed a single almost invariable T_g indifferent of the blend composition, suggesting a nearly constant composition of the amorphous phase.

On the other hand, the melting point depression in the 0–60 w/w% PMMA range indicate the compatibility of the blend component, but the small negative values of the interaction parameters, approaching zero for the higher PMMA content confirm the restricted compatibility of the PEO/PMMA pair.

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Zusammenfassung - Die Thermoanalyse des Systemes PEO/PMMA ergab für Gemische mit PMMA höheren Molekulargewichtes zwei Glasumwandlungspunkte /Tg/ im Bereich 75-80 m/m% PMMA. Eine Wärmebehandlung ist vom Verschieben dieses Bereiches mit den zwei Tg in Richtung niedrigerem PMMA-Gehalt begleitet. Weiterhin zeigt die Schmelzpunktserniedrigung im Bereich 0-60 m/m% PMMA die Kompatibilität der Gemischkomponenten. Kleine negative, mit steigendem PMMA-Gehalt des Gemisches gegen Null haltende Wechselwirkungsparameter unterstreichen die Möglichkeit einer Inkompatibilität im beobachteten Bereich der zwei Tg.

Резюме - Термический анализ системы полиэтиленоксид - полиметакрилат /PMMA/ показал, что смеси, содержащие PMMA более высокого молекулярного веса, обладают двумя температурами стеклообразования при содержании PMMA равным 75-80 вес.%. Термическая обработка этой смеси сопровождается сдвигом двух T_g в область с более низким содержанием PMMA. С другой стороны наблюдаемая точка плавления понижается в смесях с содержанием PMMA 0-60 вес.%, что указывает на совместимость компонентов смеси. Малые отрицательные параметры взаимодействия приближаются к нулю с увеличением содержания PMMA в смеси, что свидетельствует о возможной несовместимости в наблюдаемой области состава.