CHAPTER 4

RESULT AND DISCUSSION

The word "polyurethane or PU" and "semi-IPN" hereafter appeared in this Chapter refers respectively to the PCL/MMDI/TEA-based PU and the semi-IPNs of PCL/MMDI/TEA-based PU and PVC. Since there were a number of PUs and the semi-IPNs synthesized in these studies, a coding system to nomenclature samples is set.

4.1 Sample Nomenclature

Nomenclature of the particular formular of PUs or semi-IPNs composes of twelve characters. The first two characters are to be either PU or SI. PU is again abbreviated for the PCL/MMDI/TEA-based PU, and SI for the semi-IPNs of PCL/MMDI/TEA-based PU and PVC with a molecular weight of 50,625 g/mol. The subsequent two characters, i.e. the third and the forth characters, are dedicated for the value of the equivalent ratio of NCO/OH, which represents by the first two decimals of that value. For example, if the equivalent ratios of NCO/OH are equal to 0.95, 1.00, and 1.05, then the third and fourth characters are respectively 95, 00, and 05. The fifth character represents the equivalent ratio of PCL:MMDI:TEA, which in these studies they were only three ratios, namely 2:3:1, 1:2:1 and 1:3:2. The characters A, B and C are used to refer to those ratios, respectively. The sixth and the seventh characters imply the amount of PVC content in weight percentage that used to prepare the semi-IPN. If O, 5, 15 and 30 % of PVC are used in the semi-IPN compositions, then 00, 05, 15, and 30 are respectively represented them. The eighth character is a slash (/). The ninth and tenth characters are dedicated for the calculate weight percentage of crosslinking by the total weight of the resulting polymers prepared. For example, the calculated crosslinking is 20 and 30 %, then 20 and 30 are used to represent those characters respectively. In the case that those numbers contain decimals, they are omitted. The eleventh charater is a hyphen (-), and the last one is the indication of either one-shot or prepolymer processes, which are represented by “O” or “P”, respectively.

It is noted that the weight percentage crosslinking by the total weight of the resulting polymers could be calculated by taking the weight of TEA divided by the total weight of PCL, TEA, MMDI and PVC.

To provide more clear picture of the sample nomenclature, two examples are given here. A PU (obviously no PVC presented) is prepared by a one-shot process using the equivalent ratios of NCO/OH and of PCL:MMDI:TEA equal to 1.05 and 1:2:1, respectively, and the calculated crosslinking of 3.71 % by the total weight, the nomenclature for this sample is PU05B00/04-O. The other example is that the equivalent ratios of NCO/OH and PCL:MMDI:TEA are respectively 1.05 and 1:3:2 being used to prepare PU matrix, and the dispersed matrix is PVC of the amount of 30 % by the total weight. This material is the semi-IPN prepared by the prepolymer process, which has the calculated crosslinking of 4.99 % by the total weight. Therefore, the nomenclature for this sample is SI05C30/05-P.

Table 4.1 shows the ten character nomenclature of all of the polymers prepared in these studies (without indication of the one-shot or prepolymer process) together with the values of the equivalent ratios of NCO/OH and of PCL:MMDI:TEA, the amount of PVC in percent by weight contained in the resulting polymers, and the calculated weight percentage of the crosslinking of PU in the resulting polymers.

Table 4.1 Ten-character nomenclature of samples prepared in these studies.

PCL/MMDI/TEA-based PU

NCO/OH ratio	PCL:MMDI:TEA	PU/PVC (% / %)	Calculated Crosslinked*	Nomenclature
1.05	2 : 3 : 1	100/0	2.00(2)	PU05A00/02
1.05	1 : 2 : 1	100/0	3.71(4)	PU05B00/04
1.05	1 : 3 : 2	100/0	6.49(7)	PU05C00/07
0.95	1 : 3 : 2	100/0	6.66(7)	PU95C00/07
1.00	1 : 3 : 2	100/0	6.57(7)	PU00C00/07
1.10	1 : 3 : 2	100/0	6.40(6)	PU10C00/06
1.15	1 : 3 : 2	100/0	6.31(6)	PU15C00/06
1.20	1 : 3 : 2	100/0	6.23(6)	PU20C00/06

Table 4.1 Ten-character nomenclature of samples prepared in these studies. (continue)

Semi-IPN of PCL/MMDI/TEA-based PU and PVC

NCO/OH ratio	PCL:MMDI: TEA	PU/PVC (% / %)	Calculated Crosslinked*	Nomenclature
0.95	1 : 3 : 2	90/10	6.66(7)	SI95C10/07
1.00	1 : 3 : 2	90/10	6.57(7)	SI00C10/07
1.05	1 : 3 : 2	90/10	6.49(7)	SI05C10/07
1.10	1 : 3 : 2	90/10	6.40(6)	SI10C10/06
1.15	1 : 3 : 2	90/10	6.31(6)	SI15C10/06
1.20	1 : 3 : 2	90/10	6.23(6)	SI20C10/06
1.05	1 : 3 : 2	95/5	6.18(6)	SI05C05/06
1.05	1 : 3 : 2	90/10	5.90(6)	SI05C10/06
1.05	1 : 3 : 2	85/15	5.64(6)	SI05C15/06
1.05	1 : 3 : 2	80/20	5.40(5)	SI05C20/05
1.05	1 : 3 : 2	70/30	4.99(5)	SI05C30/05

* Unit in % by weight of the total weight of the resulting polymers. The members in the brackets are used to indicate the approximate number of crosslinking in the resulting polymers.

4.2 Chemical Structure of PCL/MMDI/TEA-Based PU

The crosslinked PUs prepared using the one-shot process are a transparent material. The crosslinking is due to the reaction of TEA with MMDI. Since TEA is a small molecule in comparison to PCL, which is a prepolymer of a molecular weight of 2,000 g/mol, the physical characteristics of chemical linkages resulting from those reacting with MMDI are quite different in that MMDI reacts with PCL yielding a soft segment. The chemical structures of repeating units of those are shown in Figure 4.1.

