

폴리메타아크릴레이트들과 비닐클로라이드-비닐리덴클로라이드 공중합체와의 블렌드에 관한 연구

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A Study on the Blends of Polymethacrylates with Vinyl Chloride-Vinylidene Chloride Copolymer

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요 약 : 치환기가 다른 14종의 폴리메타아크릴레이트와 비닐클로라이드와 비닐리덴클로라이드의 공중합체(P(VC-VCl₂))와의 블렌드에 대한 상용성을 시차주사 열량분석을 이용하여 연구하였다. 폴리메틸메타아크릴레이트, 폴리에틸 메타아크릴레이트, 폴리 n-프로필메타아크릴레이트, 폴리isopro필 메타아크릴레이트, 폴리 n-부틸메타아크릴레이트, 폴리isobutyl메타아크릴레이트, 폴리 s-부틸메타아크릴레이트, 폴리 n-아밀메타아크릴레이트, 폴리 n-헥실메타아크릴레이트, 폴리시클로헥실메타아크릴레이트, 폴리페닐메타아크릴레이트와 P(VC-VCl₂)와의 1:1블렌드는 상용한다는 것을 알았다. 폴리글리시딜메타아크릴레이트, 폴리히드록시프로필메타아크릴레이트, 폴리 t-부틸메타아크릴레이트와 P(VC-VCl₂)와의 1:1 블렌드는 상용하지 않았다. 폴리메타아크릴레이트들과 P(VC-VCl₂)와의 블렌드에서 알킬치환기를 가진 폴리메타아크릴레이트의 상용성은 폴리메타아크릴레이트의 알킬 치환기의 극성효과보다 입체효과에 더 의존하는 것으로 밝혀졌다. 한편, 아릴 치환기를 가진 폴리페닐메타아크릴레이트와 P(VC-VCl₂)의 블렌드는 전 조성에서 상용성을 보였으며 결정융점강화 값으로부터 구한 열역학적 상호작용 파라미터 χ_{12} 는 -0.41이었다.

Abstract : Differential scanning calorimetry was used to determine the miscibility behavior for the blends of polymethacrylates (PMA's) having various alkyl groups with the copolymer of vinyl chloride and vinylidene chloride(P(VC-VCl₂)). The 1:1 blends of polymethacrylates containing a methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, n-amyl, n-hexyl, cyclohexyl or phenyl group with P(VC-VCl₂) were found miscible. The 1:1 blends of polymethacrylates containing a glycidyl, 2-hydroxy propyl or t-butyl group with P(VC-VCl₂) were found immiscible. It was found that the miscibility of PMA's having alkyl groups in the blends of PMA's with P(VC-VCl₂) depended more heavily on the steric

effect than the polar effect of alkyl substituent groups of PMA's. The blends of poly(phenyl methacrylate (PPhMA)) with P(VC-VC₂) showed miscibility over the whole concentration ranges. From the crystalline melting point depression data on the blends of PPhMA with P(VC-VC₂), thermodynamic interaction parameter χ_{12} has been estimated to be -0.41 .

INTRODUCTION

The polymer blends have been extensively investigated from theoretical and practical standpoints.¹⁻⁴ Indeed, a large number of different materials can be prepared by simply varying the concentration of the constituents of a blend. However, the miscibility of polymer/polymer blends is a relatively rare phenomenon.

A brief review of the literature indicates that several polyesters and polymethacrylates,⁵ which have methyl, ethyl, n-propyl, isopropyl, n-butyl, n-hexyl, give miscible blends with chlorinated polymers including poly(vinyl chloride), chlorinated PVC, and Saran (a statistical copolymer of vinylidene chloride, containing 88% vinylidene chloride).

It has been suggested that the miscibility of these blends is due to specific interactions between the carbonyl groups of the polyesters^{6,7} and polymethacrylates⁵ and the hydrogen of chlorinated polymers. In this context, it is expected that further studies on the blends of polymethacrylates having various substituent groups with Saran will be fruitful both in understanding the basis and limits for miscibility and in discovering new miscible materials.

