

## Thermal and tensile properties of HTPB-based PU with PVC blends

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### ABSTRACT

Blends of HTPB (hydroxyl-terminated polybutadiene)-based polyurethane (PU) and polyvinyl chloride (PVC) membranes with various relative weight percentages were prepared by solution process. Different equivalent ratios of HTPB, 4,4'-dicyclohexyl methane diisocyanate ( $H_{12}$ MDI), and 1,4-butane diol were used to synthesize PU solution by two-stage process. The intermolecular bonding between N–H, C=O groups of PU and C–Cl group of PVC was determined via FTIR analysis by the relative absorbance of the two N–H groups and was correlated to thermal/mechanical properties. Larger part of PVC has been found to disperse in the hard domain of PU resulting in the shift in IR frequency. Thermal property, tensile strength and intermolecular bonding of membranes were function of the contents of PVC and PU's hard segment. One-year aged butadiene-containing PUs and blends still exhibit higher tensile strength than that of as-prepared ones. Hence, it is promising to replace the plasticizer, such as DOP, in PVC by these HTPB-based PU for the prevention of PVC migration as well as the enhancement of mechanical and thermal properties of blends.

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### 1. Introduction

Polyurethane (PU) is well known for its wear resistance and high toughness, however, low modulus and poor heat resistance [1,2]. Hydroxyl-terminated polybutadiene (HTPB), due to its low-temperature flexibility and low surface energy, has been widely used as the polyol of PU to induce a superhydrophobic surface of PU [3–5]. HTPB-based PU exhibits low tensile strength and breaking strength at room temperature. Unsaturation in the HTPB backbone enhances the susceptibility to aging, which causes additional oxidation and change in mechanical integrity. In this study, HTPB-based PU was expected to blend with PVC to replace the plasticizer in PVC. PVC plays an important role in plastic industry, however, it must be combined with additives, such as plasticizer (DOP) and thermal stabilizer, before processing with the virtues of toughness, abrasive resistance, acid and alkali resistance [6–9].

Polymer blending is a practical method for the development of new polymeric materials [10–13]. There are many studies on the blends of PVC with PU, such as polycaprolactone, poly(tetramethylene adipate), polypropylene glycol-based PU [14–16]. However, few studies described blends of HTPB-based PU with PVC. Adding PU to PVC would be possible to expand the characteristics of two polymers to obtain better mechanical property and compatibility

of the blends. On the other hand, exposure of polymers with the portion of double bond-containing HTPB to environments causes significant changes in their physical, chemical and mechanical characteristics [17,18].

In this study, HTPB-based PU/PVC blends were prepared by solution process. The intermolecular bonding of blends with various blend ratios and hard segment contents of PU were observed by Fourier transfer infrared (FTIR) spectra and correlated to their mechanical and thermal properties. The glass transition temperature ( $T_g$ ), storage and loss modulus were measured by dynamic mechanical analysis (DMA). Thermal gravimetric analysis (TGA) was performed to determine the thermal stability by comparing the thermal decomposition temperature ( $T_d$ ).

### 2. Experimental

#### 2.1. Materials

The chemicals used for this study were hydroxyl terminated polybutadiene (HTPB, equivalent weight 1333 g, average functionality of 2.2, R-45M of ARCO Co.), 4,4'-dicyclohexylmethane diisocyanate ( $H_{12}$ MDI, Desmodue W of Mobay Co.), 1,4-butane diol (1,4-BD) as chain extender and dibutyltin dilaurate (DBTDL) as catalyst. Dimethyl formamide (DMF) and toluene from Tedia Company were dehydrated with molecular sieves before use. PVC with molecular weight of 1800 g/mole was purchased from USI Groups in Taiwan.

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## 2.2. Preparation of membranes

### 2.2.1. Preparation of PVC solution

Designated amounts of PVC and toluene were sequentially mixed in a three-necked bottle under  $N_2$  at room temperature to obtain a homogeneous PVC solution with a solid content of 20 wt%. Continuous stirring for 2 h was followed and the final solution was stored in the refrigerator for further usage.

### 2.2.2. Synthesis of PU polymer

One equivalent weight of HTPB and two equivalent weight of  $H_{12}$ MDI were thoroughly mixed in a three-neck bottle. Small amount of DBTDL was added to the solvent containing suitable ratio of DMF and toluene at  $80^\circ C$  to prepare a polymer solution with a solid content of 80 wt% and with a theoretical NCO content. One equivalent weight of chain extender (1,4-BD) and suitable amount of solvent (DMF+toluene) were then added into the above solution and reacted for about 1 h. The resultant PU solution, with a solid content of 20 wt%, was labeled as PU121, indicating the equivalent ratio of HTPB/ $H_{12}$ MDI/1,4-BD as 1/2/1. Same procedure was applied to prepare PU154 and PU187 solutions, which imply their equivalent weight ratio of HTPB/ $H_{12}$ MDI/1,4-BD as 1/5/4 and 1/8/7, respectively.