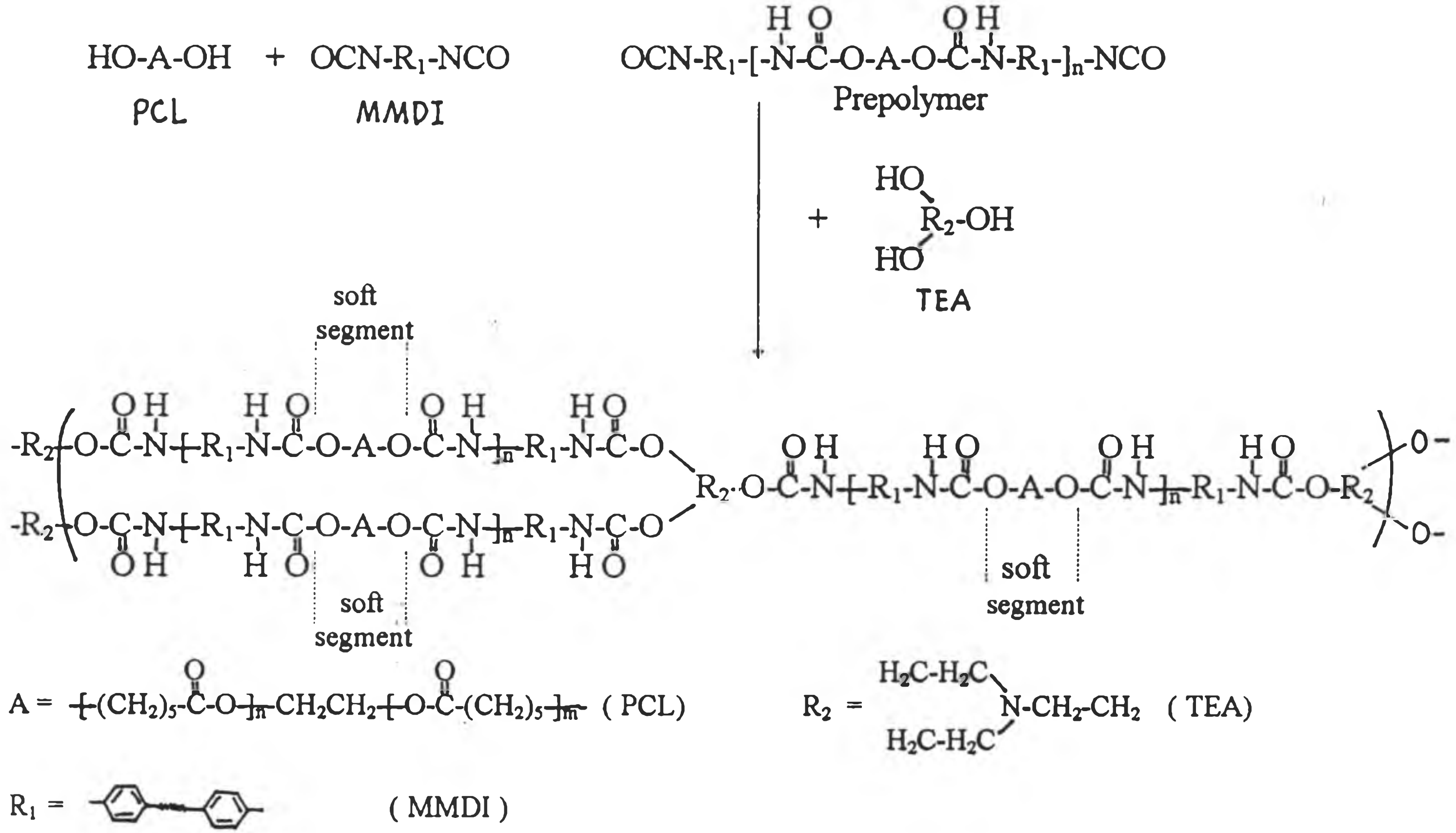


Figure 4.1 Chemical reaction and chemical structures of the repeating units of the hard and soft segments of PCL/MMDI/TEA-based PU.

4.3 The Glass Transition of PU and the semi-IPN

Since the soft segment of PU has a relatively long chain contributing from the polyester repeating unit of PCL prepolymer, its T_g should be observed and in these studies was found at -5.3 and -7.0 °C, for the one-shot and the prepolymer processes to prepare PUs, respectively. These values were measured using a technique of dynamic mechanical analysis (DMA, see Figure 4.2). It has been well known that three to five hard segments align themself to provide a characteristics of micro-crystalline regions dispersed in the amorphous matrix of the soft segment. They act as physical crosslinkings, making PU a type of semi-crystalline polymer. A melting temperature should be therefore able to observe from the DSC thermogram as an exothermic peak of heat flow (see Figure 4.3 [Hepburn,1991]). As observed from a DMA thermogram, at the melting temperature the materials flow, i.e., the viscoelastic property is destroyed, to give infinite value of tanδ. In these studies the melting temperature cannot be observed from the DMA thermogram shown in Figure 4.2. If any, the experimental temperature upto 100°C would not be high enough to detect such the transition. However, it is likely that the three-dimensional chemical crosslinking in PU should not thremodynamically allow to form the micro-crystalline region. Figure 4.4 illustrated the possible three-dimensional networking of the PU prepared in these studies, where R_2 represents the fraction of TEA molecule as indicated in Figure 4.1.

