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Head to Head Polymers. 42. Head to Head Poly(Vinyl Halide) Blends: Thermal and Degradation Behavior

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HEAD TO HEAD POLYMERS. 42. HEAD TO HEAD POLY(VINYL HALIDE) BLENDS: THERMAL AND DEGRADATION BEHAVIOR

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ABSTRACT

Improved halogenation techniques for poly(1,4-butadiene) have made well-defined head to head poly(vinyl chloride) and head to head poly(vinyl bromide) accessible in larger quantities. This allowed the preparation and study of blends of poly(vinyl chloride) or poly(vinyl bromide) with polycaprolactone and poly(methyl methacrylate); blends were also prepared between the poly(vinyl halides). The thermal behavior and the thermal degradation behavior of these blends were investigated. It was confirmed that head to head and head to tail poly(vinyl chloride) are immiscible over almost the entire range of compositions.

INTRODUCTION

Pure head to head (H-H) addition polymers, such as H-H polyolefins, H-H acrylates and H-H poly(vinyl halides) [1, 2], have been of interest in the understanding of part of the structure/ properties relationship of polymers. Regular head to tail (H-T) polymers have the substituents in the 1, 3, 5, 7, etc. position and, therefore, can be considered as alternating copolymers of methylene and alkylidenes. H-H polymers have the substituents in 1, 2, 5, 6, etc., position and, therefore, can be thought of as alternating copolymers of ethylene and 2,3-substituted ethylenes. H-H polymer structures have provided challenges of synthesis, characterization, and of the measurements of their mechanical and rheological properties.

Head to head (H-H) poly(vinyl halides) [3] of well-defined structures have become available by improved simple halogenation techniques of *cis*-1,4-polybutadiene [4, 5], using chlorine or bromine in halogenated solvents [5]. In our early work on H-H polymers [1, 2], we had studied extensively the properties of H-H polystyrene (PSt) [6], and later the thermal oxidation and photo oxidation of H-H PSt and compared its properties to that of H-T PSt [7, 8].

We had also investigated the blending behavior of H-H or H-T polymers with each other [9, 10] and with other polymers [11, 12]. For polypropylene and PSt, we found that H-H and H-T polymers are miscible over the entire range of compositions [9], polyisobutyenes, on the other hand, are immiscible [10]. H-H PSt or H-T PSt were miscible with poly(2,6-dimethyl-1,6-polyphenylene oxide) (PPO) [11]. The thermal degradation behavior of two PPO blends [12], although H-H and H-T polymers are similar in structure, and have some subtle and significant differences in details [13].

Some years ago, we had also focused on the synthesis and characterization of H-H PVC [14] and PVB [15)]. We studied briefly, the blending behavior of H-H PVC with H-T PVC and H-H PVC and H-T PVC with polycaprolactone (PCL) [16]. More recently, additional work on the blending of H-T PVC with chlorinated structures of polyethylene, including commercial samples of chlorinated polybutadiene, were undertaken [17-19].

It was the objective of this work to study the blending behavior of H-H poly(vinyl halides), to compare it with that of the corresponding H-T polymers, and, to determine the thermal and degradation behavior of these blends.

EXPERIMENTAL

A. Materials

Poly-1,4-butadiene was obtained from the Polysar Rubber Corporation. It is described as having been prepared by Ziegler-Natta "catalysis" of butadiene-1,3 in an organic solvent using Co(II)/$AlEt_2Cl$ as the catalyst system. The polymer had

TABLE 1. Molecular Weight of H-H PVC and H-H PVB

Sample type GPC characterization	H-H PVC	H-H PVB
M_n	265,300	340,700
M_w	492,100	696,300
M_z	796,000	1,127,000
M_w/M_n	1.86	2.04
M_z/M_n	3.001	3.309

a M_n of 98,000 and a M_w of 310,000. The structure of the polymer is specified as "over" 98% poly-1,4-butadiene and, within the 1,4-structure, the polybutadiene is essentially 100% cis. The sample is also described as having less than 1 mole% of a 1,2-butadiene structure.

The sample was chlorinated and brominated to H-H PVC and H-H PVB, as described before.

All the chemicals, unless otherwise mentioned, were used as received [5].

Molecular Weight

The molecular weights of H-H PVC and H-H PVB were studied by GPC with Viscotec 200 Model as the detector and had been calibrated with respect to polystyrene. The GPC column was packed with five ultrastyragel, with a pore size of $10^5/50$ nm. THF was used as the solvent for dissolving polymers and as a mobile phase for GPC measurements. The results are listed in Table 1.

After chlorination of *cis*-1,4-polybutadiene, the M_n of the polymer increased from 98,000 to 265,300 by the weight of the chlorine atoms. It should be noticed that the molecular weight of butadiene is 54 and the molecular weight of 2,3-dichlorobutane is 125. The ratio of 265,300 to 98,000 is equal to 2.5 while the ratio of 125 to 54 is 2.3. These results imply that the chlorination of PB is a pure addition reaction to the internal double bond of the polymer, furthermore, no chain cleavage seems to have occurred. On the other hand, after bromination, the number average molecular weight changed from 98,000 to 340,700 which is 3.5 times the molecular weight of the original PB. The molecular weight ratio of 2,3-dibromobutane to butadiene is 4.0. This could mean that some bond cleavage had occurred in the course of bromination.

B. Measurements

DSC Measurements

The thermal transitions of the polymer blends were determined with TA 2920 and TA 910 Differential Scanning Calorimeters equipped with a TA 2100 controller. The temperature scale of the instrument was calibrated at the desired heating rate by adjusting the temperature readout to correspond with the transition temperature of indium (m.p.= 156°C). The weight of each sample was about 5-10 mg. The heating rate was 20°C/min for each DSC measurement. The glass transition temperature was obtained by identifying the mid-point of the specific heat jump or the maximum of the derivative. (The melting transition (T_m) and crystallization temperature (T_c) are reported as the maximum peak temperature of the endothermic and exothermic peaks, respectively.

TGA Measurements

Thermogravimetric analyses were carried out with TA 2950 and TA 951 Thermogravimetric analyzer equipped with a TA 2100 controller. Measurements were carried out under a nitrogen atmosphere with a flow rate of 40 mL/min at a regular and derivative mode [20]. The heating rates were either 20°C/min or 10°C/min. For the TGA measurements, the sample weight was about 7~15 mg. The degradation temperature and the weight loss (calculated by the computer) were recorded.

C. Preparation of Head to Head Polymer Blends

Preparation of Blends of H-H Polymers with H-T Polymers

Films of H-H PVC and H-T PVC blends were prepared by casting from 2 w/v% THF solutions. The solvent was first removed by evaporating at room temperature for 3 days. Then the samples were kept at 65~80°C for 2 days at 0.1 mmHg. Blends of H-H PVB with H-T PVC, H-H PVB with H-H PVC were prepared by a similar method.

