폴리메타크릴레이트들과 염소를 포함하고 있는 고분자들의 블렌드에 관한 연구

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Blends of Polymethacrylates and Chlorine Containing Polymers

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요 약 : 치환기가 다른 14종의 폴리메타크릴레이트와 폴리비닐클로라이드(PVC), 염소화된 폴리에틸렌(CPE), 염소화된 폴리비닐클로라이드 (C-PVC : 염소함량 65 및 68%)와의 블렌드에 대한 상용성을 시차주사열량분석을 이용해서 연구하였다. 폴리메틸메타크릴레이트와 PVC 1 : 1 블렌드 및 폴리에틸메타크릴레이트, 폴리n-프로필메타크릴레이트, 폴리이소프로필메타크릴레이트, 폴리n-부틸메타크릴레이트, 폴리이소부틸메타크릴레이트, 폴리s-부틸메타크릴레이트, 폴리n-아밀메타크릴레이트, 폴리n-헥실메타크릴레이트, 폴리시클로헥실메타크릴레이트와 PVC 및 CPVC와의 1 : 1 블렌드와 폴리시클로헥실메타크릴레이트와 1 : 1 CPE와의 1 : 1 블렌드는 상용성이 있다는 것을 알았다. 폴리메틸메타크릴레이트와 CPVC 1 : 1 블렌드계는 상용성이 없었다. 폴리글리시딜메타크릴레이트, 폴리히드록시프로필메타크릴레이트, 폴리t-부틸메타크릴레이트, 폴리페닐메타크릴레이트와 PVC, CPE 및 CPVC와의 블렌드와 폴리메틸메타크릴레이트, 폴리에틸메타크릴레이트, 폴리n-프로필메타크릴레이트, 폴리이소프로필메타크릴레이트, 폴리n-부틸메타크릴레이트, 폴리이소부틸메타크릴레이트, 폴리s-부틸메타크릴레이트, 폴리n-아밀메타크릴레이트와 CPE와의 1 : 1 블렌드는 상용성이 없었다. 블렌드의 상용성은 성분들 간의 분자간 상호작용 (SIMI : specific intermolecular interaction)의 개념을 이용하여 설명하였는데, 폴리메타크릴레이트에서의 치환기의 입체효과 뿐만 아니라 염소를 포함하고 있는 고분자들의 염소 함량 및 입체형태에도 크게 의존함을 알았다.

Abstract : Differential scanning calorimetry was used to determine the miscibility behavior for the blends of polymethacrylates(PMA's) having various alkyl groups with chlorine containing polymers. For the chlorine containing polymers, poly(vinyl chloride)(PVC), chlorinated polyethylene(CPE) and chlorinated poly(vinyl chloride) (CPVC : 65 wt.% and 68wt.% chlorine) were studied. The 1 : 1 blends of polymethacrylates containing ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, n-amyl, n-hexyl, and cyclohexyl group with PVC and CPVC were found miscible. The 1 : 1 blend of poly (methyl methacrylate) with PVC was found miscible. The 1 : 1 blend of poly(cyclohexyl methacrylate) with CPE was also miscible. It was found that the following blends were immiscible ; 1 : 1 blend

of poly(methyl methacrylate) with CPVC, 1 : 1 blend of polymethacrylates containing glycidyl, 2-hydroxypropyl, t-butyl and phenyl group with PVC, CPE, and CPVC and 1 : 1 blends of poly-methacrylates containing methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, and n-amyl group with CPE. In order to explain the miscibility behavior of the blends, the concept of the specific inter-molecular interaction (SIMI) between two components was used. It was concluded that the miscibility window depends not only on the steric effect of the substituent group in PMA's but also on the chlorine content and the conformation of chlorinated polymer.

INTRODUCTION

Recently the miscibility of polymer blends has been attracted much interests from theoretical and practical standpoints.[1~3] It has been shown that miscible blends can be obtained when there is a specific interaction between two polymers in the mixture. Such specific interactions can be obtained from hydrogen bonding, from dipole-dipole forces, or from acid-base interaction, etc.