The purpose of this paper is to systematically study on the miscibility behavior of the blends of several polymethacrylates (PMA's) having alkyl and aryl substituents with the copolymer of vinyl chloride and vinylidene chloride (P(VC-VC₂)), containing 88% by weight of vinylidene chloride. The blends have been prepared from poly(methyl methacrylate), poly(ethyl methacrylate), poly(n-propyl methacrylate), poly(glycidyl methacrylate), poly(2-hydroxy propyl methacrylate), poly(isopropyl methacrylate), poly(n-butyl methacrylate), poly(isobutyl methacrylate), poly(sec-butyl methacrylate), poly(t-butyl methacrylate), poly(n-amyl methacrylate),

poly(n-hexyl methacrylate), poly(cyclohexyl methacrylate) and poly(phenyl methacrylate) with copolymer of vinyl chloride and vinylidene chloride.

The miscibility of these different blends have been analyzed by differential scanning calorimetry (DSC). Their miscibility has been estimated by the appearance of a single glass transition temperature (T_g) and a depression in crystalline melting temperature (T_m).

EXPERIMENTAL SECTION

The polymers used in this study are described in Table 1 along with their acronym, molecular weight, T_g , T_m and sources. The polymethacrylates (PMA's) are atactic. The Saran is the random copolymer of vinyl chloride and vinylidene chloride (P(VC-VC₂)), containing 88% by weight of latter repeating unit.

The molecular weights reported in Table 1 were determined by the size exclusion chromatography (SEC) using μ -styragel columns and a Waters chromatography. The measurements were conducted in tetrahydrofuran (THF) or toluene. The apparatus was calibrated with polystyrene standards and no effort was made to correct the numbers obtained by and sort of universal calibration procedures.

Polymer blends were prepared by slowly casting films from 1% solution tetrahydrofuran (THF). Solvent evaporation was conducted at room temperature. The resulting films were dried under vacuum until they reached constant weight.

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a TADS microcomputer. The DSC was calibrated with ultrapure indium (429°K). The glass transition tem-

Table 1. Characterization and Description of Polymers Used in This Study.

Polymer	Acronym	Molecular weight (kg / mole)		T _g (°K)	Source
		\overline{M}_n	\overline{M}_w		
<u>PMA's</u>					
R= methyl	PMMA	47	84	365	Fisher
ethyl	PEMA	90	147	343	Aldrich
n-propyl	Pn-PMA	210	270	325	Polysciences
glycidyl	PGMA	11	58	291	Aldrich
2-hydroxypropyl	PHPMA	36	110	374	Aldrich
i-propyl	Pi-PMA	150	460	358	Aldrich
n-butyl	Pn-BMA	88	150	302	Aldrich
i-butyl	Pi-BMA	220	310	328	Aldrich
s-butyl	Ps-BMA	22	66	321	Aldrich
t-butyl	Pt-BMA	54	102	368	Aldrich
n-amyl	Pn-AMA	22	61	270	Polysciences
n-hexyl	Pn-HMA	80	109	259	Aldrich
cyclohexyl	PCHMA	36	84	358	Polysciences
phenyl	PPhMA	38	80	393	Aldrich
<u>Copolymer</u>					
Poly(vinyl chloride-co-vinylidene chloride)	P(VC-VC1 ₂)	—	100	281	Polysciences

peratures(T_g) reported were recorded at the half-height of the corresponding heat capacity jump. Reported crystalline melting temperatures(T_m) were recorded at the end of the melting curve.

After insertion of samples in the DSC apparatus, all samples were first cooled at 173°K and maintained at that temperature for 5 min. The first scan was made at a heating rate of 40°K/min, up to 460°K, and then the sample was maintained for 2 minutes at that temperature. It was quenched at 360°K and maintained at that temperature for 15 minutes to allow the crystallization of Saran. This sample was then quenched at 173°K, it was again left for 10 minutes at this temperature before the second scan at a heating rate of 20°K/min, and reheated at 460°K. The T_g 's, T_m 's and the enthalpy of fusion(ΔH_f) of Saran were always recorded during the second scan.

In this paper, the following terminology is adopted: a sample is declared miscible when it gives for a given composition a single T_g intermediate between those of its pure components, even if crystals of components 1 and / or 2 are formed. A sample exhibiting two T_g 's at a given composition

is declared immiscible. According to this terminology, it suffices to observe two T_g 's at one composition in order to conclude that the sample is immiscible, even if the possibility of observing a single T_g at other composition.