Preparation of Blends of H-H and H-T Poly(vinyl halides) with Other Polymers

Appropriate amounts of H-H PVC, H-T PVC or H-H PVB (2% solutions) were mixed with *atactic*-PMMA or *isotactic*-PMMA (2% solutions in butanone-2). The mixtures were allowed to remain at room temperature to remove most of the solvent, then the polymer films were heated to 110°C and 0.1 mmHg for two days.

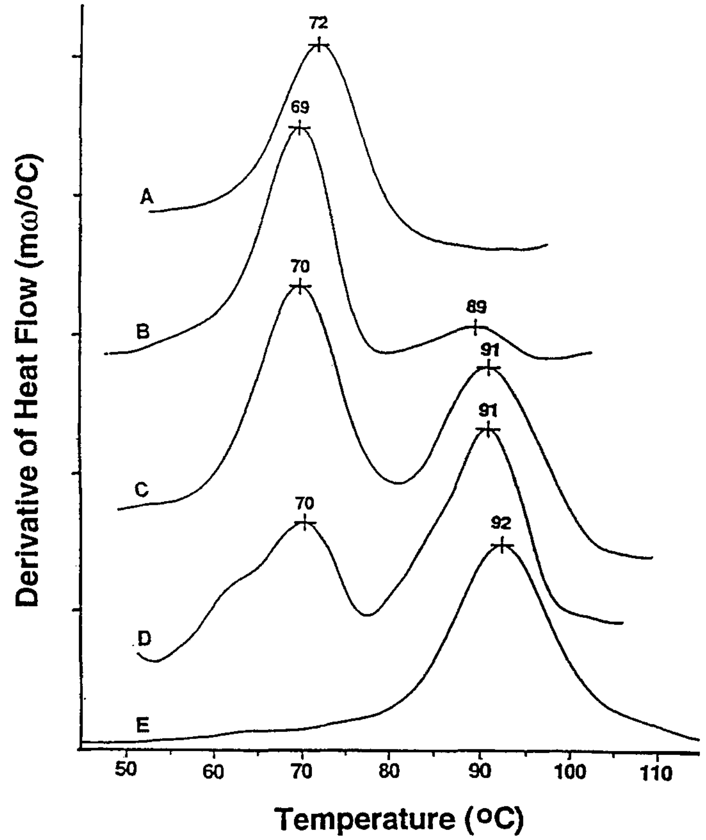


Figure 1. DSC results of blends of H-H PVC with H-T PVC. a) 100% H-H; b) H-H:H-T=75:25; c) H-H:H-T=50:50; d) H-H:H-T=25:75; e) 100% H-T

H-H, H-T PVC, or H-H PVB (2.00 g) and poly(ε-caprolactone)(PCL) (2.00 g) were separately dissolved in fresh THF (100 mL) under nitrogen. Appropriate amounts of H-H PVC and PCL were mixed and the solvent was evaporated at room temperature (4 days). Blends of H-H PVB with PCL were prepared in a similar manner as described above.

Head to Head Polymer Blends

Miscibility Study of Head to Head Polymer Blends

The blending behavior of H-H polymers has been studied in the past [9-11, 14-19]. Blends of H-H or H-T polymers with each other [6, 9, 10, 14] and with

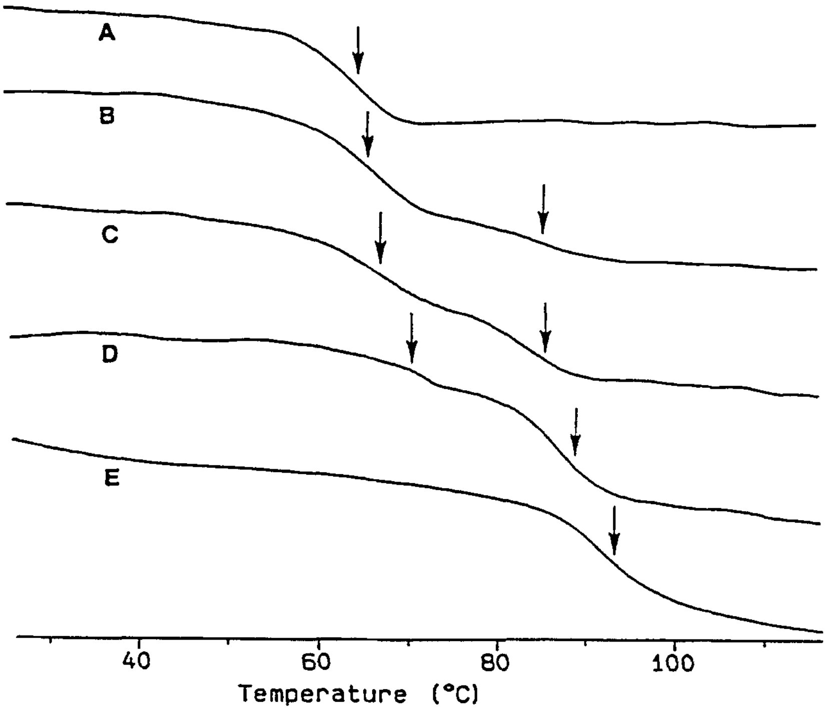


Figure 2. DSC results of blends of H-H PVB with H-T PVC. a) 100% H-H; b) H-H:H-T=75:25; c) H-H:H-T=50:50; d) H-H:H-T=25:75; e) 100% H-T

other polymers [11-19, 22] were investigated. By DSC measurements, H-H and H-T polypropylene were found miscible over the entire composition range (9,22), while H-H and H-T polyisobutylene were almost totally immiscible. H-H and H-T PSt are miscible with each other and miscible with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [11] and H-H and H-T PVC are both are miscible with polycaprolactone (PCL) [16]. In this work [21], a much more detailed study of blends of H-H poly(vinyl halides) with various polymers was carried out.

a. H-H Poly(vinyl halides) and H-T Poly(vinyl halides) Blended with Each Other

Figure 1 shows the derivative of the heat flow obtained for various compositions of the blends. The individual T_g's of the two components of the blends are clearly recognizable over the entire range of compositions that we investigated. Our H-H PVC had a T_g of 70°C and the H-T PVC had a T_g of 90°C. The area of each peak in the derivative plot is proportional to the concentration of each polymer, indicating complete immiscibility.