### 2.2.3. Preparation of PU/PVC blend solutions

Different weight ratios, 90:10, 70:30, 50:50, 30:70 and 10:90, of prepared PU and PVC solutions were blended for 2 h under  $N_2$  atmosphere. The resultant PU/PVC blend solutions were stored at refrigerator for further usage and labeled as PU121 (or PU154, PU187)/PVC=90/10, 70/30, 50/50, 30/70 and 10/90, respectively.

### 2.2.4. Preparation PU/PVC blend membranes

The above PU/PVC blend solution was poured and knife-coated on a glass plate to obtain polymer films with a thickness of  $160\ \mu m$ , followed by vacuum dried at  $50^\circ C$  for 2 h. After most of the solvent was removed from the film, further drying was performed in a circulation oven with temperature programming. Through the three steps of heating at  $80^\circ C$  (1 h),  $100^\circ C$  (1 h) and  $150^\circ C$  (1 h), golden and semi-transparent solid membranes were obtained. The thickness of all PU/PVC blend membranes was in the range of 90–100  $\mu m$  in the dry state. After one week, some of the prepared membranes were under a series of measurements and regarded as as-prepared samples. Other unused membranes were stored in-between transparent sheets at room temperature without any direct light exposure. Membranes under the latter condition for one year were regarded as one-year-aged samples.

## 2.3. Measurements

The functional groups of PU and PU/PVC blend membranes were examined using a FTIR spectrophotometer (Nicolet PROTEGE-460). Spectra were collected between the wave number of 4000 and  $400\ cm^{-1}$  at a resolution of  $2\ cm^{-1}$ . TGA was performed by Du Pont TGA-950 from  $60^\circ C$  to  $800^\circ C$  at a heating rate of  $20^\circ C/min$  under nitrogen atmosphere. The decomposition temperature ( $T_d$ ) was determined by the TGA curve. The glass transition temperature ( $T_g$ ) and tensile property were analyzed by a thermal analyzer, DMA-2980, from  $-100^\circ C$  to  $300^\circ C$ , at a frequency of 1 Hz and a heating rate of  $3^\circ C/min$ . All the above measurements were carried out on as-prepared membranes. The tensile properties and FTIR spectra of one-year-aged samples were also under investigation.

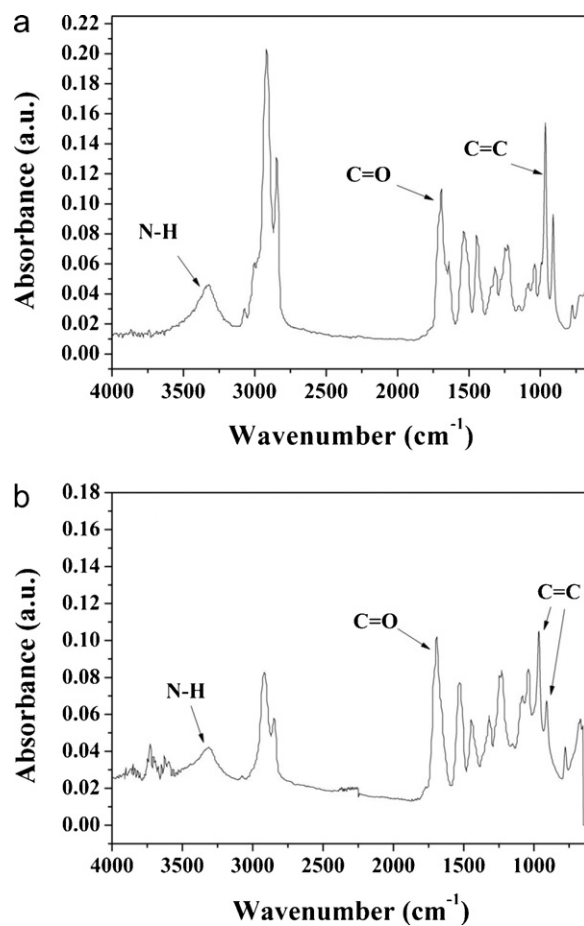


Fig. 1. FTIR spectra of (a) HTPB-based PU and (b) PU154/PVC = 90/10 blends.

## 3. Results and discussion

### 3.1. FTIR measurements

FTIR spectroscopy has been proved to be a useful technique for characterization of intermolecular interactions between groups in self-polymer or different polymer molecules in blend systems. These intermolecular interactions, mainly hydrogen bonding and dipole–dipole interaction, lead to either shifts in frequency or changes in absorbance of specific functional groups [19].

Fig. 1 shows the FTIR spectra of a typical HTPB-based PU and a blend, PU154/PVC = 90/10. The characteristic absorption peaks of PU and blend at 970 and  $912\ cm^{-1}$  were assigned as the out-of-plane bending vibration of C–H of  $R_1CH=CHR_2$  [20] and could be considered as trans-1,4 and trans-1,2 forms of (C=C) group of soft HTPB segments, respectively. Meanwhile, the characteristic absorption peaks at 1698 or  $1716\ cm^{-1}$  and the ones at 3320 or  $3442\ cm^{-1}$  were assigned as C=O and N–H groups, respectively. The peak at  $1698\ cm^{-1}$  was considered as the hydrogen bonded C=O stretching and the one at  $1716\ cm^{-1}$  was the free bonded C=O stretching. The hydrogen bonded N–H stretching and free N–H stretching represented absorption peaks at  $3320\ cm^{-1}$  and  $3442\ cm^{-1}$ , respectively [5,21].