A brief review of the literatures indicates that several polyesters are miscible with chlorinated polymers, including poly(vinyl chloride), chlorina-ted PVC, and a statistical copolymer of 88% of vinylidene chloride and 12% of vinyl chloride.[4~6] It has been suggested that the miscibility of these blends is due to specific interactions between the carbonyl groups of the polyesters and the hydro-gen of chlorinated polymers. It was reported that the polyacrylates and polymethacrylates were broadly comparable with the polyesters in the mis-cibility behavior of the blends containing PVC or other chlorinated polymers except that the ester group lies in the side chain.[4,7] In fact, recent studies of blends of chlorinated polymers with a range of polyacrylates and polymethacryl-ates with ester side chains have also shown similar results due to the creation of similar specific interaction.[7~11]

In this context, it is expected that further studies on the blends of polymethacrylates having various substituent groups with poly (vinyl chloride) (PVC), chlorinated polyethylene (CPE) and chlorinated PVC(CPVC) will be fruitful both in understanding the basis and limits

for miscibility and in discovering new miscible materials.

The purpose of this paper is a systemmatic study on the miscibility behavior of the blends of polymethacrylates having various substituents with PVC, CPE, and CPVC. The blends have been pre-pared from poly(methyl methacrylate)(PMMA), poly(ethyl methacrylate)(PEMA), poly(n-propyl methacrylate)(Pn-PMA), poly(iso-propyl meth-acrylate)(Pi-PMA), poly(2-hydroxypropyl meth-acrylate)(PHPMA), poly(glycidyl methacrylate) (PGMA), poly(n-butyl methacrylate)(Pn-BMA), poly(isobutyl methacrylate)(Pi-BMA), poly(sec-butyl methacrylate)(Ps-BMA), poly(t-butyl metha-crylate)(Pt-BMA), poly(n-amyl methacrylate)(Pn-AMA), poly(n-hexyl methacrylate)(Pn-HMA), poly(cyclohexyl methacrylate)(PCHMA), and poly (phenyl methacrylate)(PPhMA) with PVC, CPE, and CPVC.

Their miscibility behavior has been estimated by the measurement of the glass transition tempera-ture(T_g) of the blends, using differential scanning calorimetry(DSC).

EXPERIMENTAL SECTION

The polymers used in this study are described in Table 1 along with their acronym, molecular weights, T_g's and sources. The polymethacrylates (PMA's) were atactic. The chlorinated polyethyl-ene(CPE-48) contained 48 weight % chlorine. Two different CPVC's contained 65 (CPVC-65) and 68 (CPVC-68) weight % chlorine, respect-ively.

The molecular weights reported in Table 1 were

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

Polymer	Acronym	Molecular Weight (Kg/mole)		Tg(K)	$\Delta C_p \times 10^2$ (cal/gdeg)	Source
		Mn	Mw			
PMA's						
R = methyl-	PMMA	47	84	365	8.08	Fisher
ethyl	PEMA	90	147	343	7.24	Aldrich
n-propyl	Pn-PMA	210	270	325	6.20	Polysciences
glycidyl	PGMA	11	58	291	11.23	Aldrich
2-hydroxypropyl	PHPMA	36	110	374	8.24	Aldrich
i-propyl	Pi-PMA	150	460	358	8.20	Aldrich
n-butyl	Pn-BMA	88	150	302	4.05	Aldrich
i-butyl	Pi-BMA	220	310	328	5.32	Aldrich
s-butyl	Ps-BMA	22	66	321	4.24	Aldrich
t-butyl	Pt-BMA	54	102	368	3.95	Aldrich
n-amyl	Pn-AMA	22	61	270	4.36	Polysciences
n-hexyl	Pn-HMA	80	109	259	6.54	Aldrich
cyclohexyl	PCHMA	36	84	358	5.50	Polysciences
phenyl	PPhMA	38	80	393	6.79	Aldrich
Chlorinated Polymers						
chlorinated						
polyethylene	CPE-48	...	...	281	7.18	Polysciences
poly(vinyl chloride)	PVC	...	80	352	5.29	Polysciences
chlorinated PVC	CPVC-65	60	112	359	3.99	Polysciences
	CPVC-68	...	100	389	1.00	Polysciences

determined by size exclusion chromatrography (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 universal calibration procedure. The T_g values reported in Table 1 were determined in the present study.