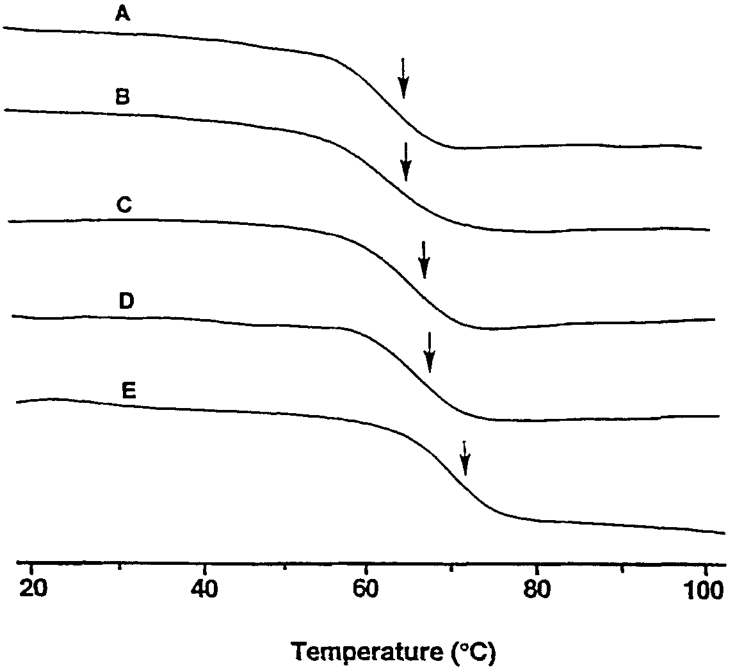


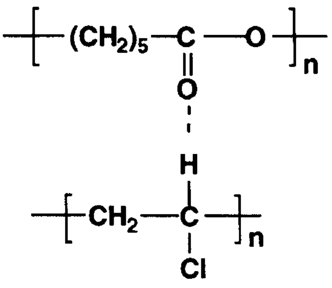
Figure 3. DSC results of blends of H-H PVB with H-H PVC. a) 100% H-H PVB; b) PVB:PVC=75:25; c) PVB:PVC=50:50; d) PVB:PVC=25:75; e) 100% PVC

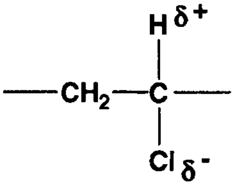
H-H PVB showed some miscibility with H-T PVC. The H-H PVB had a T_g of 66°C. Each of three blends showed two separate T_g's, but both were displaced by a few degrees: the higher T_g (at 92°C for H-T PVC) was displaced to as low as 84°C (Figure 2), and the lower T_g (H-H PVB), upward to about 70°C.

H-H PVB and H-H PVC have similar T_g at 66°C and 72°C, respectively. The T_g difference of these two polymers is too small to draw any conclusion about their miscibility (Figure 3).

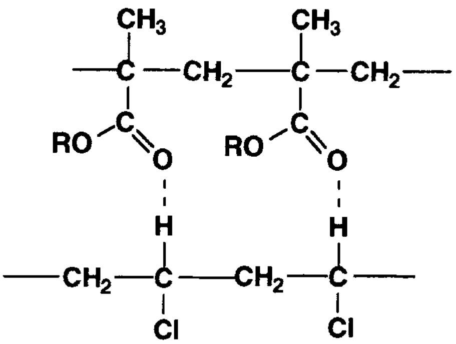
b. Poly(vinyl halides) Blends with Other Polymers

PVC represents one of the most rigorously investigated components of polymer blends [23]. It has been found to be miscible with a number of structurally different polymers and copolymers. A weak specific interaction is possible with PVC. The α-hydrogen atom of PVC is capable of hydrogen bonding, particularly with polymers which have "basic" properties (i.e., amides, carbonyl) [24]. Many of the systems miscible with PVC, for example, PCL, PMMA, butadiene/acrylonitrile copolymer, ethylene/vinylacetate copolymer etc., have a common denominator in that they contain structural units (proton acceptors) capable of hydrogen bonding with the α-hydrogen of PVC.





The specific interaction can also be a hydrogen bonding interaction involving the β-hydrogen of PVC or a dipole-dipole interaction between carbonyl carbon atoms of the C=O groups and the chlorine atom of the C-Cl groups of PVC. The possibility of a charge-transfer interaction with PVC has also been proposed [25], involving the ester oxygen and the pendant chloride for the miscible blend of PVC and poly(ε-caprolactone).



The several different types of interactions may all contribute to miscibility. In consideration of the availability of H-H PVC and H-H PVB, we have undertaken the investigation of blend behavior of these H-H polymers with PMMA and PCL as blending partners.

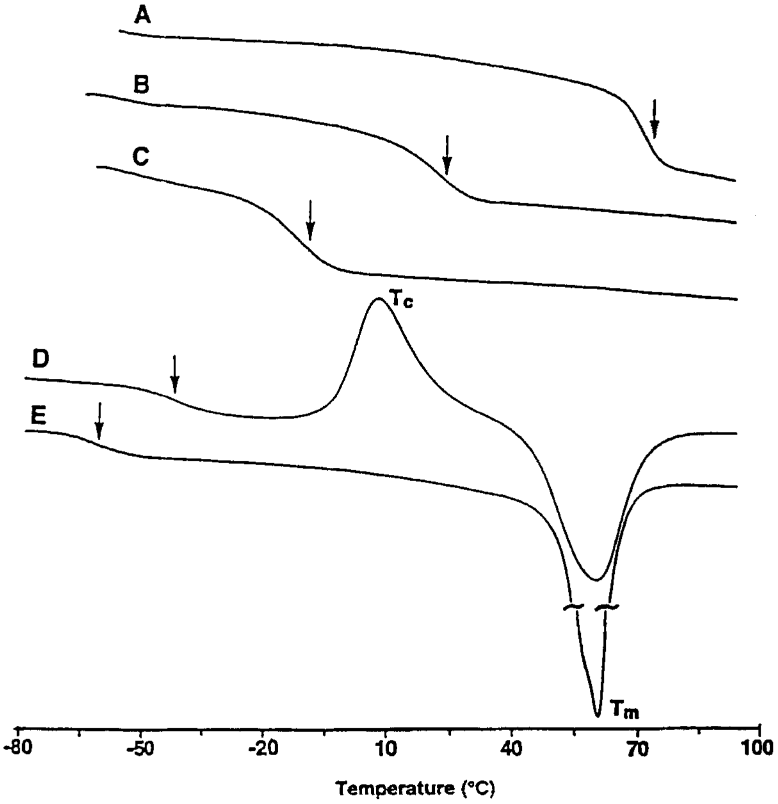


Figure 4. DSC results of blends of H-H PVC with PCL. a) H-H PVC; b) H-H PVC/PCL=75:25; c) H-H PVC/PCL=50:50; d) H-H PVC/PCL=25:75; e) PCL

i. Poly(vinyl halides) Blends with Poly(ε-caprolactone)

The thermal behaviors of a series of blends of H-H PVC, H-T PVC and H-H PVB with PCL show only one glass transition temperature for each blend in the DSC scans. PCL is a crystalline polymer with the degree of crystallinity depending on the history of the sample [26]. It has a T_m of 60°C. The T_g is affected by crystallinity and was reported to be around -62°C; our PCL sample had a T_g of -61°C.