The split of C=O and N–H peaks observed in Fig. 1 may be due to the presence of inter-hydrogen bonding in urethanes. It is known that the primary intermolecular interaction, self-association, occurring in urethanes is hydrogen bonding between urethane C=O and urethane N–H groups from different chains. Hence, the inter-chains of hydrogen-bonded urethane groups were formed and two non-hydrogen-bonded groups, free C=O and free N–H, were at the other ends of these chains. The hydrogen-bonded

N–H (or C=O) groups were believed in the interior of the PU hard segments, whereas the free bands may correspond to those groups in the hard segment domains or in the soft domains or at PU's interface [22]. In the butadiene-containing PUs, hydrogen bonding occurs only between urethane segments of the N–H and C=O group, since the carbonyl groups in the urethane linkage and the urethane alkoxy oxygen are the only available proton acceptors.

The dipole–dipole interaction between N–H groups of PU and C–Cl groups of PVC will occur with the addition of PVC into PU. There are some explanations: First, the HTPB soft segment contains only nonpolar groups, such as  $-\text{CH}_2$ ,  $\text{C}=\text{C}$  and  $-\text{CH}_3$ . Second, the intermolecular bonding between HTPB-based PU and PVC will occur only on N–H, C=O groups of PU hard segment and C–Cl group of PVC due to hydrogen bonding and dipole–dipole interaction [14,16]. However, bad compatibility between PVC and HTPB segment of PU is expected as the solubility parameter of HTPB,  $8.4 \text{ (cal/cm}^3)^{1/2}$ , is lesser than that of PVC and normal PU,  $10.5 \text{ (cal/cm}^3)^{1/2}$ . Another possible reason is that the rigid character of PVC segment can easily aggregate in PU hard segment. Hence, the added PVC will tend to distribute in the hard domain of PU.

Landro et al. [23] have reported that a large number of N–H forms hydrogen bonds with C=O and N–H groups on different chains in the case of PU with fewer polyether chain, resulting in a higher IR absorbance (A) ratio of bonded N–H to free N–H. In this respect, the extent of N–H groups participating in the intermolecular bonding can be expressed by the  $R_{\text{I,N-H}}$  value, which is defined as the ratio of relative absorbance of the bonded and free N–H groups, i.e.  $R_{\text{I,N-H}} = A_{\text{N-H,bonded}}/A_{\text{N-H,free}}$ . A larger  $R_{\text{I,N-H}}$  value indicates a stronger intermolecular bonding present in a polymer system. The addition of PVC, which possesses C–Cl groups, will enhance the bonding with N–H groups of PU segment. Hence, a majority of bonded N–H groups will agglomerate to the hard segment domain of PU and free N–H groups distribute in the soft HTPB domain. Intuitively, the absorbance of bonded N–H peak and the  $R_{\text{I,N-H}}$  values of blends will increase with the increase of PVC content. However, the presence of C–Cl in PVC will create repulsion to the C=O groups in PU. The bonded C=O groups will disperse in PU's soft HTPB domain, rather than in hard PU domain. The controversy effect of C–Cl on the interaction between C=O and N–H groups is expected for the synthesized blends.

Table 1 shows the  $R_{\text{I,N-H}}$  values obtained from IR measurements on various PU/PVC blends.  $R_{\text{I,N-H}}$  was increased from 1.18 to 1.53 for the blends with relative PU/PVC ratio of 100/0 to 10/90. That is,  $R_{\text{I,N-H}}$  is increased with the PVC content, no matter the type of PU. It indicates stronger interactions occur between C–Cl and N–H groups that more N–H groups were bonded in the hard PU domain. Meanwhile, the repulsion between C–Cl and C=O groups was enhanced that hydrogen bonding between N–H and C=O groups was limited resulting in less bonded C=O groups in hard PU domain. Most C=O groups will be free bonded and distribute in the soft HTPB domain. The increase in PVC content will push more C=O group into HTPB soft domain and then strengthen the repulsion between HTPB domain with C=O or C–Cl groups. These competitive effects on interactions within hard and soft domains will affect the interaction of the constituents during aging period. The changes in  $R_{\text{I,N-H}}$  provide the information of interaction within blends.

$R_{\text{I,N-H}}$  values shown in Table 1 were also function of the content of hard domain in PU, that is, increased from PU121, PU154 to PU187. The increase in the content of hard segment will enlarge the amount of polar groups, N–H and C=O, aggregating in the hard segment of PU, rather than dispersing in the soft HTPB domain. The greater  $R_{\text{I,N-H}}$  value indicates the increased participation of the N–H groups in bonding with C=O group or C–Cl group of PVC in the hard PU domain.