RESULTS AND DISCUSSION

T_g Behaviors

Table 2 gives the T_g values measured for PMA's / P(VC-VCl₂) blends of a 1 : 1 composition. The blends of PMMA, PEMA, Pn-PMA, PHMA, Pi-PMA, Pn-BMA, Pi-BMA, Ps-BMA, Pn-AMA, Pn-HMA, PCHMA and PPhMA with P(VC-VCl₂) were found miscible since these blends exhibited a single T_g values at a temperature intermediate between those of the corresponding homopolymers. This observation means that we were unable to detect two phases by DSC measurements. From a DSC point of view, these blends are homogeneous. However, we must keep in mind that the size scale of the T_g measurement is of the order of 15nm, therefore, the measurement of a single T_g does not necessarily imply molecular

Table 2. DSC Analysis of the 1 : 1 Blends of PMA's / P(VC-VCl₂), T_g of P(VC-VCl₂) : 281°K.

PMA's	T _g (°K)	
	PMA's	PMA's / P(VC-VCl ₂)
PMMA	365	331
PEMA	343	315
Pn-PMA	325	299
PGMA	291	276 and 289
PHPMA	374	282 and 327
Pi-PMA	358	317
Pn-BMA	302	289
Pi-BMA	328	301
Ps-BMA	321	297
Pt-BMA	368	290 and 350
Pn-AMA	270	271
Pn-HMA	259	269
PCHMA	358	320
PPhMA	393	335

Table 3. Glass Transition Temperature (T_g) of Pi-BMA / P(VC-VCl₂).

Pi-BMA (weight %)	T _g (K)	Phase
	Pi-BMA / P(VC-VCl ₂)	
0	281	I
15	281 and 317	
35	281 and 319	M
50	305	
65	311	M
85	316	
100	328	

I : immiscible M : miscible

homogeneity.

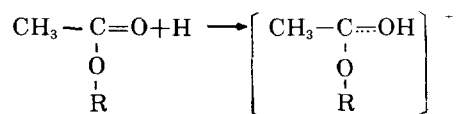
The PGMA / P(VC-VCl₂), PHPMA / P(VC-VCl₂) and Pt-BMA / P(VC-VCl₂) blends exhibit two T_g values which are close to the T_g values of the corresponding homopolymers. By our criterion concerning miscibility or immiscibility, these blends are immiscible, with the formation of two phases composed of mixed component containing two homopolymers. It is obvious from Table 2 that the T_g values of PAMA and P(VC-VCl₂) are very close, making any decision upon the miscibility of these two polymers uncertain. Since this blend was optically clear, it has been declared miscible. Our results on the miscibility of the 1 : 1 blends

of PMMA, PEHA, PPMA, Pi-PMA, PBMA, PAMA, PHMA and PCHMA with P(VC-VCl₂) are in agreement with those of the literature.⁵

Table 3 gives the T_g values measured for Pi-BMA / P(VC-VCl₂) blends of various compositions. The Pi-BMA / P(VC-VCl₂) mixture exhibits two T_g's at Pi-BMA contents of 15 and 35% and, therefore, these two mixtures are immiscible. However, the Pi-BMA / P(VC-VCl₂) blends are miscible at Pi-BMA contents of 50, 65 and 85% since these blends exhibit a single T_g.

Substituent Effect of PMA's

Taft studied the reaction kinetics of the acid catalyzed hydrolysis in aliphatic esters and pointed out the polar and the steric effect of the alkyl substituents are major two factors to govern the reaction rates of the systems represented by the following scheme^{8,9}:



He reported that the reaction rate increased with increasing electron releasing ability of alkyl substituents, R, and with decreasing bulkiness of the substituents and proposed the following equation⁹:

$$\log(k/k_0) = \rho^* \sigma^* + \delta E_s \quad (1)$$

where k and k₀ are reaction rate constant of substituted aliphatic ester and unsubstituted ester, respectively, ρ*: reaction constant measuring the susceptibility of the reaction to polar effect, σ*: the substituent constant relating to the polar effect of alkyl substituent R relative to the standard CH₃, δ: reaction constant measuring the susceptibility of the reaction to steric effect and E_s is the substituent constant relating to the steric effect of alkyl substituents.