Interestingly, the DSC scans of two sets of PVC blends (H-H and H-T) with PCL were somewhat different (Figures 4 & 5). For the blends of H-T PVC with PCL, a single T_g was evident for each blend and no crystallization for PCl was observed over the range of composition from 25% to 75% of PCL (Figure 5). This indicates that H-T PVC disrupted the crystal structure of PCL completely and

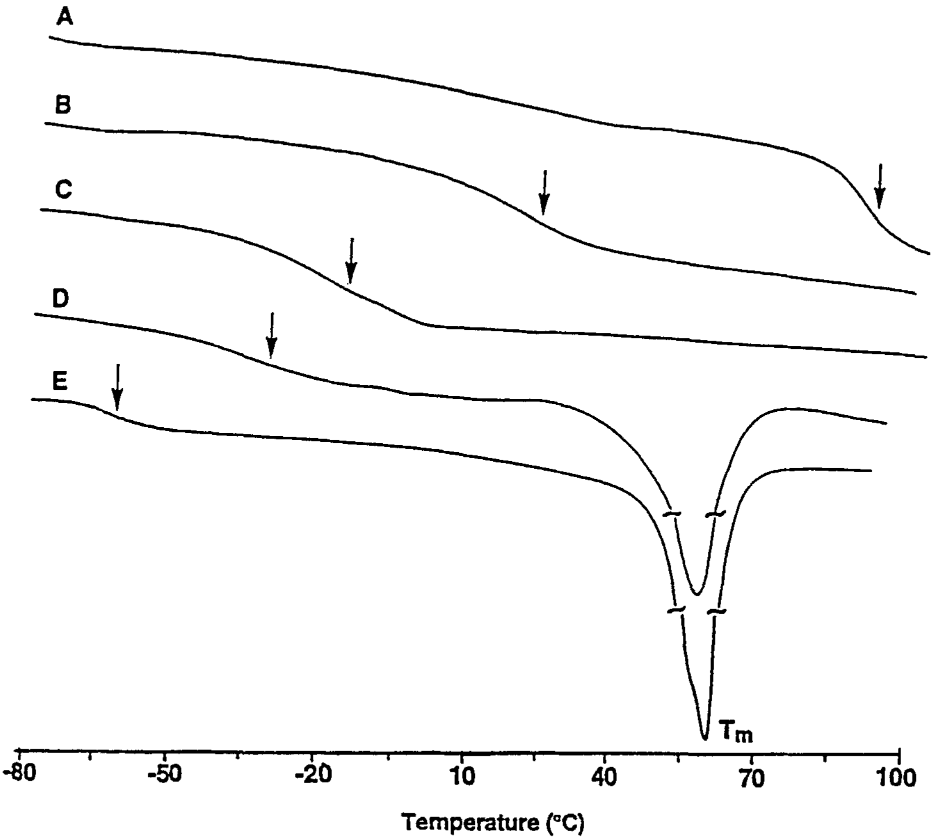


Figure 5. DSC results of blends of H-T PVC with PCL. a) H-T PVC; b) H-T PVC/PCL=75:25; c) H-T PVC/PCL=50:50; d) H-T PVC/PCL=25:75; e) PCL

miscibility of the two homopolymers is the result. This result is somewhat different from that obtained by Kondo [16] in which a crystallization exotherm (T_c) and a melting endotherm (T_m) were observed in the blends of 25% H-T PVC and 75% PCL.

For blends of H-H PVC with PCL, with a PCL content of 50% or 25%, again only one T_g and no crystalline melting point was observed for PCL. However, the DSC scans of blends containing 75% PCL showed not only one T_g, but also a crystallization exotherm (T_c) at 8°C followed by a melting endotherm (T_m) at 60°C which is the same as the T_m of PCL itself. This phenomena suggest that at higher temperature (above 5°C) some of the PCL crystallizes, resulting in two phases and then melts when the T_m of PCL is reached.

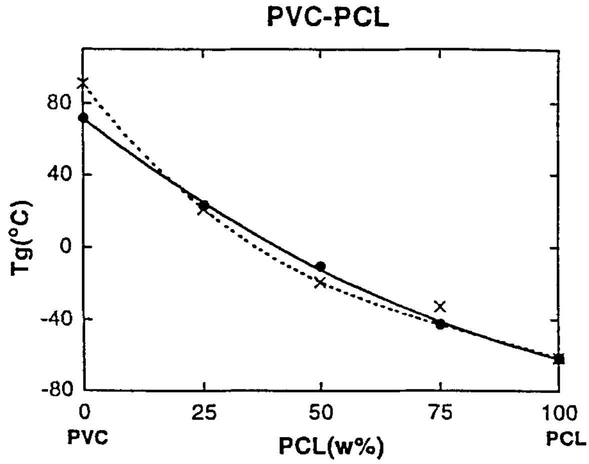


Figure 6. Glass transition temperature of H-H PVC/PCL and H-T PVC/PCL blends as a function of composition. (—) H-H PVC blends with PCL. (·····) H-T PVC blends with PCL.

Figure 6 shows the T_g for H-H PVC/PCL and for H-T PVC/PCL blends as a function of blend composition. Both curves have the same pattern with slight concave deviations from linearity. The T_g's of H-H PVC/PCL blends fit very well with the theoretical calculations from the Fox equation, while the T_g's of H-T PVC/PCL blends have a slight deviation from the theoretical calculation.

The DSC results of blends of H-H PVB with PCL are similar to those of blends of H-H PVC with PCL. There is only one T_g over the entire range of composition (Figure 7) which indicates that H-H PVB and PCL blends are miscible. When the content of H-H PVB was 75%, no crystalline melting point was observed in the scan. When the PCL concentration was around 50%, a crystallization exotherm as well as a melting endotherm was found. When the H-H PVB content was smaller (25%), the presence of H-H PVB shifted the T_g of the major phase from -62°C to -36°C , but the crystalline phase of PCL remained. This result is interesting because H-H PVB has much higher molecular weight per segment than H-H PVC but the same degree of polymerization. The same weight percentage of PVB and PVC means a much smaller mole percentage of PVB as compared to that of PVC. If the blends were made according to mole fractions instead of weight percentage, a more similar DSC behavior should be expected for the blends of H-H PVC/PCL and of H-H PVB/PCL.