As discussed in the previous reports [24,25], the shift of IR absorption frequency was used as a measure of the average strength

of intermolecular interactions in PU with the present of PVC. The absorption frequency of bonded N–H groups,  $\nu_{\text{N-H,bonded}}$ , listed in Table 1, was increased with the increase of PVC content for all PU/PVC blends. It shifted from  $3320$  to  $3335 \text{ cm}^{-1}$  when the PVC composition was increased from 0 to 90. The shift to a higher frequency was due to the enhanced attraction between C–Cl and N–H groups. In addition, the C–Cl stretching peak at  $833 \text{ cm}^{-1}$  slightly shifts to  $835 \text{ cm}^{-1}$  for the blends, no matter the variation of PU content. It could be explained that the increase in PVC content (i.e. the amount of C–Cl groups) enhances the dipole–dipole bonding with N–H groups.

Table 1 also lists the relative IR absorbance of C=O to C=C,  $A_{\text{C=O}}/A_{\text{C=C}}$ , for as-prepared and one-year-aged samples. A decrease in the strength of C=C band in HTPB segment is expected as oxidation or cross-linking reaction may occur after one-year aging. Larger value of  $A_{\text{C=O}}/A_{\text{C=C}}$  indicates more C=O (or lesser C=C) segment content presented in blends. The value of  $A_{\text{C=O}}/A_{\text{C=C}}$  was increased from 1.07 to 1.14 for PU121 to PU187 as more hard segments, i.e. C=O groups, presents in PU187. This value was larger for one-year-aged than as-prepared HTPB-containing membranes, indicating more C=C band oxidized or cross-linked. For example,  $A_{\text{C=O}}/A_{\text{C=C}}$  was increased from 1.14 to 1.18 for PU187 series membranes.

### 3.2. Mechanical properties

The stress–strain results of PU, PVC and blends were presented in Table 2. The tensile strength of blends was significantly increased with the increase of PVC contents and the strain of blends was between that of pure PU and PVC. Meanwhile, the increase in the content of PU hard segment, e.g. from PU121, PU154 to PU187, enhances the tensile strength, however, decreases the strain. The presence of PVC in PU/PVC blends is believed to increase the strength of polymers because of the interlocking of polymeric chains on blends as well as the dipole–dipole interaction between N–H groups in PU and C–Cl groups in PVC [26,27]. Those may be the reasons that the more the PVC content, the higher the tensile strength but the less the elongation at break of blends.

The results shown in Table 2 indicate the stress of PU-containing membranes after 1 year aging was greater than that of as-prepared ones. The difference in strain of these membranes was also revealed for aged and as-prepared membranes. The increasing increment of stress of PU121 and PU121-based blends are larger than those of PU154 or PU187 and blends. The reason is that HTPB soft segment, containing unsaturated double bonds, C=C, will be oxidized or crosslinked under the exposure to ambient condition. More HTPB presented in PU121-based blends than other PU-based samples that the intermolecular cross-linkage of PU121 blends was more promising. The destroy of C=C double bonds (e.g. by oxidation or crosslink) of these membranes can be proved from the decrease in peak intensity from trans-1,4 form of C=C peak at  $972 \text{ cm}^{-1}$  and 1,2 form at  $912 \text{ cm}^{-1}$ . The relative absorbance,  $A_{\text{C=O}}/A_{\text{C=C}}$ , is expressed in Table 1. It increases with the decrease of C=C groups, that is, with the increase of PU hard segment content in samples. The oxidation or crosslink of C=C bands of HTPB-containing PU or blends leads to the increase in  $A_{\text{C=O}}/A_{\text{C=C}}$  for samples under 1-year aging. The destruction of C=C band is the reason for the changes in stress and strain observed for one-year-aged butadiene-containing PU and blends.

As indicted in Table 2, the stress and strain of some one-year-aged blends were failed to measure, including PU121-based 50/50 blends and all blends with the composition of 70/30. Significant destruction and severe phase separation of the above four membranes were viewed by naked eyes as bad PU–PVC compatibility occurs. Relatively, other blends exhibit better compatibility

**Table 1**  
FTIR results of PU and PU/PVC blends.

Property	Sample	Composition (PU/PVC)						
		PU type	Composition (PU/PVC)					
			100/0	90/10	70/30	50/50	30/70	10/90
$R_{I,N-H}$ value	PU121	1.18	1.19	1.21	1.24	1.26	1.28	
	PU154	1.36	1.37	1.40	1.43	1.44	1.45	
	PU187	1.43	1.45	1.47	1.50	1.52	1.53	
$\nu_{N-H}$ , bonded ( $\text{cm}^{-1}$ )	PU121	3320.8	3323.3	3325.4	3326.7	3328.8	3330.6	
	PU154	3320.8	3325.7	3327.3	3330.2	3332.1	3335.2	
	PU187	3320.8	3326.5	3330.7	3332.4	3333.2	3335.5	
$(A_{C=O}/A_{C-C})^a$	PU121	1.07	1.07	1.07	1.07	1.07	1.07	
	PU154	1.11	1.11	1.11	1.11	1.11	1.11	
	PU187	1.14	1.14	1.14	1.14	1.14	1.14	
$(A_{C=O}/A_{C-C})^b$	PU121	1.15	1.15	– <sup>c</sup>	– <sup>c</sup>	1.14	1.14	
	PU154	1.16	1.15	– <sup>c</sup>	1.15	1.14	1.14	
	PU187	1.18	1.18	– <sup>c</sup>	1.17	1.17	1.16	

<sup>a</sup> For as-prepared membranes.<sup>b</sup> For one-year-aged membranes.<sup>c</sup> Failed to perform measurement due to membrane rupture.**Table 2**  
Tensile properties of PU, PVC and PU/PVC blends.