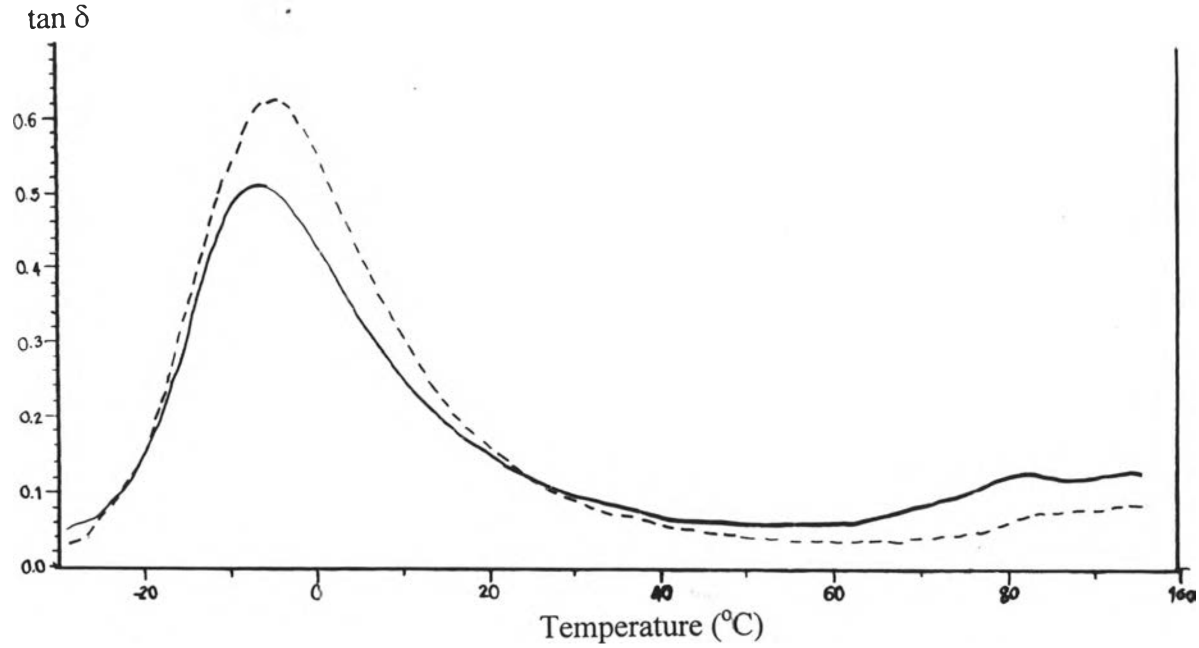


Figure 4.2 The dynamic mechanical response of PU prepared by one-shot (------) and prepolymer (——) processes : Temperature ranges from -30 to 100°C, temperature scanning rate 2K/min, frequency 1 Hz.

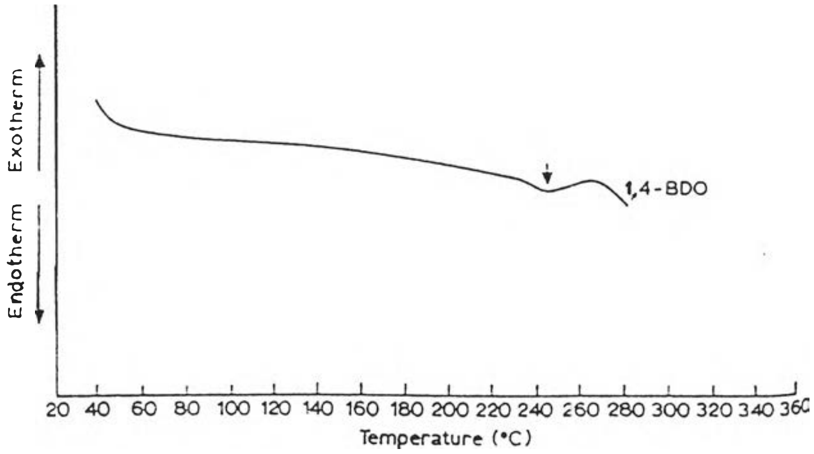


Figure 4.3 DSC scans of diol chain-extended polyurethane elastomers (arrow designates the position of the transition). [Hepburn,1991]

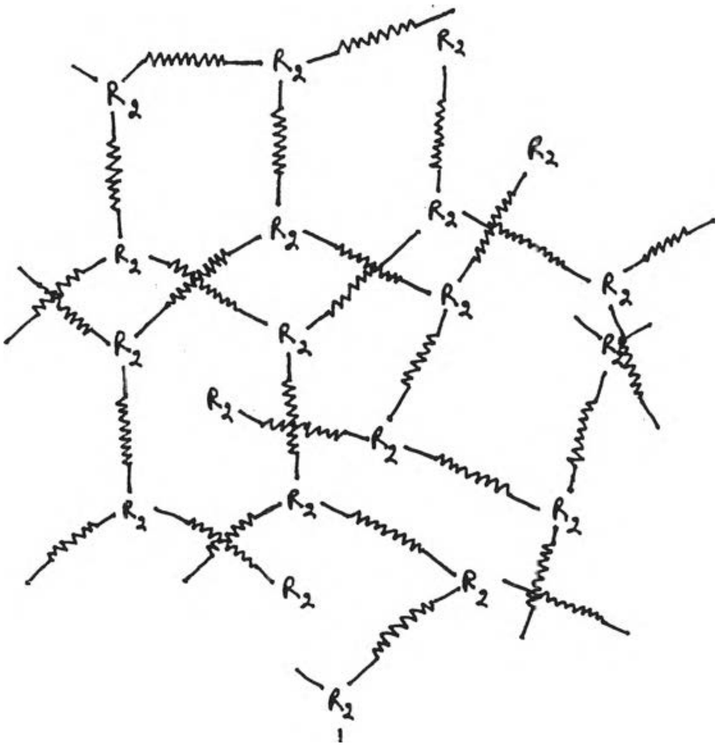


Figure 4.4 Possible three-dimensional network of crosslinked PU prepared in these studies.

For the semi-IPNs (fix the equivalent ratio of PCL:MMDI:TEA = 1:3:2 and 10 % of PVC), the one-shot method gave higher values of T_g's than the prepolymer process (see Table 4.2). The differences of these values are due to the different in the method of preparation. Excluding the effect of the equivalent ratio of NCO/OH, the calculated T_g for the semi-IPN containing PVC of 10 % by weight should be respectively 2.7 and 1.2 for the one-shot and the prepolymer processes. The calculation was based on Equation (2.1) in Chapter 2, and again shows here

$$T_g = W_{(PU)}T_{g(PU)} + W_{(PVC)}T_{g(PVC)}$$

where $W_{(PU)}$ = weight fraction of PU, $W_{(PVC)}$ = weight fraction of PVC, $T_{g(PVC)}$ = 83.5 [Penn,1971] , $T_{g(PU)}$ = -5.3°C (one-shot process) and -7.0°C (prepolymer process).

When the compatible semi-IPN obtained by the prepolymer process, the narrower DMA-tanδ peak is observed (see Figure 4.5). Totally incompatible PU and PVC in the resulting semi-IPN yields two T_g's, being belongs to that of PVC and of the soft segment of PU.