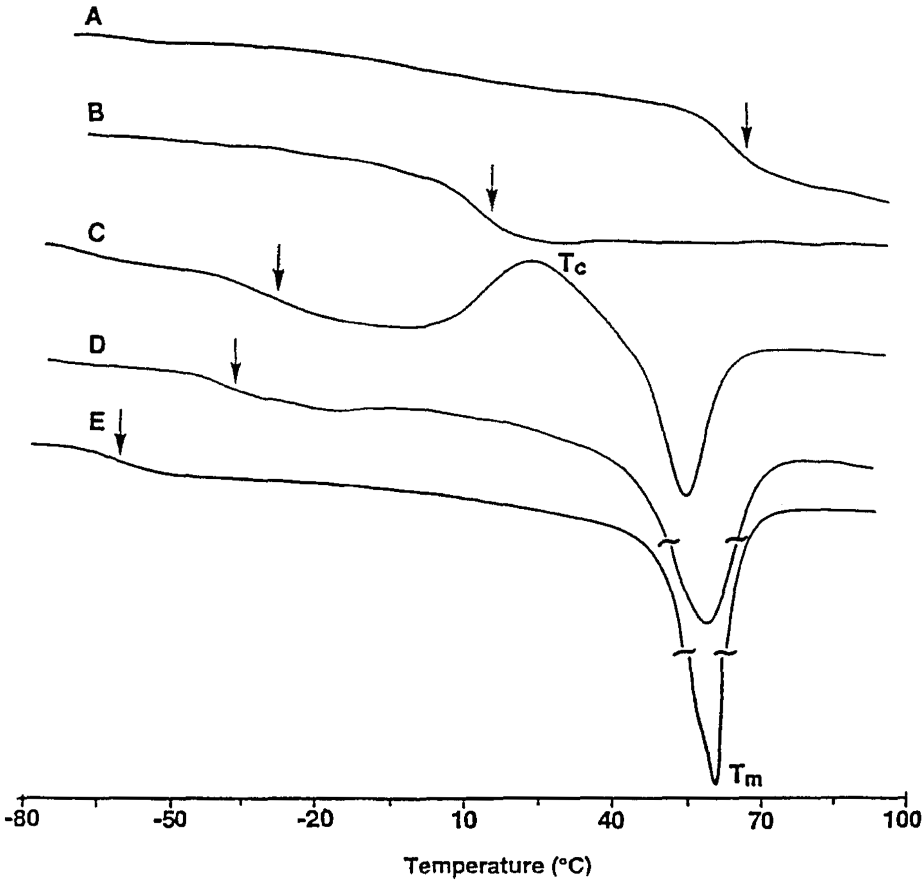


Figure 7. DSC results of blends of H-HPVB with PCL. a) H-H PVB; b) H-HPVB/PCL=75:25; c)H-H PVB/PCL=50:50; d) H-H PVB/PCL=25:75; e) PCL

The relationship between the glass transition temperature of H-H PVB-PCL blends and the composition shows also relatively small deviation from linearity (Figure 8).

Our DSC studies of H-H and H-T poly(vinyl halides) (PVH) blends with PCL show that the PVHs are completely miscible with PCL and the phase behaviors of these blends are similar.

ii. Poly(vinyl halides) blends with poly(methyl methacrylate)

The miscibility study of PVC with PMMA, especially the influence of the tacticity of PMMA on the miscibility with PVC, was first carried out by Challa in

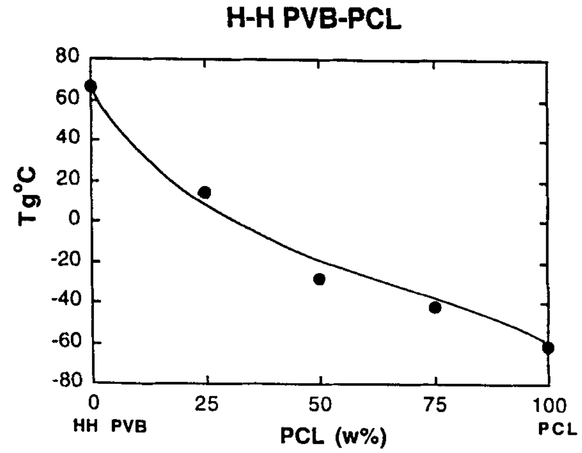


Figure 8. Glass transition temperature of H-H PVB/PCL blends as a function of composition.

1975 [27]. A more detailed study on this matter was done by the same group in 1985 [28]. They concluded that PVC was more miscible with *syndiotactic* PMMA (*syn*-PMMA) than with isotactic PMMA (*iso*-PMMA). With *iso*-PMMA, immiscible blends with PVC were observed over the entire range of composition. With *syn*-PMMA, however, miscible blends resulted up to a blend composition corresponding to a monomer weight ratio of PMMA:PVC 1:1. At higher *syn*-PMMA contents, two-phase behavior was observed with one phase consisting of *syn*-PMMA and the other phase corresponding to the 1:1 PMMA: PVC composition [26]. The samples for these experiments, however, were prepared by heating the samples at 170°C for 10 minutes to remove the last trace of solvent DMF. It is highly possible that at such a high temperature, the polymer blends had already phase separated.

In our experiments, sample preparation was carried out at a lower temperature. The evaporation temperature was 110°C and the temperature during the DSC measurement did not exceed 140°C.

Blends of H-H PVC, H-T PVC with conventional PMMA (obtained by radical polymerization with a *syndiotactic: isotactic* dyad ratio of 80:20), and the blends of H-H PVC, H-T PVC with isotactic PMMA were investigated. H-H PVC was found to be completely miscible with atactic-PMMA (*at*-PMMA) and *iso*-PMMA under our experimental condition. Figure 9 shows the relationships be-

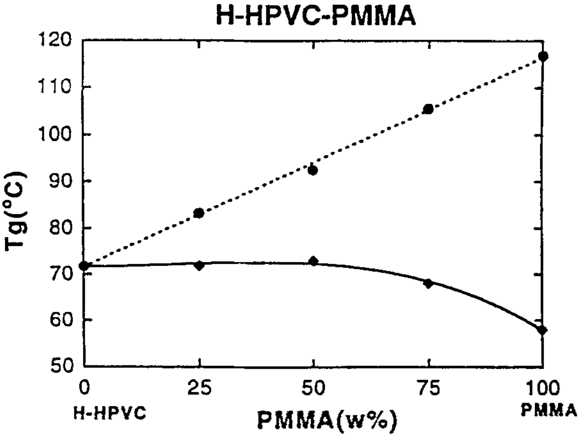


Figure 9. Glass transition temperature of H-H PVC/*at*-PMMA and H-H PVC/*iso*-PMMA blends as a function of composition. (····) H-H PVC blends with *at*-PMMA. (—) H-H PVC Blends with *iso*-PMMA.

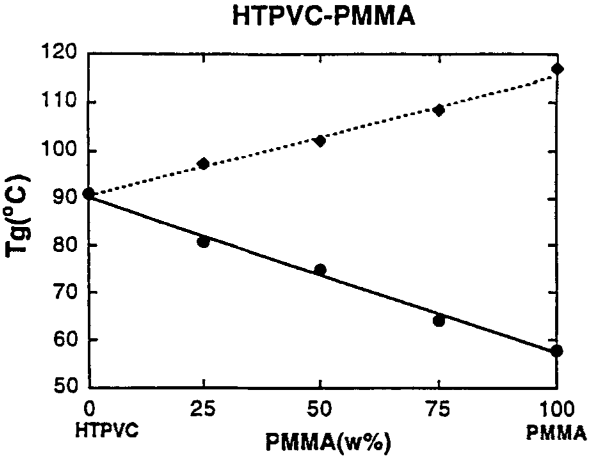


Figure 10. Glass transition temperature of H-T PVC/*at*-PMMA and H-T PVC/*iso*-PMMA blends as a function of composition. (····) H-T PVC blends with *at*-PMMA. (—) H-T PVC blends with *iso*-PMMA.