Property	Sample	Composition (PU/PVC)							
		PU type	Composition (PU/PVC)						
			100/0	90/10	70/30	50/50	30/70	10/90	0/100
Stress <sup>a</sup> (MPa)	PU121	1.98	4.28	7.33	11.64	21.75	46.90	175	
	PU154	4.35	9.29	21.37	32.18	53.45	67.53	175	
	PU187	6.89	15.23	31.56	48.15	65.17	74.26	175	
Stress <sup>b</sup> (MPa)	PU121	4.12	7.71	– <sup>c</sup>	– <sup>c</sup>	18.27	65.67	–	
	PU154	6.53	13.00	– <sup>c</sup>	30.09	65.21	74.28	–	
	PU187	7.76	17.07	– <sup>c</sup>	45.26	72.34	81.69	–	
Strain <sup>a</sup> (%)	PU121	1298	119.4	50.48	33.06	17.75	16.86	13.11	
	PU154	874.3	92.51	43.25	27.56	17.34	15.83	13.11	
	PU187	686.7	83.64	37.53	23.18	14.39	13.48	13.11	
Strain <sup>b</sup> (%)	PU121	1387	132.9	– <sup>c</sup>	– <sup>c</sup>	15.63	20.23	–	
	PU154	927.8	103.5	– <sup>c</sup>	24.67	19.50	16.30	–	
	PU187	872.2	86.13	– <sup>c</sup>	21.78	15.27	14.36	–	

<sup>a</sup> For as-prepared membranes.<sup>b</sup> For one-year-aged membranes.<sup>c</sup> Failed to perform measurement due to membrane rupture.

between PU and PVC. It is believed that HTPB is more nonpolar than PVC that repulsion of soft domain of 70/30 blends is too large to form compatible blends. And the PU121-based 50/50 blend possesses more HTPB soft segment content than the other two blends of PU154 and PU187-based 50/50. Then the PU121-based 50/50 blend reveals bad compatibility. The remaining blends reveal better compatibility between PU and PVC because a suitable equilibrium between the repulsion interaction, from HTPB and C=O or C–Cl groups, and the attraction interaction, from N–H and C–Cl groups of hard domain may exist.

### 3.3. DMA measurements

Many reports have demonstrated that the polyester PU blends with PVC or CPVC formed a miscible system, whereas immiscible for polyether PU system [16,28]. In this manuscript, the effects of PU hard segment content and PVC content on  $T_g$  and storage modulus were studied by DMA measurements. The  $T_g$  value indicates the interaction between hard segment of HTPB-based PU and PVC. As HTPB contains only nonpolar soft segment, most PVC will agglomerate to the hard segment of PU and less PVC distributes in nonpolar and soft HTPB segment, as discussed in Section 3.1.

Figs. 2–4 show that the storage modulus decreased with the decrease of PVC content, i.e. following the rank of pure PVC, blends 10/90, 30/70, 50/50, 70/30, 90/10 and pure PU. The reason is that PVC is a rigid segment that possesses higher storage modulus.

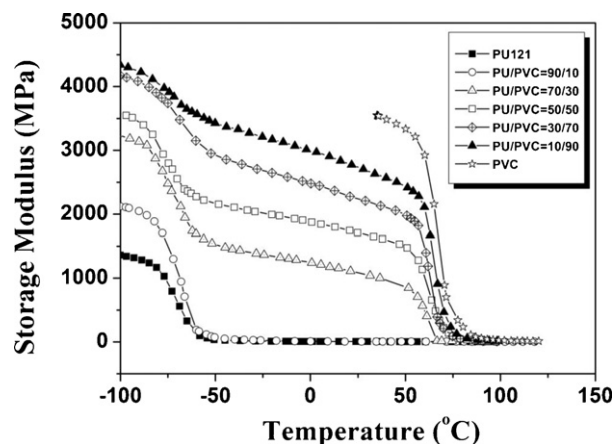


Fig. 2. Storage modulus of PU121, PVC and PU121/PVC blends.

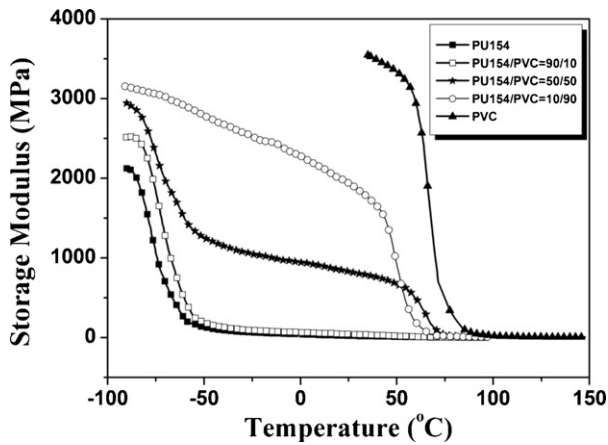


Fig. 3. Storage modulus of PU154, PVC and PU154/PVC blends.