However, they were not observed in the tanδ-temperature DMA thermogram, which means that partially compatible of PVC in the semi-IPN is obtained. The confirmation of this evident was made using the SEM technique. SEM microgaphs of the uncompatible and compatible semi-IPNs are shown in Figures 4.6 and 4.7, respectively. For the one-shot process, the white particles associated to the PVC phase disperse in the dark PU matrix (Figure 4.6) is observed. The higher the weight percentage of PVC in the one-shot semi-IPNs was, the larger the white particles observed, indicating that the PVC could not be well dispersed in the PU matrix.

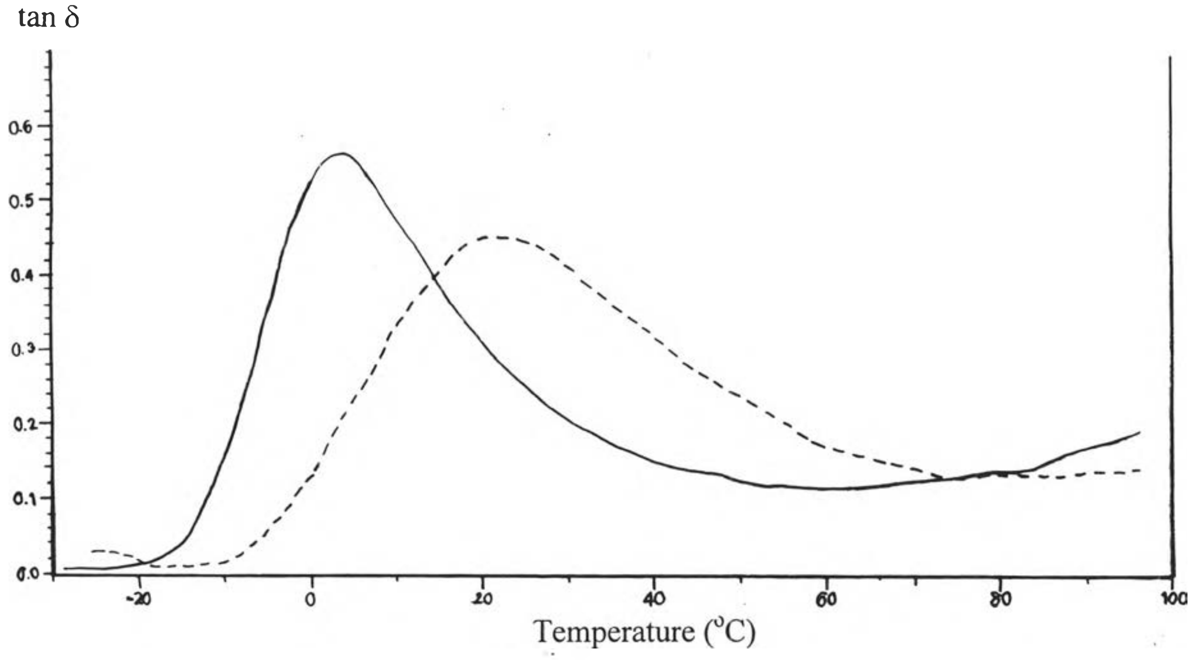
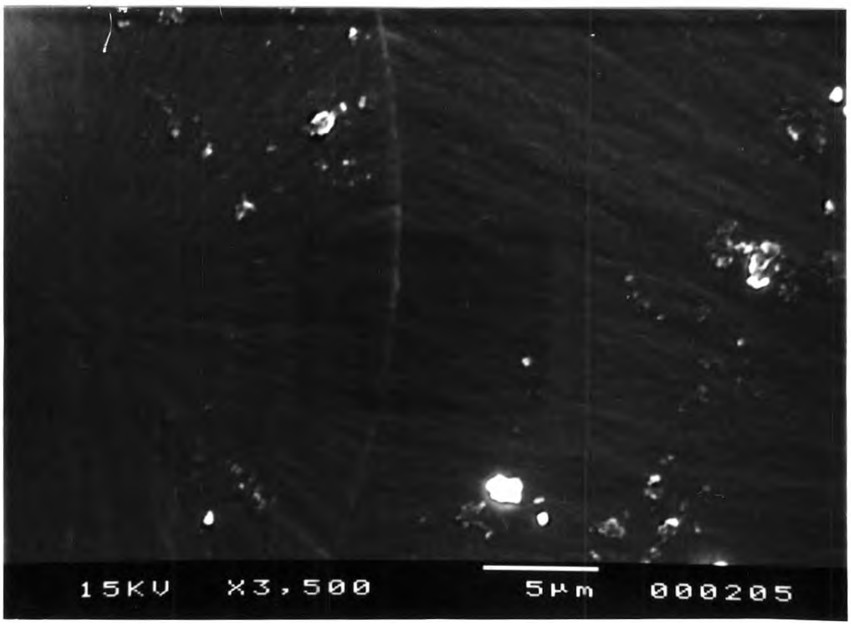
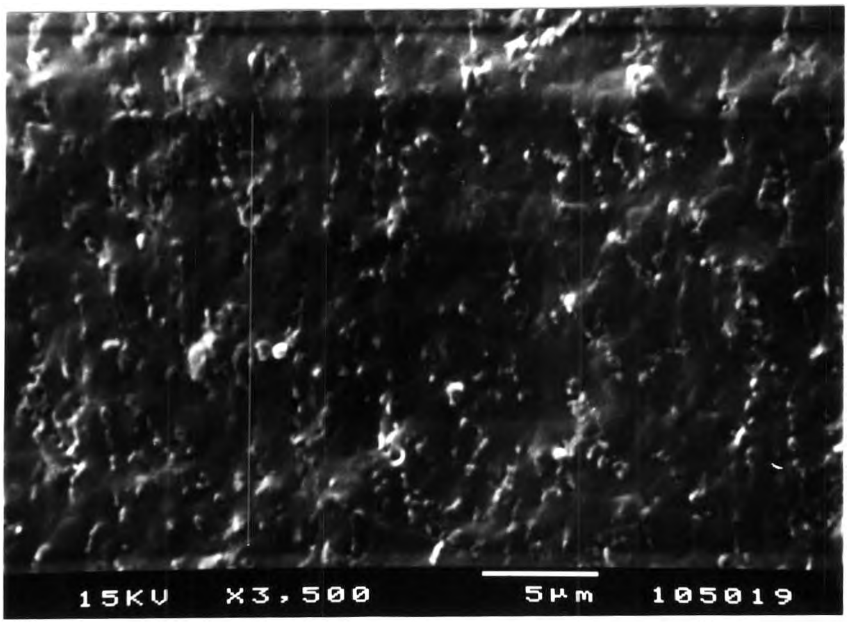


Figure 4.5 The dynamic mechanical response of the semi-IPN prepared by one-shot (-----) and prepolymer (——) processes : the semi-IPN was based on PCL/MMDI/TEA-based PU80%(the equivalent ratios of NCO/OH = 1.05 and of PCL:MMDI:TEA = 1:3:2) and PVC20%; temperature ranges from -30 to 100°C, temperature scanning rate of 2 K/min, frequency of 1 Hz.