Polymer films were generally cast from 1% solutions. For that purpose, various solvents were used : THF for PVC, CPVC, and blends involving these polymers ; 2-butanone or amyl acetate for CPE and blends containing CPE. Solvent evaporation was normally conducted at room temperature. The resulting films were dried under vacuum until they reached constant weight. Film thicknesses

were about 40 μm. The composition of the blends was fixed at 50 : 50 ratio by weight, unless otherwise noted.

Differential scanning calorimetry(DSC) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a thermal analysis data software. The DSC was calibrated with ultrapure indium(m. p. 429 K). The glass transition temperature(T_g) reported was recorded at the halfheight of the corresponding heat capacity jump. After insertion of samples in the DSC apparatus, all samples were first cooled at 173 K and maintained for 5 min. A 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. This sample was then quenched at 173 K. It was again left for 10 minutes at this tem-

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perature before the second scan at a heating rate of 20°C/min and reheated at 460 K. The T_g's of the blends were always recorded during the second scan.

In this paper, a sample is defined as miscible when it gives a single T_g intermediate between those of its pure components at a given composition. A sample exhibiting two T_g's at a given composition is defined as immiscible.

RESULTS AND DISCUSSION

T_g Behaviors

Table 2 gives the T_g values measured for the 1 : 1 blends of CPE-48 with PMA's(Pi-PMA, PH-PMA, PGMA, Pi-BMA, Ps-BMA, Pt-BMA and PPhMA). These blends exhibit two T_g's which are close to the T_g's of the corresponding homopolymers. These blends are therefore immiscible, forming two phases composed almost entirely of pure PMA and pure CPE-48. The observed T_g's of blends of CPE-48 with Pi-BMA, Ps-BMA and Pt-BMA are shifted to slightly high temperature, compared to that of the pure corresponding PMA. This phenomenon may be ascribed to the fact that the CPE-48 molecules are entangled partially to

PMA's chain having a relatively bulky side group by segmental motions of CPE-48 molecules even in immiscible domain at higher temperture than its T_g, because the heat capacity increment of CPE-48 at T_g is relatively large as shown in Table 1. If the entanglement is formed partially, micro-Brownian motion of molecule is difficult. The T_g is therefore shifted to higher temperature.

The 1 : 1 PCHMA/CPE-48 blend is found miscible since this blend exhibits a single T_g at a temperature intermediate between those of the corresponding homopolymers. It should be noted, however, that the miscibility of the blends depends on the composition of PCHMA. We observed a single T_g at 50, 65, and 85% but two T_g's at 15 and 35% by weight of PCHMA(see Table 7). It can be supposed that the phase separation in CPE rich phase is ascribed to the solubilization power of solvent on CPE in the film casting. These results are in agreement with the study of Walsh and Cheng,[7] stating that the PMA's/CPE blends are immiscible in case of chlorinated polyethylenes containing less than 49% of chlorine except the PCHMA/CPE-48 blend.

In Table 2, the PGMA/PVC and Pt-BMA/PVC blends are immiscible since they show two T_g's. The Pi-BMA/PVC and Ps-BMA/PVC blends exhibit a single T_g at a temperature intermediate between those corresponding homopolymers and are therfore clearly miscible. A single T_g was observed over the entire composition ranges as shown in Table 5 and Table 6.

The Pi-PMA/PVC and PCHMA/PVC blends exhibit a single T_g. The decision upon the miscibility of these blends were difficult because the T_g's are very close. However since these blends were optically clear, they have been declared miscible.

The PHPMA/PVC and PPhMA/PVC blends exhibit a single T_g which is close to that of PVC. The films were slightly turbid and showed phase separation. Our criterion concerning the miscibility or inmiscibility is mentioned at the Experimental Section. We have declared these blends immiscible because the exhibited one T_g value does not indi-

Table 2. Glass Transition Temperature of 1 : 1 blends of PMA's with CPE-48 and PVC ; Tg of CPE-48 : 281 K, Tg of PVC : 352 K

PMA's	Tg(K)		Phase	Tg(K)	Phase
	PMA's	PMA's/CPE-48 blend		PMA's/PVC blend	
Pi-PMA	358	282 and 357	I	355	M*
PHPMA	374	282 and 373	I	357	I
PGMA	291	282 and 287	I	310 and 345	I
Pi-BMA	328	284 and 334	I	341	M
Ps-BMA	321	282 and 329	I	343	M
Pt-BMA	368	282 and 372	I	352 and 363	I
PCHMA	358	316	M	356	M*
PPhMA	393	283 and 382	I	357	I

I : Immiscible, M : Miscible, M* : Miscibility determined by optical clarity of film

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cate at a temperature intermediate between the T_g's of the homopolymers.