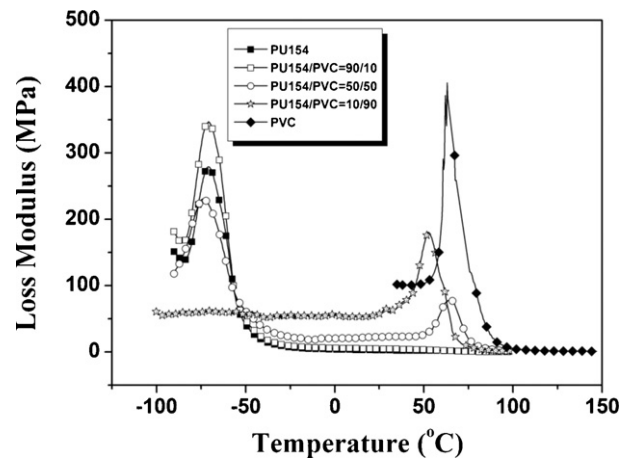


Fig. 6. Loss modulus of PU154, PVC and PU154/PVC blends.

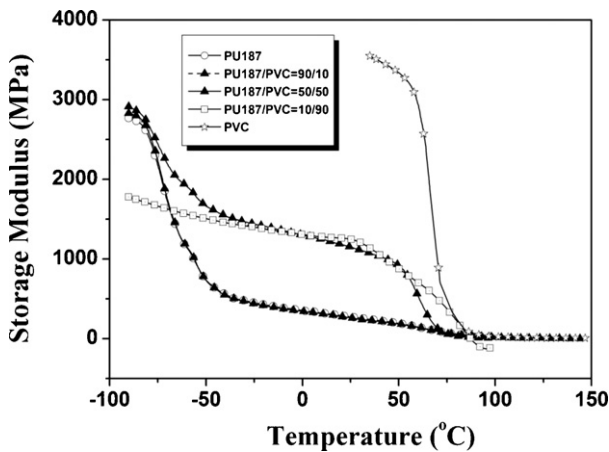


Fig. 4. Storage modulus of PU187, PVC and PU187/PVC blends.

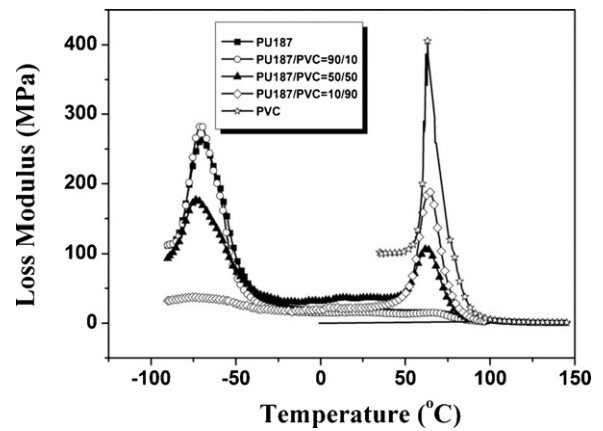


Fig. 7. Loss modulus of PU187, PVC and PU187/PVC blends.

Meanwhile, the storage modulus increased from PU121, PU154 to PU187, which contains increased PU hard segment. The increase in the content of PU hard segment will increase the intermolecular attraction owing to the formation of intermolecular hydrogen bonding between N–H and C=O groups.

Figs. 5–7 show the loss modulus curves of PVC, PU and blends and the corresponding  $T_g$  values, which were determined by the peak position, were summarized in Table 3. The  $T_{g1}$  of all pure PUs is at  $-72.8^\circ\text{C}$  and the  $T_{g2}$  of pure PVC is at  $80.5^\circ\text{C}$ .  $T_{g1}$  is the  $T_g$  value

of HTPB soft segment, meanwhile, the  $T_{g2}$  is the one from the combination of PU hard segment and PVC segment or pure PVC only. The  $T_{g1}$  values are all increased with the increase of PVC content. The following two reasons may explain the increase in  $T_{g1}$  value. First, some part of PVC segment will disperse into PU's soft domain.

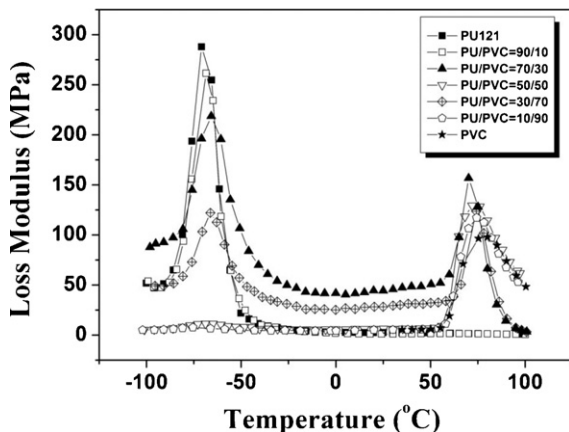


Fig. 5. Loss modulus of PU121, PVC and PU121/PVC blends.

Table 3

DMA and TGA results of PU, PVC and PU/PVC blends.