The polar constant (σ*) means that the more electron releasing group has larger negative value which can favorably interact with positive part (H⁺). Steric constant (E_s) indicates that much

Table 4. Polar(σ^*) and Steric(E_s) Constants¹ for Alkyl Groups of PMA's and Miscibility or Immiscibility of 1:1 Blends of PMA's with P(VC-VCl₂).

Substituent group of PMA's	$-\sigma^*$	$-E_s$	Phase
Me	0.00	0.00	M
Et	0.10	0.07	M
n-Pr	0.115	0.36	M
i-Pr	0.19	0.47	M
n-Bu	0.13	0.39	M
i-Bu	0.125	0.93	M
s-Bu	0.21	1.13	M
t-Bu	0.30	1.54	I
n-Am	0.16	0.40	M

M : miscible I : immiscible

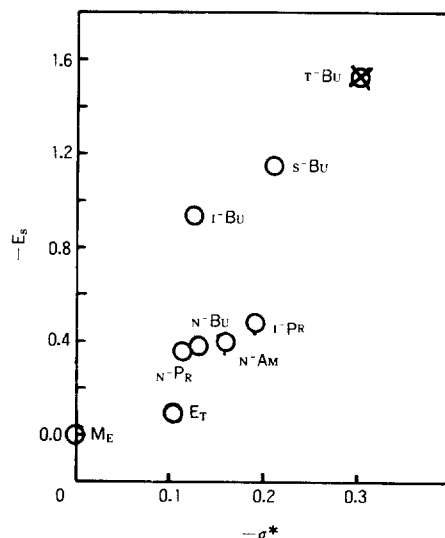
+ Data from Ref. 9.

bulkier group has greater negative value which signifies the difficulty of approach toward the specific intermolecular interaction sites between the components : positive part and oxygen at carbonyl group.

It is assumed that the interaction sites are similar in the Taft's reaction systems of the acid catalyzed alkyl esters and in the blends of PMA's and P(VC-VCl₂) studied in this work because of the similar molecular structure of the interacting components having alkyl substituent groups in the two systems.

Thus, we suggests that the two factors also play an important role in the miscibility behavior of PMA's / P(VC-VCl₂) blend ; the polar and steric effect of the PMA's as host polymer, and the copolymer as guest, although Taft's consideration was originated from the relationship between structure and reactivity. The polar and steric effect of PMA's is depicted in Fig. 1.

Table 4 summarizes the miscibility or immiscibility behavior of the substituent effect of PMA's for the blends of PMA's with P(VC-VCl₂). The order of the effect of increasing electron release is Me<Et<n-Pr<i-Bu<n-Bu<n-Am<i-Pr<s-Bu<t-Bu as shown by the increasingly more negative values of σ^* . E_s is near-quantitative measure of the total steric effect associated with a given

**Fig. 1.** Miscibility or immiscibility in the blends of PMA's with P(VC-VCl₂).

○ : miscible ⊗ : immiscible

substituent relative to the standard of comparison (-CH₃). The order of increasing ($-E_s$) values is Me<Et<n-Pr<n-Bu<n-Am<i-Pr<s-Bu<t-Bu.

From Table 4 and Figure 1, it is concluded that the miscibility of PMA's in the blends of PMA's with P(VC-VCl₂) depends more heavily on the steric effect than the polar effect of substituent group of PMA's.

It must be realized that the miscibility phenomenon results from a competition between interactions. In order to create A / B interactions and a miscible blend, A / A and B / B interactions must be broken. If the A / A interactions are stronger than A / B interactions they will not be broken and the A / B blends will be immiscible.