Table 3 gives the T_g values and phase information determined for 1 : 1 PMA's/CPVC-65 and 1 : 1 PMA's/CPVC-68 blends. The PGMA/CPVC-65, PGMA/CPVC-68, and Pt-BMA/CPVC-68 blends are found to be immiscible whereas the Pi-BMA/CPVC-65, Ps-BMA/CPVC-65, PPhMA/CPVC-65, Pi-PMA/CPVC-68, Pi-BMA/CPVC-68, Pi-BMA/CPVC-68, Ps-BMA/CPVC-68, and PCHMA/CPVC-68 blends are miscible. A single composition dependent T_g was found at whole compositions in these miscible blends except the Ps-BMA/CPVC-68 blends(see Tables 4 through 7).

Table 3. Tg of 1 : 1 blends of PMA's with CPVC-65 and CPVC-68. Tg of CPVC-65 : 359 K, Tg of CPVC-68 : 389 K

PMA's	Tg(K)		Phase	Tg(K)	Phase
	PMA's	PMA's/CPVC -65 blend		PMA's/CPVC -68 blend	
Pi-PMA	358	358	M*	370	M
PHPMA	374	360	I	375	I
PGMA	291	290 and 352	I	288 and 346	I
Pi-BMA	328	342	M	352	M
Ps-BMA	321	340	M	349	M
Pt-BMA	368	358	I	369 and 378	I
PCHMA	358	358	M*	366	M
PPhMA	393	371	M	ND	

ND : Not Determined

Table 4. Tg as a Function of Pi-PMA Contents in the Pi-PMA/CPVC-68 Blend

Pi-PMA (weight %)	Tg(K)
	Pi-PMA/CPVC-68 blend
0	389
15	377
35	375
50	370
65	366
85	359
100	358

The two T_g's were observed in Ps-BMA/CPVC-68 blend at Ps-BMA contents of 65 and 85% whereas a single T_g was observed for the blends of other composition as shown in Table 6. We can

Table 5. Tg as a Function of Pi-BMA Contents in the Blends of Pi-BMA with PVC, CPVC-65, and CPVC-68

Pi-BMA (weight %)	Tg(K)		
	Pi-BMA/ PVC	Pi-BMA/ CPVC-65	Pi-BMA/ CPVC-68
0	352	359	389
15	348	351	364
35	343	346	358
50	341	342	352
65	336	338	343
85	331	332	334
100	328	328	328

Table 6. Tg as a Function of Ps-BMA Contents in the Blends of Ps-BMA with PVC, CPVC-65, and CPVC-68

Ps-BMA (weight %)	Tg(K)			Phase
	Ps-BMA/ PVC	Ps-BMA/ CPVC-65	Ps-BMA/ CPVC-68	
0	352	359	389	
15	348	350	370	M
35	346	345	358	M
50	343	340	349	M
65	342	335	309 and 371	I
85	337	332	320 and 354	I
100	321	321	321	

Table 7. Tg as a Function of PCHMA in Blends of PCHMA with CPE-48 and CPVC-68

PCHMA (weight %)	Tg(K)	Phase	Tg(K)	Phase
	PCHMA/ CPE-48		PCHMA/ CPVC-68	
0	281		389	
15	277 and 345	I	376	M
35	282 and 341	I	370	M
50	316	M	366	M
65	333	M	364	M
85	340	M	360	M
100	358		358	

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deduce that the phase separation in Ps-BMA rich phase is ascribed to the decreased specific intermolecular interaction (SIMI) between Ps-BMA and CPVC-68.

The Pi-PMA/CPVC-65 and PCHMA/CPVC-65 blends exhibit a single T_g, but small difference between the T_g's of the homopolymers make difficult any intepretation. However since these blends were optically clear, we have finally decied in favor of the miscible blend. The PHPMA/CPVC-65 and Pt-BMA/CPVC-65 blends exhibit a single T_g which is close to the T_g's of CPVC-65. The films were, however, slightly turbid and showed phase separation. These blends are thus defined as immiscible. The PHPMA/CPVC-68 blend showed a single T_g which is close to that of PHPMA. The film is also turbid and phase separation. This blend is therefore immiscible. The T_g's of PPhMA/CPVC-68 blend was not measured because the T_g's of two homopolymers are very close.