Property	Sample	PU type Composition (PU/PVC)						
		100/0	90/10	70/30	50/50	30/70	10/90	0/100
$T_{g1}$ ( $^\circ\text{C}$ )	PU121	-72.8	-69.4	-67.0	-66.3	-64.9	a	a
	PU154	-72.8	-67.6	-65.8	-64.7	a	a	a
	PU187	-72.8	-66.3	-65.7	-65.9	a	a	a
$T_{g2}$ ( $^\circ\text{C}$ )	PU121	a	a	70.2	74.1	75.0	76.0	80.5
	PU154	a	a	71.8	75.4	77.1	78.2	80.5
	PU187	a	a	73.2	77.2	78.5	79.1	80.5
$T_{d1}$ ( $^\circ\text{C}$ )	PU121	283	261	265	263	270	273	275
	PU154	285	283	274	246	258	249	275
	PU187	287	285	278	254	254	256	275
$T_{d2}$ ( $^\circ\text{C}$ )	PU121	450	446	443	441	438	435	432
	PU154	453	450	447	446	445	442	432
	PU187	457	449	447	446	443	438	432
Residue (%)	PU121	4.89	4.63	4.77	5.34	5.87	6.82	9.71
	PU154	4.15	4.32	4.25	4.79	5.16	6.24	9.71
	PU187	3.87	4.08	4.16	4.35	4.68	5.85	9.71

<sup>a</sup> Failed to perform measurement.

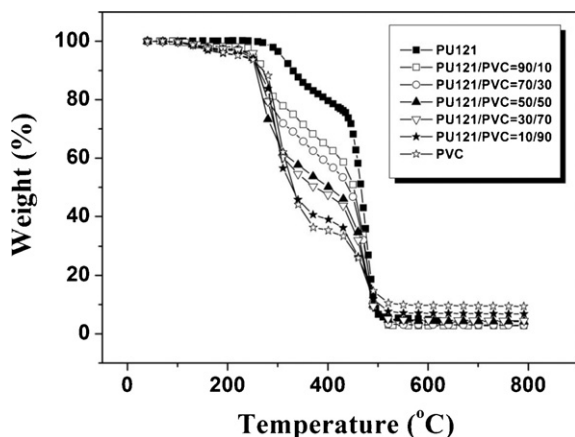


Fig. 8. TGA curves of PU121, PVC and PU121/PVC blends.

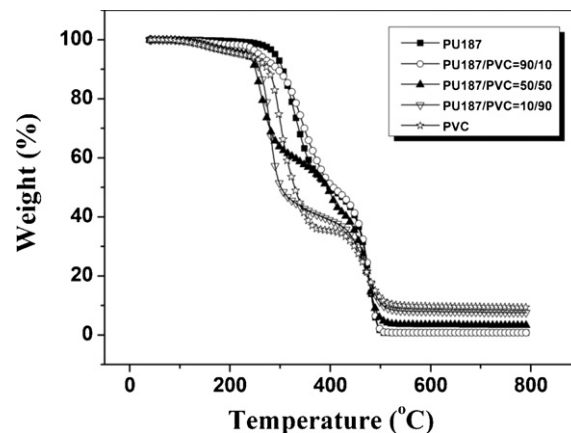


Fig. 10. TGA curves of PU187, PVC and PU187/PVC blends.

Secondly, most part of PVC segment will interact with  $-NH$  groups of PU's hard segment and then agglomerate resulting more free bonded  $C=O$  groups in PU's soft domain. On the other hand, the  $T_{g2}$  values of all blends decreased with the increase of PU content (or the decrease of PVC content). Most PVC tends to agglomerate within PU's hard segment, which is softer than PVC and then the  $T_{g2}$  value decreases with the combination of PU into PVC segment.

Blends of all 70/30, 50/50 composition and PU121-based 30/70 composition respectively possess one  $T_{g1}$  value as well as one  $T_{g2}$  value. All the 70/30 blends and PU121-based 50/50 blend are immiscible and the other two blends of PU154 and PU187-based 50/50 blend are miscible. The explanation may be that too much HTPB nonpolar soft segment contained in the former four blends and the intermolecular repulsion increased as stated in the above section.

However, Table 3 also depicts that the pure PVC, pure PU, blends of three 90/10 and three 10/90 and two 30/70 composition of PU154 and PU187-based present only one  $T_{g1}$  value or one  $T_{g2}$  value, respectively and these eight blends are miscible. The explanation is that former three 90/10 blends containing only 10 wt% of PVC content and latter five blends containing lesser PU content and then the repulsion interaction between PU and PVC is lower.