tween the T_g and the composition of H-H PVC/*at*-PMMA and of H-H PVC/*iso*-PMMA. For the H-H PVC/*at*-PMMA blends, the T_g increased regularly as the amount of *at*-PMMA in the blends increased, and there is a linear relationship between T_g and composition. The blends of H-H PVC/*iso*-PMMA show a curve

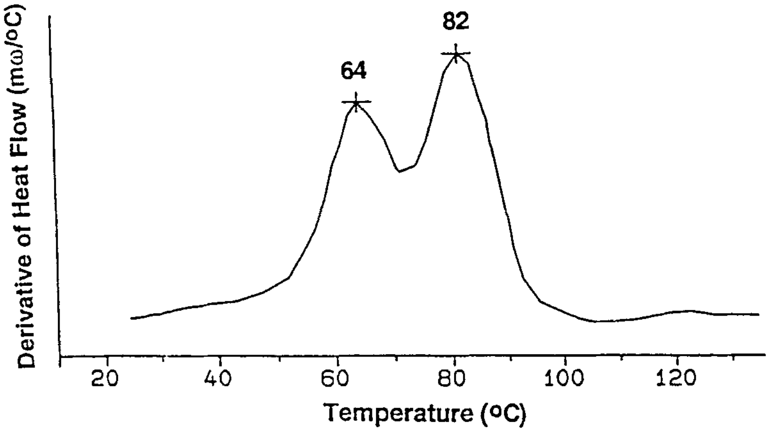


Figure 11. DSC thermogram of H-T PVC/*iso*-PMMA 50:50 after annealing at 180°C for 20 minutes.

with a convex variation from linearity, that is, the T_g values are much higher than expected. This result seems to imply the existence of a definite intermolecular interaction between H-H PVC and *iso*-PMMA.

For mixtures prepared by our technique, H-T PVC was found completely miscible with *at*-PMMA and *iso*-PMMA over the entire range of composition (Figure 10). Both H-T PVC/*at*-PMMA and H-T PVC/*iso*-PMMA blends have a linear relationship between the T_g and the composition.

The results we obtained conflict with those obtained by Challa [27]. The reason for the difference probably lies in sample preparation. The polymer blends we made were never heated over 110°C, while Challa's group heated the blends to above 170°C. Their samples may already have phase separated when heated to 170°C. To prove this point, we heated the H-T PVC/*iso*-PMMA blends to a higher temperature. Indeed, phase separation occurred above 170°C. Furthermore, we found that the phase separation temperature varied according to the different compositions of the blends. When a H-T PVC/*iso*-PMMA 50:50 film was annealed at 180°C for 20 minutes, slowly cooled, and the DSC scan repeated, the thermogram showed two clearly distinguishable T_g's. Figure 11 shows the derivative of the heat flow of the DSC scan. One peak is at 63°C which is the T_g of the *iso*-PMMA rich phase, and the other peak is at 83°C, which is the T_g of the H-T PVC rich phase. For the H-T PVC/*iso*-PMMA 25:75 sample, phase separation already occurred when the sample was annealed at 160°C for 20 minutes. For the

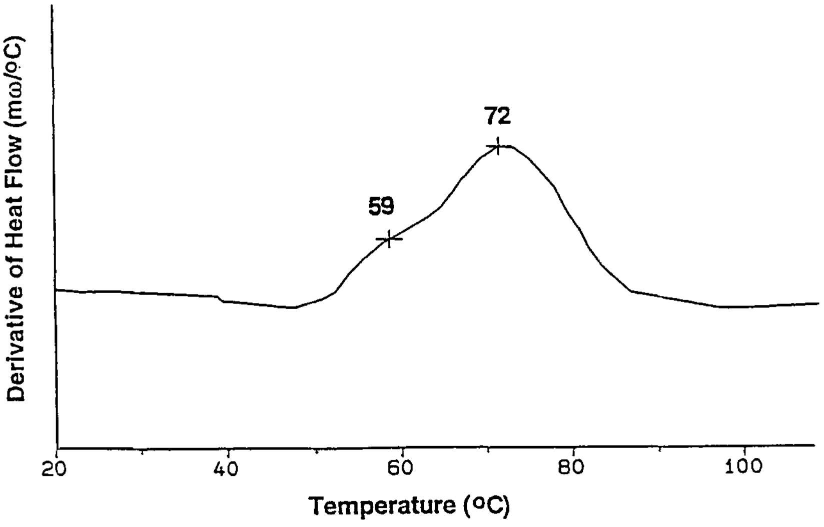


Figure 12. DSC thermogram of H-H PVC/*iso*-PMMA 50:50 after annealing at 210°C for 20 minutes.

75:25 H-T PVC/*iso*-PMMA sample, phase separation occurred only after the sample was annealed at 200°C. It seems that the higher the PVC content, the higher was the phase separation temperature.

H-H PVC/ *iso*-PMMA blends have a higher cloud point than H-T PVC/*iso*-PMMA blends. Sample H-H PVC/*iso*-PMMA 50:50 was heated to 160°C, 180°C, 200°C and 210°C, respectively and annealed for 20 minutes. The sample was then cooled slowly to 0°C, and the DSC scan was taken again. This sample was not phase separated until the annealing temperature reached 210°C (Figure 12). Since the sample H-T PVC/iso-PMMA reached its phase separation point at 180°C, it is concluded that H-H PVC/*iso*-PMMA has better miscibility.

H-H PVB is completely immiscible with *at*-PMMA under the same sample preparation condition that we used for blending PVC with PMMA. When blended with PCL, H-H PVB has similar phase behavior as H-H and H-T PVC: all these polymers are miscible with PCL, which implies that PVH is better miscible than with PCL than with PMMA. Although the α-H in PVB seems to be less acidic than the α-H in PVC it is still strong enough to interact with a strong acceptor such as the C=O group in PCL and form a miscible blend.

Figure 13 shows the T_g's of different H-H PVB/*at*-PMMA blends. There are always two T_g's in each blend, corresponding to the individual polymers, which indicates substantial immiscibility.

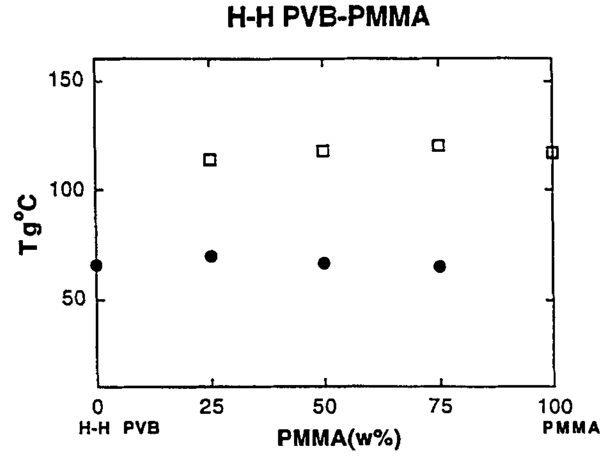


Figure 13. Glass transition temperature of H-H PVB/PMMA blends as a function of composition.