For our works, in order to create PMA's and P(VC-VCl₂) interactions and a miscible blend, PMA's / PMA's and P(VC-VCl₂) / P(VC-VCl₂) interaction must be broken. If PMA's / PMA's interactions are stronger than PMA's / P(VC-VCl₂) interactions they will not be broken and PMA's / P(VC-VCl₂) blends will be immiscible. This situation may occur in Pt-BMA / P(VC-VCl₂) blend since the steric effect of bulky t-

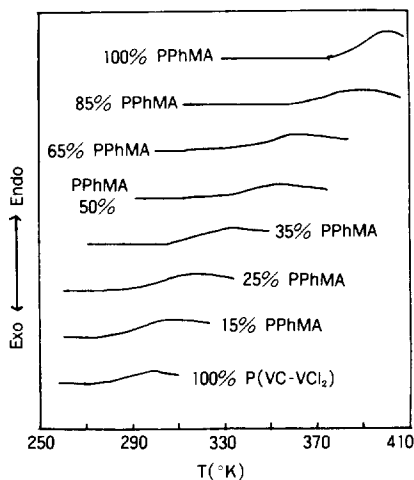


Fig. 2. DSC curves in the T_g transition zone for PPhMA / P(VC-VCl₂) blends. The lowest curve is for P(VC-VCl₂) and the highest one for PPhMA. The intermediate curves, from bottom to top, correspond to blends with 15, 25, 35, 50, 65 and 85% by weight of PPhMA, respectively.

Table 5. Glass Transition Temperature(T_g), Crystalline Melting Temperature(T_m) and Enthalpy of Fusion (ΔH_f) of PPhMA / P(VC-VCl₂).

PPhMA (weight %)	$T_g(^{\circ}\text{K})$	$T_m(^{\circ}\text{K})$	ΔH_f (KJ / mole)
0	281	445	22
15	290	437	19
25	298	436	16
35	327	431	12
50	335	427	8
65	349	419	6
85	376	—	—
100	393	—	—

butyl group interferes the approaching of hydrogen in P(VC-VCl₂) to oxygen of carbonyl group in PMA's.

PPhMA/P(VC-VCl₂) Blend

The blends of PPhMA and P(VC-VCl₂) is of interest since the blends showed miscibility over all concentration ranges.

In order to confirm the miscibility of the PPhMA / P(VC-VCl₂) blends, DSC measurements were

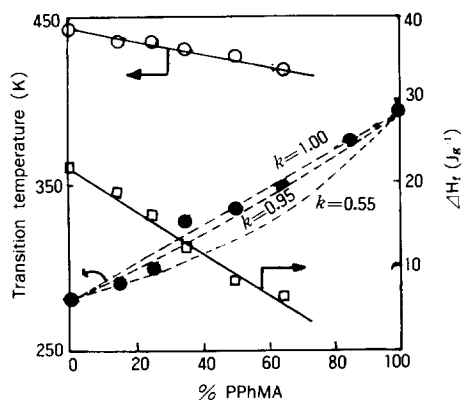


Fig. 3. Phase diagram of PPhMA / P(VC-VCl₂). The dotted lines obey equation (4). Three parameter k 's are denoted in the figure to fit the experimental T_g data as function of composition. \circ : T_m , \bullet : T_g , \square : enthalpy of fusion.

conducted at nine compositions ranging from 15 to 85%. For illustrative purpose, DSC curves in the T_g transition zone for PPhMA / P(VC-VCl₂) blends are shown in Fig. 2. T_g , T_m and ΔH_m values are reported in Table 5 and Fig. 3. All the blends exhibit a single T_g at each composition indicating miscibility and T_g values increase regularly with composition of PPhMA.

The variation of T_g of miscible blends as a function of composition can be expressed by several equations.^{10,11} The simple mixing rule is

$$T_g = w_1 T_{g1} + w_2 T_{g2} \quad (2)$$

where T_g is the glass transition temperature of the blend, and T_{g1} and T_{g2} are those of components 1 and 2, and w_1 and w_2 are the corresponding weight fractions.

Equation (2) predicts a linear T_g versus composition relation. However, a negative deviation is often observed. Negative deviations can be simulated by using the Fox equation.¹⁰

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (3)$$

or the Gordon-Taylor equation,¹¹

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (4)$$

where k is the ratio between the volume expansion coefficients of the homopolymers of the blend. When k is equal to unity, eq. (4) reduces to eq. (2). The smaller is the value of k , the greater is the concavity of the T_g versus composition curve. The dotted lines drawn in Figure 3 was obtained from equation (4) with parameter k (without correction for the real composition of the amorphous phase). The figure shows that k is 0.55 for P(VC-VCl₂)-rich blends and 0.95 for PPhMA-rich blends. Similar variations were reported in the polycaprolactone / P(VC-VCl₂) blend systems.⁷

The degree of miscibility of blends where one component is semicrystalline can be also followed by measurement of T_m . As shown in Table 5 and Figure 3, T_m of P(VC-VCl₂) decreases with increasing PPhMA contents in the blends.