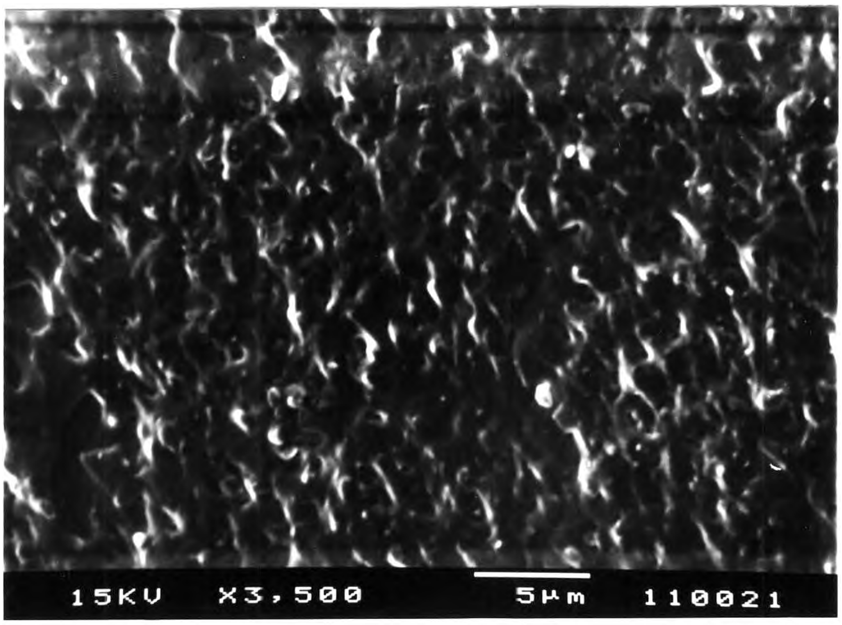
Figure 4.6 SEM micrographs of semi-IPNs PU and PVC (one-shot process) in various amount of PVC.