As shown in Table 2 and 3, PHPMA and PGMA are immiscible with halogenated polymers. This means that the hydroxyl group in PHPMA or ethylene oxide group in PGMA interfere the SIMI between PMA's and halogenated polymers. Because the intramolecular interaction is possible between oxygen at carbonyl and hydrogen at hydroxyl part in the substutuent group of PHPMA, and the intramolecular dipole-dipole interaction is also possible between carbonyl and ethylene oxide in the side chain of PGMA. If this sort of intramolecular interaction occurs, the SIMI is difficult between PHPMA or PGMA with halogenated polymers.

In Table 3, the PPhMA is miscible with CPVC-65 although it has the electron withdrawing phenyl group. The delocalization of π-electron is known to be possible between ester and phenyl part in side chain. The negative nature of delocalizing π-electron can interact with positive part of CPVC-65. But this sort of interaction is weaker than that of localized polar interaction. Therefore PPhMA is immiscible with PVC which has low content of halogen than CPVC-65.

Table 8. Polar(σ^*) and Steric(E_s) Constants of Substituent Group in PMA's and Miscibility or Immiscibility of 1 : 1 Blends of PMA's with CPE-48, PVC, and CPVC

Substituent group in PMA's	$-\sigma^*$	$-E_s$	Miscibility or Immiscibility			
			CPE-48 (Cl : 48%)	PVC (Cl : 56%)	CPVC-65 (Cl : 65%)	CPVC-68 (Cl : 68%)
Methyl	0.00	0.00	I	M	I	I
Ethyl	0.10	0.07	I	M	M	M
n-Propyl	0.115	0.36	I	M	M	M
i-Propyl	0.19	0.47	I	M	M	M
n-Butyl	0.13	0.39	I	M	M	M
i-Butyl	0.125	0.93	I	M	M	M
s-Butyl	0.21	1.13	I	M	M	M
t-Butyl	0.30	1.54	I	I	I	I
n-Amyl	0.16	0.40	I	M	M	M
cyclohexyl	0.15	0.79	M	M	M	M

Table 8 summarizes the effect of substituent groups in PMA's on the miscibility or immiscibility behavior in the blends of PMA's with chlorinated polymers.

Substituent Effect of PMA's

The two factors play important roles in the miscibility behavior of PMA's/chlorinated polymer blends ; the polar and the steric effect of the PMA's as host polymer, and the chlorine contents and conformation of chlorinated polymer as guest. The polar and steric effect of PMA's is depicted in Fig. 1.

The polar constant(σ^*) means that the more electron releasing group has larger negative value which can favorably interact with positive part. Steric constant(E_s) indicates that much bulkier group has greater negative value which signified the difficulty of approach between the SIMI site.[12~14]

In spite of larger negative σ^* value of the tertiary butyl group, Pt-BMA is immiscible with chlorinated polymers as shown in Table 8 and Fig. 1. This means that the approach of chlorinated polymers to carbonyl group site of Pt-BMA is diffi-
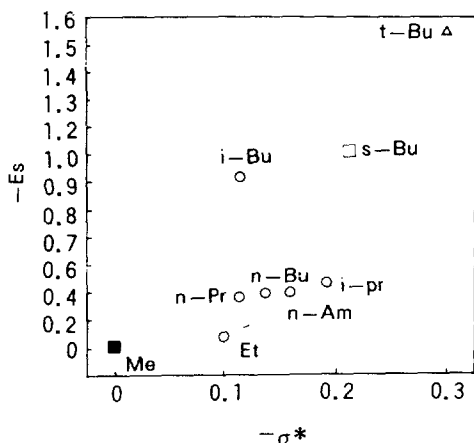
Fig. 1. Miscibility or immisibility in the blends of PMA's with PVC, CPVC-65 and CPVC-68 : (○) miscible, (△) immiscible, (■) immiscible with CPVC, (□) Borderline of miscibility.

cult by the steric hindrance of bulky butyl group. Although the smallest σ^* value of methyl group, PMMA is miscible with PVC as shown in Table 8.

From these results, we can confirm that the miscibility of PMA's in the blends of PMA's with chlorinated polymers depends profoundly on the steric effect than the polar effect of substituent group.