This result can be also interpreted as being due to extensive mixing of the segments of the blends. Quantitatively, it has been shown that depression in the melting point data can be interpreted according to the equation,¹²

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = - \frac{R V_2}{\Delta H_2 V_1} \chi_{12} \phi_1^2 \quad (5)$$

where T_m is the melting point of the blend, T_m° is the melting point of pure P(VC-VCl₂), R is the gas constant, ΔH_2 is the molar heat of fusion of the repeating units in P(VC-VCl₂), V_1 and V_2 are the molar volumes of the repeating units of P(VC-VCl₂) and PPhMA, and χ_{12} is the PPhMA / P(VC-VCl₂) thermodynamic interaction parameter. As shown in Fig. 4, a plot of $1/T_m$ as a function of ϕ_1^2 leads to straight line, from which χ_{12} can be calculated. If V_2 and V_1 are taken equal to 57 cm³/mole¹³ and 133.88 cm³/mole¹⁴, respectively, and ΔH_2 is equal to 6.3 KJ/mole,^{15,16} χ_{12} is -0.41 for the PPhMA

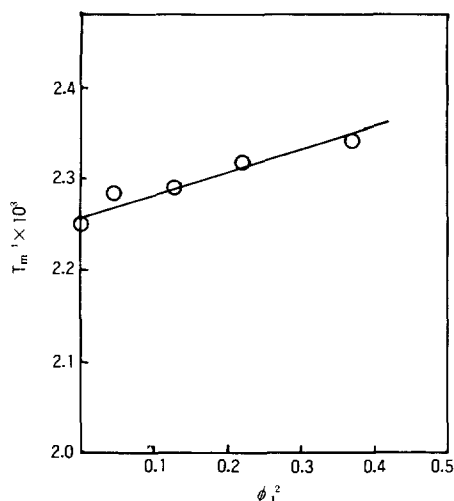


Fig. 4. Plot of $1/T_m$ vs. ϕ_1^2 in PPhMA / P(VC-VCl₂) blends, $\chi_{12} = -0.41$.

/P(VC-VCl₂) blend. A negative value of χ_{12} indicates the formation of a thermodynamically miscible blend above the melting point of P(VC-VCl₂).

Values of the enthalpy of fusion, ΔH_2 reported in units of kilojoules per gram of P(VC-VCl₂), are also given in Table 5. Blends containing more than 85% PPhMA do not allow P(VC-VCl₂) to crystallize. Blends containing from 15 to 65% PPhMA have value of ΔH_2 which decrease regularly as the composition in PPhMA increases. Similar examples can be found in the literature for several other blends.⁷

CONCLUSIONS

1. The 1 : 1 blends of polymethacrylates (PMA's) containing methyl (PMMA), ethyl (PEMA), n-propyl (Pn-PMA), i-propyl (Pi-PMA), n-butyl (Pn-BMA), i-butyl (Pi-BMA), s-butyl (Ps-BMA), n-amyl (Pn-AMA), n-hexyl (Pn-HMA), cyclohexyl (PCHMA) and phenyl group (PPhMA) with P(VC-VCl₂) were found miscible since these blends exhibited a single T_g value at a temperature

intermediate between those of the corresponding homopolymers.

2. The 1 : 1 blends of polymethacrylates containing glycidyl(PGMA), hydroxy propyl(PHPMA) and t-butyl group(Pt-BMA) with P(VC-VCl₂) were exhibited two T_g values of the corresponding homopolymers. These blend were found immiscible.

3. It is concluded that the miscibility of PMA's with P(VC-VCl₂) depends more heavily on the steric effect than the polar effect of substituent groups of PMA's.

4. The blends of poly(phenyl methacrylate) (PPhMA) with P(VC-VCl₂) were exhibited a single T_g over all composition ranges which increased regularly with composition of PPhMA.

5. The calculated thermodynamic interaction parameter χ_{12} value for the blends of PPhMA with P(VC-VCl₂) has been estimated to be -0.41.

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