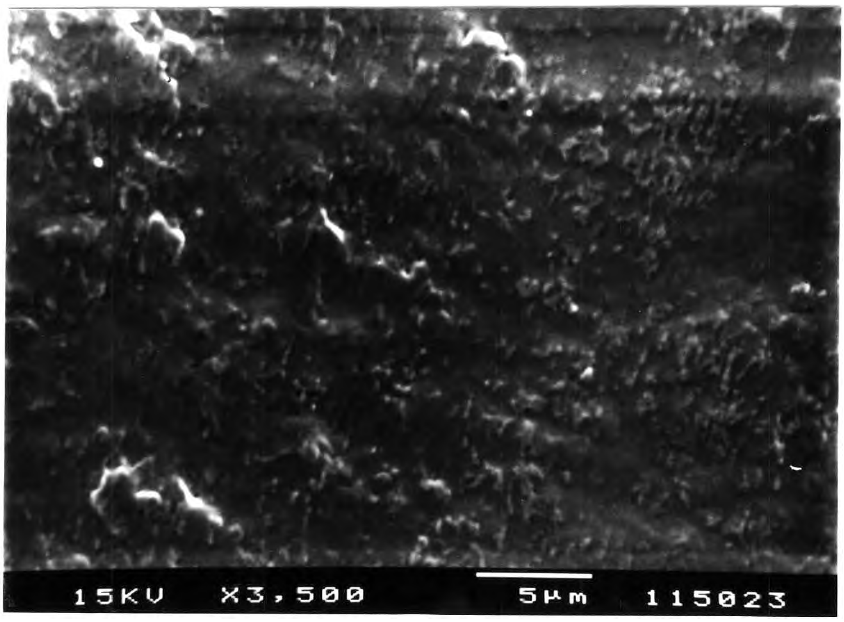
(a) PU 100%



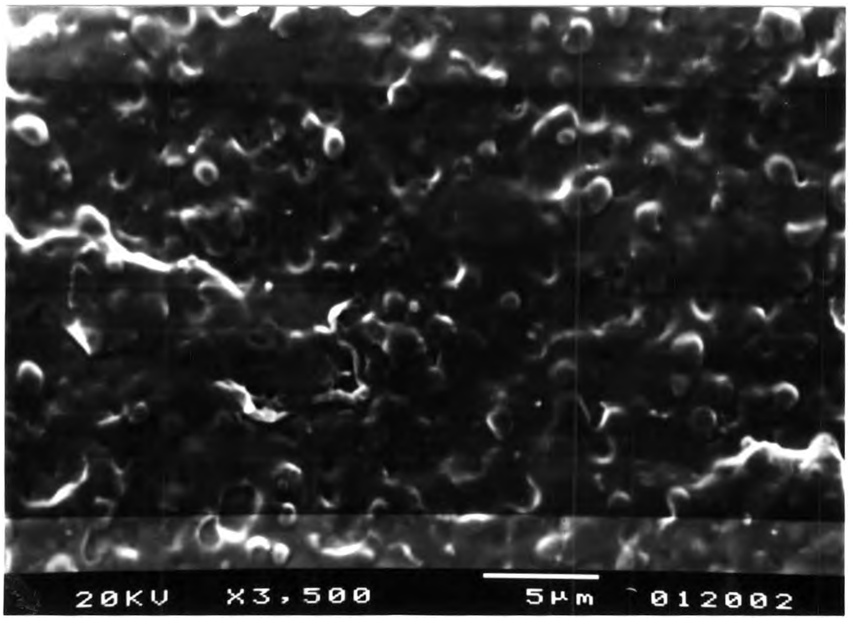
(b) PU 95% / PVC 5%



(c) PU 90% / PVC 10%

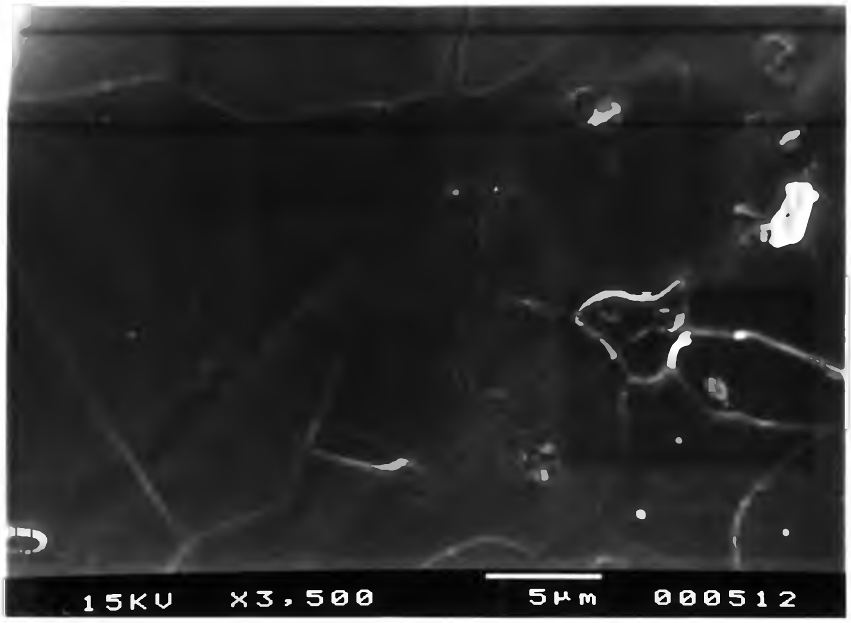


(d) PU 85% / PVC 15%

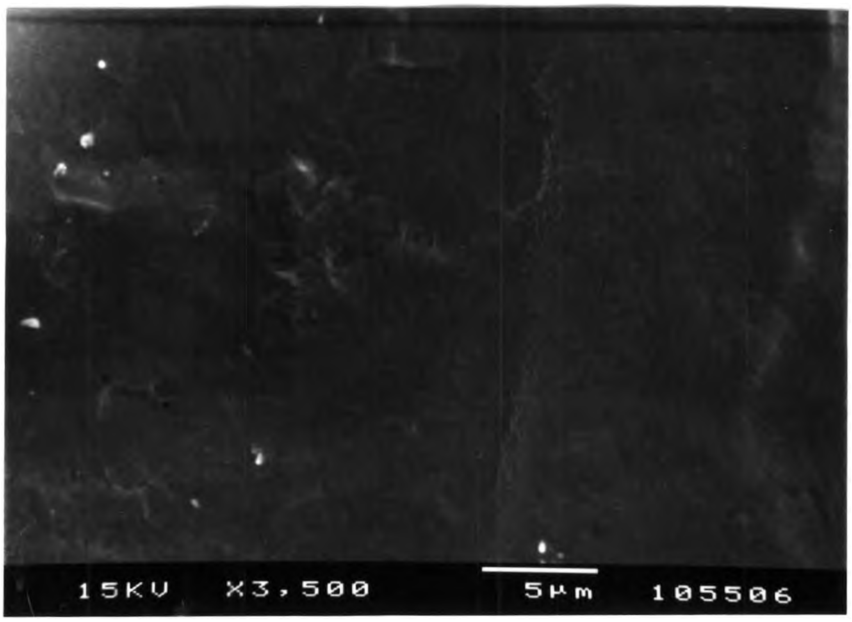


(e) PU 80% / PVC 20%

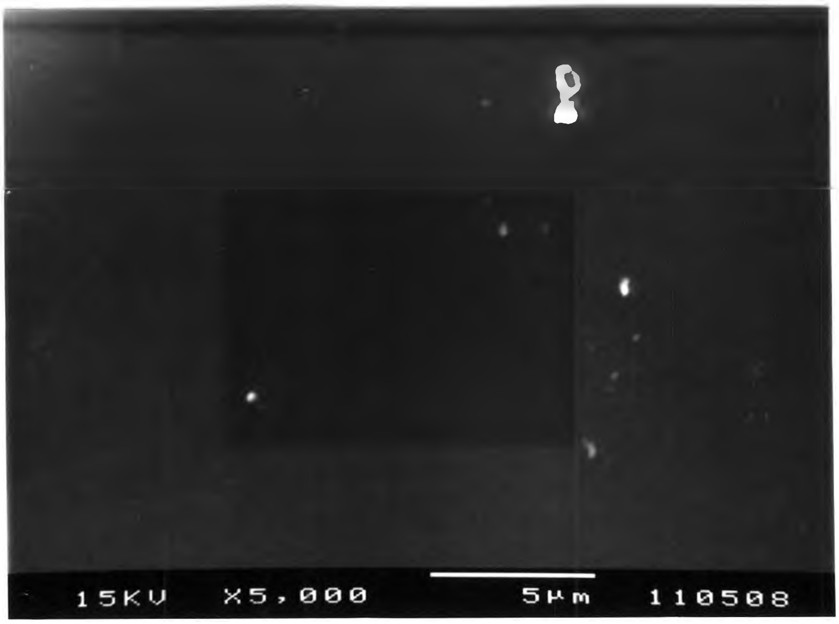
Figure 4.7 SEM micrographs of the semi-IPN PU and PVC (prepolymer process) in various amount of PVC.