On the other hand, PMMA is immiscible with CPVC-65 and CPVC-68 although chlorine contents of both CPVC are higher than those of PVC. This result indicates the intramolecular interaction between β-chlorine and α-hydrogen in CPVC shield from both side of chlorine atom in CPVC, because the structure of repeating unit of CPVC is similar to 1,2-dichloroethane. The interaction intensity between β-chlorine and α-hydrogen in CPVC varies with the conformation of polymer. Since this kind of interaction is weak, it is not important for PMA's having larger σ^* value.

The Ps-BMA is immiscible with CPVC-68 which contains less than 35 percent in the blend. This result is ascribed to the fact that the SIMI site of Ps-BMA is hiden by bulky secondary butyl group because the probability of encountering of Ps-BMA and Ps-BMA is larger than that of Ps-BMA and

CPVC-68 in Ps-BMA rich phase. Additionally the phase separation caused by the intramolecular interaction between β-chlorine and α-hydrogen, and the shielding of α-hydrogen in CPVC.

Table 8 indicates that at low chlorine contents, chlorinated polymers are not miscible with PMA's except PCHMA, because a large number of interactions is required between the two polymers in order to counteract the dispersion or van der Waals forces opposing to the miscibility. At low chlorine contents the number of interactions is too small ; at high chlorine contents, it becomes sufficient. This conclusion is in accordance with their results by Walsh et al.,[11] stated that the critical chlorine content concerning about the number of interactions is given at 49% for PMMA/chlorinated polyethylene blends. It is also in agreement with the general behavior of linear polyester/CPE polymer blends[4,5] and aromatic polyester/CPE blends for which chlorine contents of 30 and 50%, respectively, are required to observe miscibility.

In the PMA's/chlorinated polymer blends, the miscibility behavior depends on the chlorine contents and the conformation of chlorinated polymer. It should be stressed that the chlorine contents of chlorinated polymer are necessary condition but not sufficient condition to miscibility. From the above results, thus, the miscibity window depends not only on the steric effect of the substituent group in PMA's as host polymer but also on the chlorine contents and the conformation of chlorinated polymer as guest.

It must be realized that the miscibilty phenomenon results from a competition of 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 the A/B interactioins, they will not be broken and the A/B blends will be immiscible.

In the present study, it is suggested that SIMI occurs between the carbonyl groups of the PMA's and the chlorinated polymers ; these interactions could be similar to those occuring between polyesters and chlorinated polymers even though the

ester group lies in the side chain[6~11,15~17]. This SIMI can be hydrogen bonding interactions involving the β-hydrogens of the chlorinated polymers or dipole-dipole interactions between the C=O groups of the polymethacrylates and C−Cl groups of the chlorinated polymers. At first sight and by analogy with the polyester/chlorinated polymers behavior, the α-hydrogen bonding interactions seem favored.

Composition Dependence of T_g

The variation of T_g of miscible blends as a function of composition can be expressed by several equations[18~22]. The simplest one is the law of mixture.

$$T_g = w_1 T_{g1} + w_2 T_{g2} \tag{1}$$

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

Equation (1) predicts a linear T_g-composition relation. However, a negative deviation is often observed.[15] Negative deviations can be simulated using the Fox equation[18]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{2}$$

or the Gordon-Taylor equation[19]

$$T_g = (w_1 T_{g1} + k\ w_2 T_{g2})/(w_1 + k\ w_2) \tag{3}$$

where k is the ratio between the volume expansion coefficients of the homopolymers of the mixture ; $k = \Delta e_1 / \Delta e_2 = (e_1 - e_g)_1 / (e_1 - e_g)_2$, $e_{1g} = (\partial V/\partial T)p$, the thermal specific expansivity in the liquid and glassy state, respectively(dim. cm^3/gK). When k is equal to unity, equation(3) reduces to equation (1). The smaller the value of k, the larger is the concavity of the T_g-composition curve.