Thermal Codegradation Behavior of Head to Head Polymer Blends

Codegradation of polymer blends as demonstrated also with H-H blends was first carried out by Kryszewski and Vogl. They studied the thermal degradation of blends of H-H and H-T PSt with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [11, 12]. Although these two components are completely miscible, they degrade quite independently from each other. In H-T PSt/PPO blend, degradation of one component did not effect the other component, while in H-H PSt/PPO blend, a decrease in the stability of the PPO fraction of the blends was noticed in the presence of the degrading of H-H PSt [12]. Immiscible blends of H-H polyisobutylene (PIB) and H-T PIB show no interaction between the two polymers during the thermal degradation process [29].

a. Miscible Blends

i. PVC blends with PMMA

The degradation of H-T PVC/PMMA blends has been the subject of a detailed study [30]. It was found that in the early stages of degradation, there was an acceleration of the PMMA decomposition and a retardation of dehydrochlorination reaction. In the later stages of the degradation of the mixture, less MMA was produced than in pure PMMA and the rate of maximum degradation moved to higher temperatures. These results were best interpreted in terms of two types of interaction process, one involving the reaction of the chlorine radical with

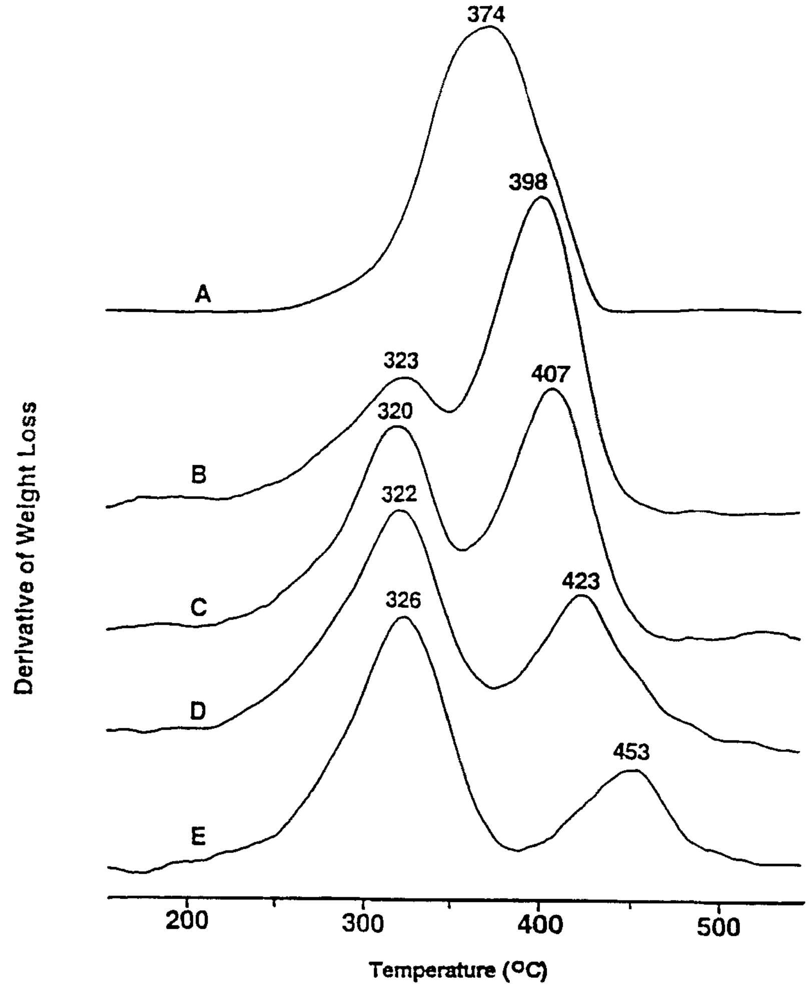


Figure 14. Differential thermogravimetric curve of H-H PVC/PMMA blends; a) PMMA; b) PVC/PMMA=25:75; c) PVC/PMMA=50:50; d) PVC/PMMA = 75:25; e)PVC

PMMA, leading to a considerable destabilization of PMMA for radical degradation, and the other involving the reaction of hydrogen chloride, producing some thermally more stable structure in the degrading PMMA chain.

Our results of the thermal degradation of miscible blends of H-H PVC/PMMA and H-T PVC/PMMA are shown in Figures 14 and 15. For H-H PVC/PMMA blends (Figure 14), PMMA seems to have no effect on the H-H PVC degradation. The dehydrochlorination temperature remains the same for the entire

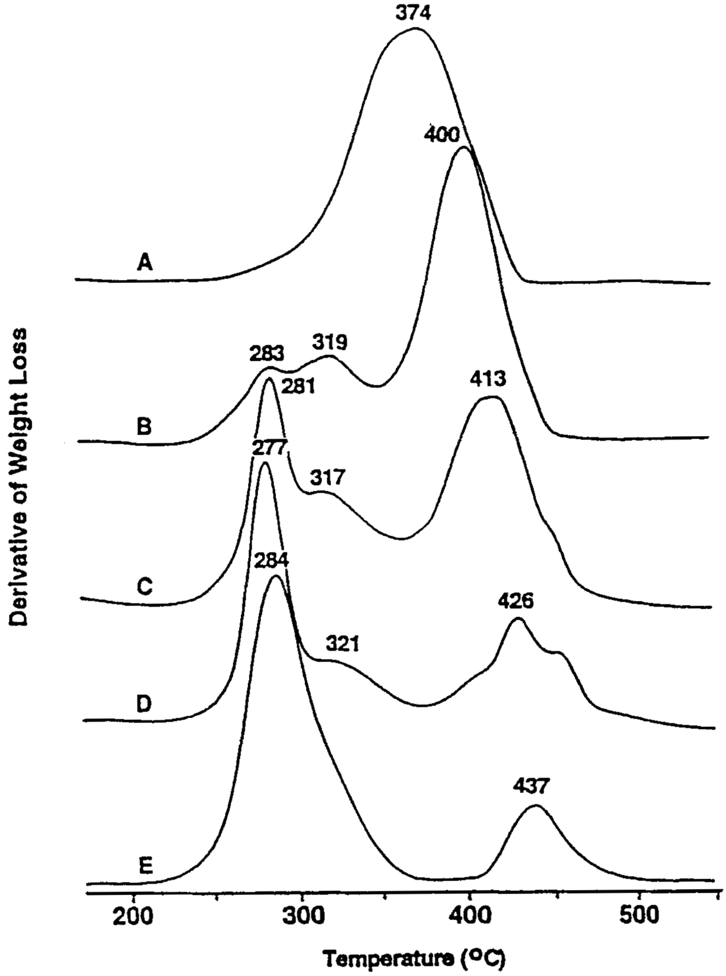


Figure 15. Differential thermogravimetric curve of H-T PVC/PMMA blends; a) PMMA; b) PVC/PMMA=25:75; c) PVC/PMMA=50:50; d) PVC/PMMA =75:25; e) PVC

range of H-H PVC/PMMA blend composition which is around 320°C. The degradation of PMMA, however, seems to be retarded by the presence of H-H PVC. In a blend containing 25% of H-H PVC, the temperature for the maximum degradation rate (T_{md}) increased from 374°C to 398°C. Furthermore, the higher the H-H PVC content, the higher the maximum degradation rate temperature for PMMA in the blends. It might be noticed that the second T_{md} for H-H PVC is 453°C which corresponds to the degradation of the main chain. The peak area