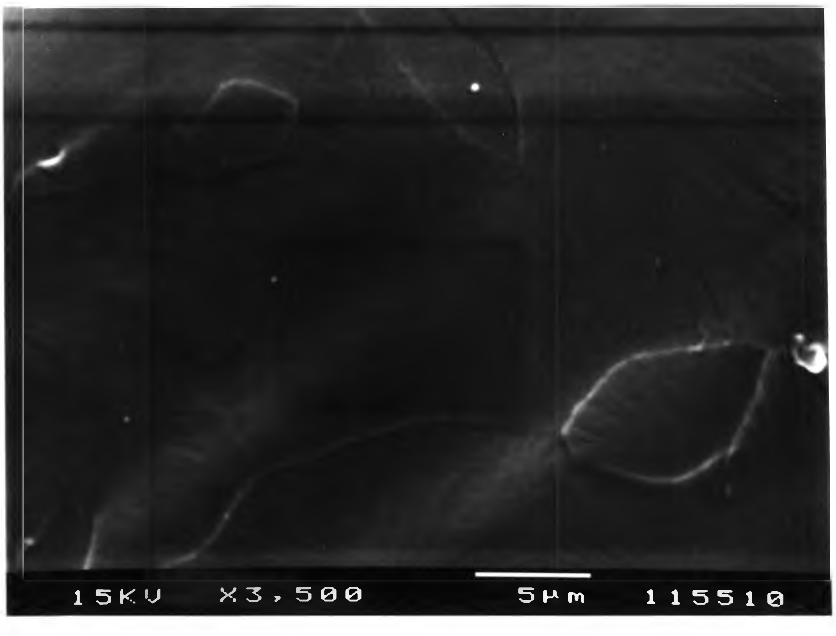
(a) PU 100%



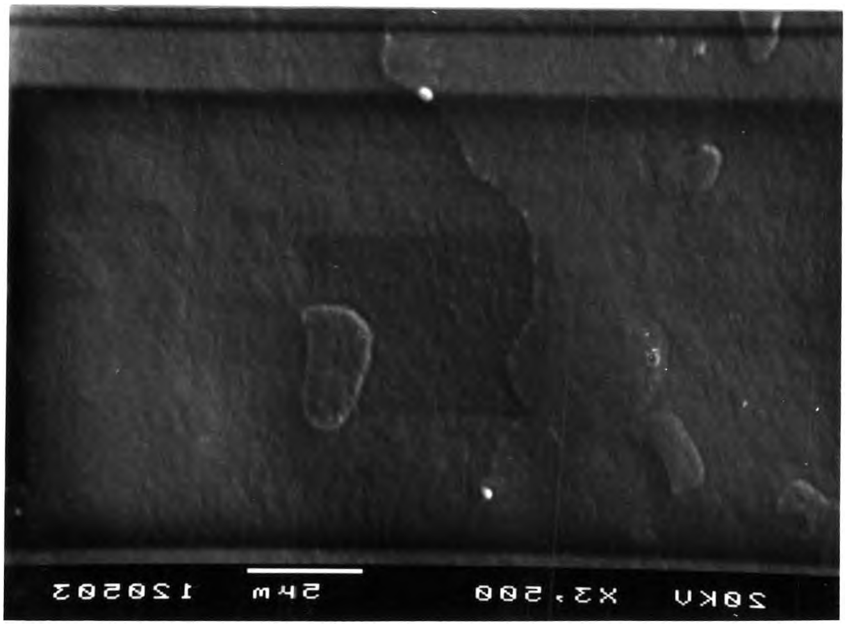
(b) PU 95% / PVC 5%



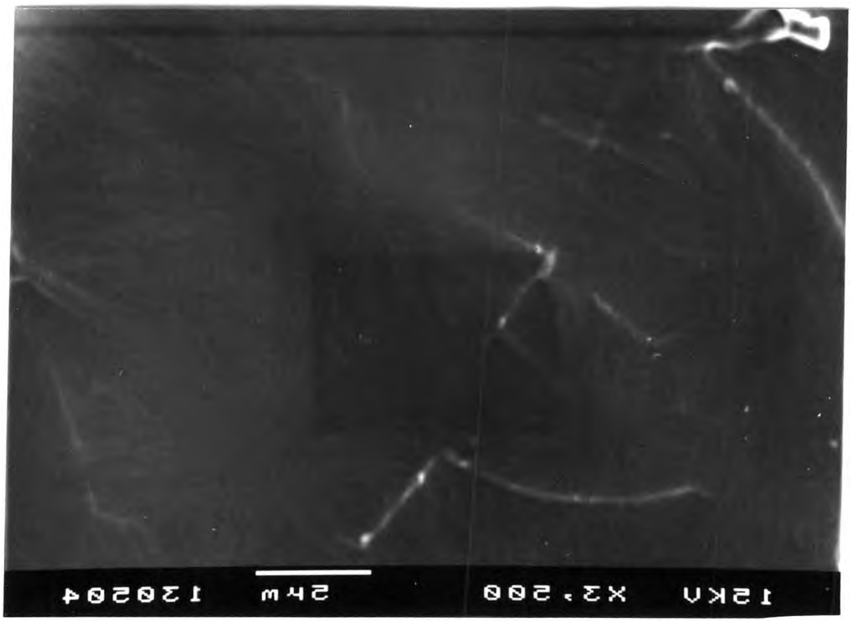
(c) PU 90% / PVC 10%



(d) PU 85% / PVC 15%



(e) PU 80% / PVC 20



(f) PU 70% / PVC 30%

For the one-shot semi-IPN, T_g's are significantly dependent upon the equivalent ratio of NCO/OH even through the equivalent ratio of PCL:MMDI:TEA and the weight percentage of PVC in the resulting materials are fixed. This may be attributed to the chemical crosslinking of the secondary reaction to form allophanate induced better imcompatibility between PVC and PU of the resulting semi-IPNs. In effect the broader tan δ peaks observed for the higher the equivalent ratios of NCO/OH (see Figure 4.8). This seem to be contrast for the semi-IPNs prepared by the prepolymer process in that the narrower tan δ peaks obtained (see Figure 4.9). In these studies, it could be concluded that T_g of the compatible semi-IPNs (10 % PVC) is in the ranges of -3.5 - 5.1°C.

Figure 4.10 and 4.11 show DMA thermogram of the semi-IPNs prepared by one-shot and prepolymer process respectively, when the amount of PVC was varied from 0-30%. Table 4.3 shows the values of T_g of the one-shot and of the prepolymer semi-IPNs together with the calculated ones. Disaccount on the effect of the different preparation processes, when the amount of PVC increases, T_g also increases. The larger the amount of PVC contributes to the higher the values of T_g, which this trend can also find in the case of calculated T_g's. However, the calculated values differ from the experimental ones because the former depends upon many assumptions for the derivation of Equation (2.1). Again the one-shot process gave the higher values of Tg than the prepolymer technique due to the imcompatibility of PVC in the PU matrix of the resulting Semi-IPNs.