More recently, Couchman has derived an expression which takes into account the heat capacity increments, ΔCp_1 and ΔCp_2, of homopolymers 1 and 2 at T_g(expressed per unit mass), assuming that ΔCp_1 and ΔCp_2 are temperature independent and that the molar entropy of the two homopolymers in the liquid state is equal to their entropy

in the glassy state at T_g[20] ;

$$\ln T_g = \frac{w_1 \Delta Cp_1\ \ln T_{g1} + w_2 \Delta Cp_2\ \ln T_{g2}}{w_1 \Delta Cp_1 + w_2 \Delta Cp_2} \tag{4}$$

Both negative and positive deviations can be obtained using equation(4).

For miscible PMA's/chlorinated polymer blends, the T_g-composition curves are usually close to equation (1) and (2), but exhibit negative deviation. Equation (3) can hardly fit the experimental parameter k which varies as a function of composition as shown in Figs. 2~5.

Table 9 indicates that the k value of Pi-BMA is larger than that of Ps-BMA. This means that the jump in thermal specific expansivity around T_g is also affected by chlorine content and conformation of polymers.

It can be predicted from equation (4) since $\Delta Cp_1 = \Delta Cp_2 \cong 0.05$ cal/g for the blends of PVC with Pi-BMA as shown in Table 1. For values of ΔCp_1 close or equal to ΔCp_2, equation(4) leads to a small concavity in agreement with the experimental results. In fact, when $\Delta Cp_1 = \Delta Cp_2$, equation (4) reduces to

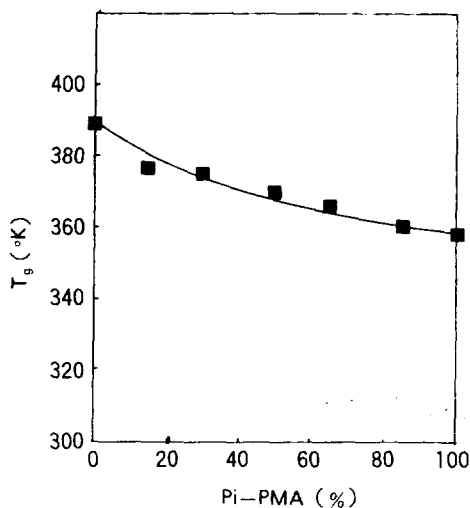$$\ln T_g = w_1 \ln T_{g1} + w_2 \ln T_{g2} \tag{5}$$

Fig. 2. T_g of Pi-PMA/CPVC-68 blends as a function of weight percent of Pi-PMA(k=0.24).

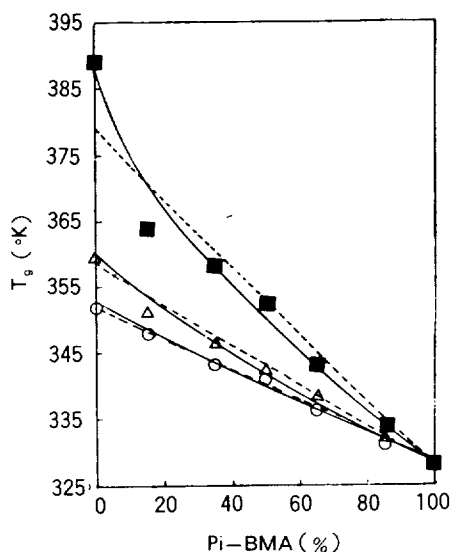which is the equation suggested recently by Po-chan et al. on an empirical basis[22].

Fig. 3. T_g as a function of weight percent of Pi-BMA in the blends of Pi-BMA with PVC, CPVC-65, and CPVC-68 : (○) Pi-BMA/PVC (k=0.87), (△) Pi-BMA/CPVC-65 (k=0.44), (■) Pi−BMA/CPVC-68 (k=0.20).
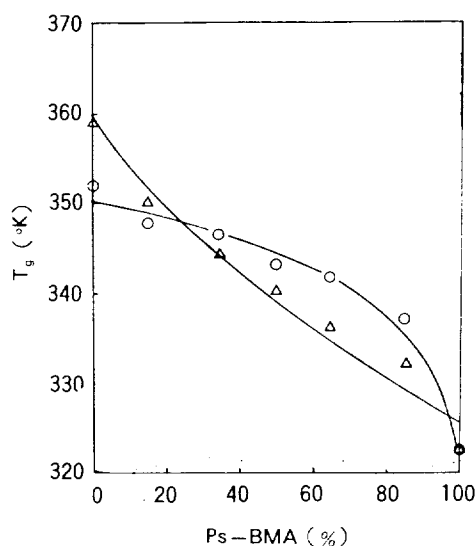