### 3.4. TGA measurements

Figs. 8–10 show the TGA results taken in the temperature range of 50–550°C at a heating rate of 20°C/min in nitrogen. Two-step degradation curves were observed for pure PU, PVC and PU/PVC

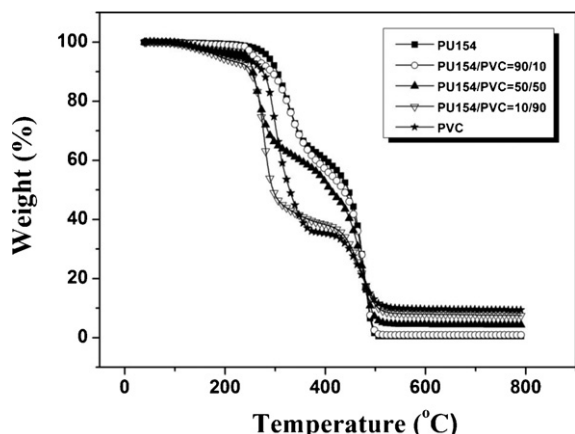


Fig. 9. TGA curves of PU154, PVC and PU154/PVC blends.

blends, which were completely degraded around 500°C. The first and second step of PU decomposition is corresponding to the breaking of urethane bond and decomposition of polyol, respectively [29]. PVC samples exhibit two-step decomposition process as well [14,30]. And the first and second step of PVC decomposition is corresponding to the breaking of  $-C-Cl$  segment and decomposition of  $-CH_2$  segment, respectively. Table 3 depicts these two decomposition temperatures ( $T_{d1}$  and  $T_{d2}$ ) for each prepared sample. The  $T_{d1}$  of PVC (275°C) is lower than those of pure PUs (PU121: 284°C, PU154: 285°C and PU187: 286°C). The value of  $T_{d1}$  for all blends decreases with the increase of PVC content and lies between that of the corresponding PU and PVC. There are two contrary effects on  $T_{d1}$  values: One is that the introduction of PVC segment onto hard domain will destruct the original hydrogen bonding of PU's hard domain. Hence,  $T_{d1}$  value decreases with the increase of PVC content. However, the increase in PVC content increases the attractive interaction between  $C-Cl$  and  $-NH$  groups, resulting to a greater  $T_{d1}$  value. The obtained results indicate the former repulsive effect possesses superiority that the decrease in  $T_{d1}$  values revealed for samples containing less PU.

Meanwhile, the  $T_{d2}$  value of PVC (432°C) is lower than that of PUs (PU121: 450°C, PU154: 453°C and PU187: 457°C). The  $T_{d2}$  value of all blends is lower than that of the corresponding PU and decreases with the increase of PVC content as well. The explanation is that the repulsive interaction between PVC and soft HTPB segment will contribute to the decrease in  $T_{d2}$  values of the blends. As shown in Table 3, the decomposition temperatures ( $T_{d1}$  and  $T_{d2}$ ) of pure PUs increased, following the rank of PU121, 154–187. With the increase of PU hard segment content, stronger attraction between PU's hard segment as well as more free bonded  $C=O$  or  $N-H$  groups dispersed in PU's soft segment will be achieved that greater  $T_{d1}$  and  $T_{d2}$  values were obtained.

The residues of all blends after thermal treatment were all larger than those of pure PU membrane and increased with the increase of PVC content. Membranes with less hard segment (i.e. with higher HTPB content) or higher PVC content possess more carbon and chlorine atoms in the system. It is more difficult for carbon and chlorine elements to decompose than for oxygen and nitrogen in PU's hard segment do. These may be the reasons that more residues remain after thermal treatment for the membranes with more PVC present.

## 4. Conclusion

The molecular level interactions between PU, PVC and blends are successfully resolved by FTIR analysis. Large amount of PVC comes into the hard domain of PU with the addition of PVC to PU.

A larger  $R_{\text{I,N-H}}$  value indicates a stronger intermolecular bonding, which increases with the increasing PVC content. The IR absorption frequency of bonded N–H,  $\nu_{\text{N-H,bonded}}$ , increases with the increase of PVC content for all PU/PVC blends. Membranes with the PU/PVC composition of 70/30 and 50/50 blends of PU121 as well as 70/30 blends of PU154 and PU187 with PVC are regarded as bad compatibility between PVC and PU. While the other blends possess better PU–PVC compatibility. The storage modulus of samples decreases in the rank of PVC, blends, and pure PU, following the trend of decreasing PVC content. The  $T_{g_1}$  of all pure PUs are all at  $-72.8^\circ\text{C}$ , while the  $T_{g_2}$  of pure PVC is at  $80.5^\circ\text{C}$ . Blends possess only one  $T_{g_1}$  value and only one  $T_{g_2}$  value. The  $T_{g_1}$  values enlarge with the increase of PVC content; however, the  $T_{g_2}$  values reduce with the increase of PU content (or the decrease of PVC content). The first decomposition temperature ( $T_{d_1}$ ) of PVC is lower than that of PUs. For all blends,  $T_{d_1}$  lies between the one of corresponding PU and PVC and reduces with the increase of PVC content. Meanwhile, the decomposition temperature ( $T_{d_2}$ ) of PVC is lower than PUs. Similar trend is observed for  $T_{d_2}$  values of all blends, which is lower than that of corresponding PU and decrease with the increase of PVC content. The decomposition temperature of pure PUs is increased, following the rank of PU121, PU154 to PU187. Both the increase in the content of PVC and PU's hard segment enhance the tensile strength of the blends. The strain of blends are in-between the one of pure PU and PVC. A strange phenomenon was observed that the stress and strain of 1-year-aged PU-containing membranes are all larger than those of as-prepared ones. This could be explained by the variation in  $A_{\text{C=O}}/A_{\text{C=C}}$  ratio, which increases with the samples with more PU's hard segment or under longer aging process.

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