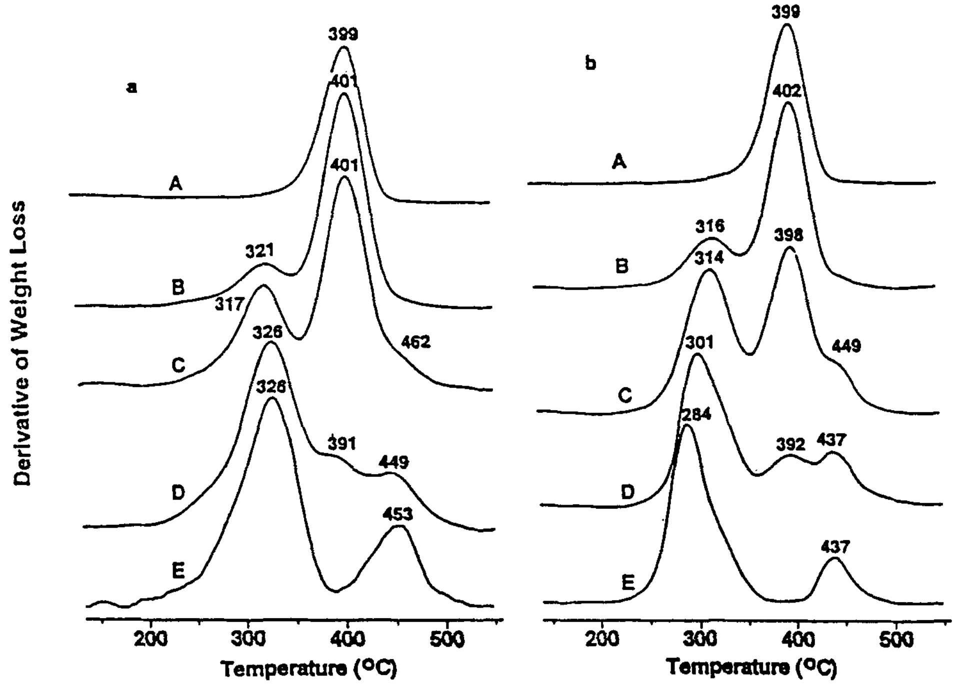


Figure 16. Differential thermogravimetric curve of H-H PVC/PCL and H-T PVC/PCL blends; (a) H-H PVC/PCL blends; (b) H-T PVC/PCL blends. A) PCL; B) PVC/PCL=25:75; C) PVC/PCL=50:50; D) PVC/PCL=75:25; E) PVC

ratio of the dehydrochlorination and the backbone degradation is about 3:1 for 100% H-H PVC. It can be concluded that the degradation which occurred above 400°C in H-H PVC and PMMA blends is related to the decomposition of PMMA.

The degradation of H-T PVC and PMMA blends show similar behavior (Figure 15) as their H-H PVC counterparts. PMMA has no effect on the dehydrochlorination of H-T PVC. The T_{md} is always at 280°C over the entire range of composition. At the later stage of degradation, the T_{md} of PMMA decomposition is shifted to higher temperatures. The amount of the temperature shift is proportional to the concentration of H-T PVC. In the blends of H-T PVC/PMMA 75:25 and H-T PVC/PMMA 50:50, there is a shoulder at about 440°C which represents the backbone degradation of H-T PVC. This result implies that PMMA also has no effect on the backbone degradation of PVC. Comparing the TGA thermogram of the two homopolymers (curve A and E), with those of the blends, there is an additional peak at around 320°C. This peak is not affected by the concentration of

TABLE 2: Temperature o Maximum Degradation Rate of H-H Polymer Blends at Different Composition.

H-H PVC-H-TPVC

	HH 100	HH:HT75:25	HH:HT50:50	HH:HT25:75	HT 100
Tmd1 (°C)	326	317	309	309	284
Tmd2 (°C)	453	450	450	454	437

H-H PVB-H-H PVC

	PVB 100	PVB:PVC75:25	PVB:PVC50:50	PVB:PVB25:75	PVC100
Tmd1(°C)	225	211	211	215 ~	324
Tmd2(°C)	610	454	450	457	448

H-H PVB-H-T PVC

	HH 100	HH:HT75:25	HH:HT50:50	HH:HT25:75	HT 10C
Tmd1(°C)	225	229	251	226	284
Tmd2(°C)	610	452	451	461	437

H-T PVC. This may be related to the acceleration of the PMMA decomposition which is also in agreement with the result obtained by McNeill [30].

ii. PVC blends with PCL

The thermal decomposition of H-H PVC/PCL blends is almost the superimposition of the degradation processes of the homopolymers H-H PVC and PCL, although these two polymers are completely miscible (Figure 16). The specific interaction between H-H PVC and PCL that makes the blends miscible does not affect the degradation behavior. The temperatures of maximum degradation rate of H-H PVC are at 326°C and 450°C, while the temperature of maximum degradation rate of PCL is at 400°C. For H-T PVC/PCL blends, the existence of PCL seems to retard the dehydrochlorination of H-T PVC and shift the T_{md} of dehydrochlorination from 284°C to 316°C (Figure 16).

b. Immiscible Blends

Immiscible blends of H-H PVC/H-T PVC, H-H PVB/H-T PVC were subjected to codegradation studies. Although it was not possible to judge the miscibility of blends of H-H PVB/H-H PVC, by a DSC study (due to the too small T_g

difference) we also included this blend in the category on immiscible blends. We found that the codegradation behavior of the polymer blends investigated in this study was very similar to the combination of the thermal degradation behavior of the individual polymers in the blends. Table 2 shows a list of the temperatures of maximum degradation rates of different the blends at different composition.

CONCLUSIONS

The miscibility and degradation behavior of H-H PVC, H-H PVB and H-T PVC blends with each other and with other polymer especially with PMMA of different tacticity and of PCL were investigated. Both H-H and H-T) PVC and H-H PVB form miscible blends with PMMA of different tacticities. They are also completely miscible with PCL. A certain degree of interaction between PVC's and PMMA are found by the delay of degradation temperature of the PMMA part in the TGA studies. However, blends between H-H and H-T PVH were immiscible. The lack of interaction between these two polymers was further demonstrated by the TGA behavior which was the superposition of the thermal degradation of the two individual polymers.

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