Fig. 4. T_g as a function of weight percent of Ps-BMA with PVC and CPVC-65 : (○) Ps-BMA/PVC (k= 0.48), (△) Ps-BMA/CPVC-65 (k=0.40).
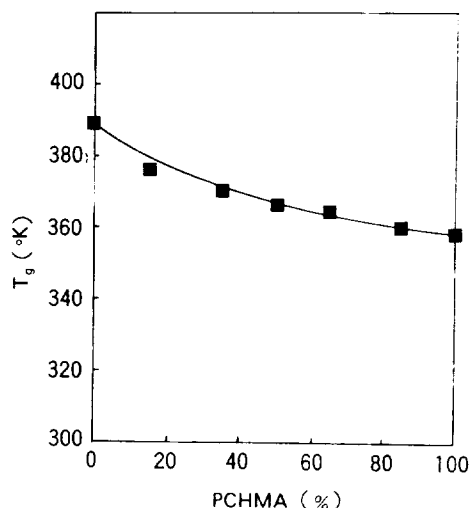

Fig. 5. T_g of PCHMA/CPVC-68 blends as a function of weight percent of PCHMA(k=0.22).

Table 9. k Value of PMA's/Chlorinated Polymer Blends

	k Value		
	PVC	CPVC-65	CPVC-68
Pi-PMA	—	—	0.24
Pi-BMA	0.87	0.44	0.20
Ps-BMA	0.48	0.40	—
PCHMA	—	—	0.22

CONCLUSIONS

PMA's/chlorinated polymer blends are often miscible if the substituent constants of PMA's are given as followings : σ^* value is less than zero and Es value is larger than -1, and the chlorine content of chlorinated polymers is high enough and the conformation of chlorinated polymers is within the so-called miscibility window.

REFERENCES

1. D. P. Kang, C. S. Ha, R. E. Prud'homme, and W. J. Cho, *Polymer(Korea)*, **12**, 7, 634 (1988).

2. D. P. Kang, C. S. Ha, and W. J. Cho, *J. Poly. Sci., Polym. Chem. Ed.*, **27**, 1401 (1989).

3. O. Olabishi, L. M. Robeson, and M. T. Shaw, "Polymer-Polymer Misibility", Academic Press, New York, (1979).

4. R. E. Prud'homme, *Polym. Eng. Sci.*, **22**, 90 (1982).

5. J. J. Ziska, J. W. Barlow, and D. R. Paul, *Polymer*, **22**, 918 (1981).

6. E. M. Woo, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **28**, 1347 (1983).

7. D. J. Walsh and G. L. Cheng, *Polymer*, **25**, 499 (1984).

8. C. Tremblay and R. E. Prud'homme, *J. Polym. Sci. Poly. Phys., Ed.*, **22**, 1857 (1984).

9. M. Aubin and R. E. Prud'homme, *Macromolecules*, **13**, 365 (1980).

10. M. Aubin, Y. Bedard, M. Morrissette, and R. E. Prud'homme, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 223 (1983).

11. D. J. Walsh, J. S. Higgins, and C. Zhikuan, *Polymer*, **23**, 336 (1982).

12. J. Shorter, "Correlation Analysis in Organic Chemistry", Clarendon Press, Oxford (1980).

13. R. A. Y. Jones, "Physical and Mechanistic Organic Chemistry", Cambridge Univ. Press., U. K., Chap. 3 (1979).

14. R. P. Gilliom, "Introduction to Physical Organic Chemistry", Addison-Wesley, Reading, U. S. A., pp. 157-159(1970).

15. R. E. Prud'homme, *Polym. Eng. Sci.*, **23**, 1138 (1983).

16. M. M. Coleman and J. Zarian, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 837 (1979).

17. D. F. Varnell, E. J. Moskala, P. C. Painter, and M. C. Coleman, *Polym. Eng. Sci.*, **23**, 658 (1983).

18. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).

19. M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 1 (1952).

20. P. R. Couchman, *Macromolecules*, **11**, 1156 (1978).

21. M. Aubin and R. E. Prud'homme, *Macromolecules*, **21**, 2945 (1988).

22. J. M. Pochan, C. L. Beaty, and D. F. Pochan, *Polymer*, **20**, 879 (1979).