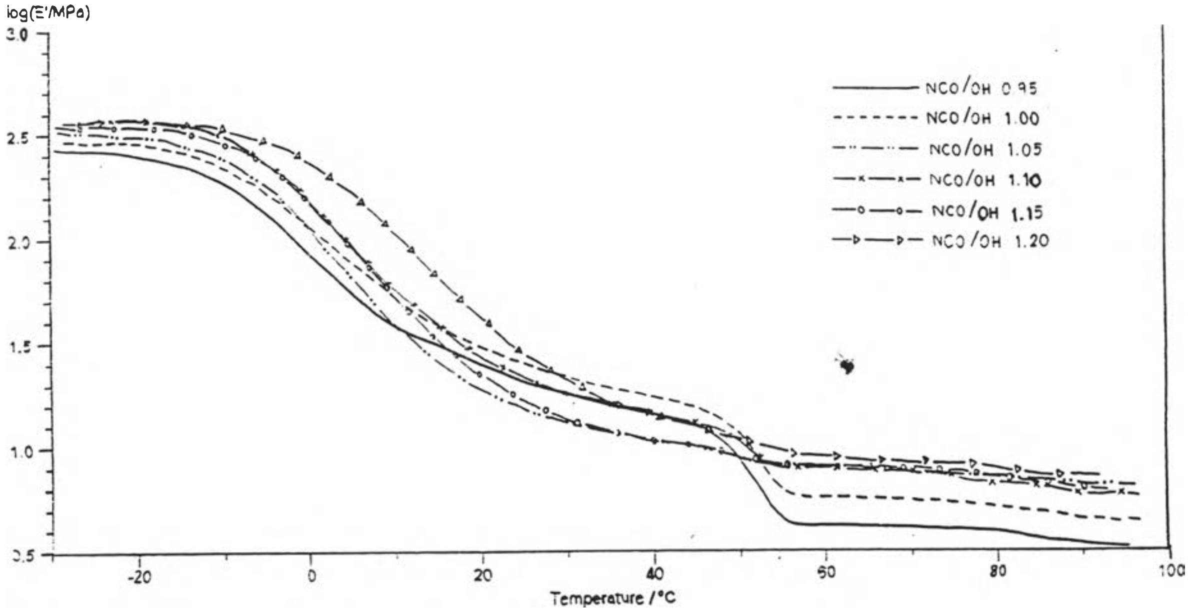
Table 4.2 Values of T_g of the semi-IPNs measured by DMA technique at various equivalent ratios of NCO/OH.

Sample	NCO/OH ratio	T_g (°C) (one-shot)		T_g (°C) (prepolymer)	
		obtain	calculate	obtain	calculate
SI95C10/O7	0.95	3.7	2.7	-3.5	1.2
SI00C10/07	1.00	7.1		-2.1	
SI05C10/07	1.05	8.4		-0.9	
SI10C10/06	1.10	10.2		0.7	
SI15C10/06	1.15	11.4		1.8	
SI20C10/06	1.20	19.6		5.1	

Table 4.3 Values of Tg of the semi-IPNs measured by DMA technique at various weight percentage of PVC.

Sample	% PVC	T_g (°C) (one-shot)		T_g (°C) (prepolymer)	
		obtain	calculate	obtain	calculate
SI05C05/06	5	5.7	-0.86	-4.0	-2.48
SI05C10/06	10	8.4	2.69	-0.9	1.15
SI05C15/06	15	18.6	6.24	1.3	4.77
SI05C20/05	20	21.9	9.80	3.2	8.39
SI05C30/05	30	-	-	8.6	13.82

Figure 4.8 The plots of E' and tan δ against temperature of the semi-IPN of PU and PVC prepared by one-shot process with the variation of the NCO/OH ratio.



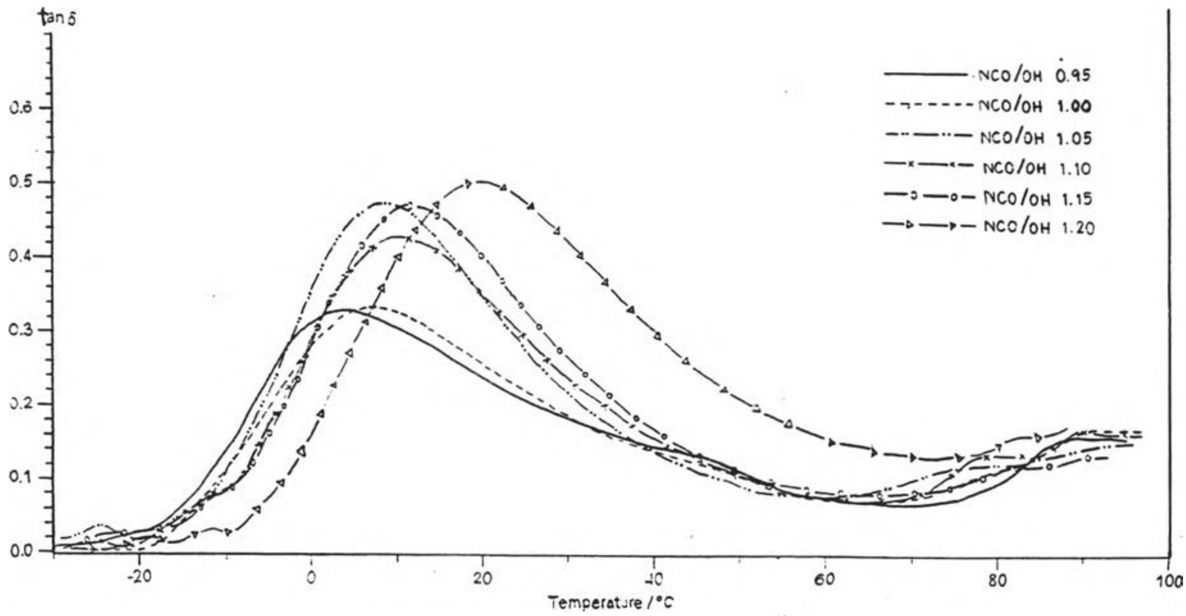


Figure 4.9 The plots of E' and tan δ against temperature of the semi-IPN of PU and PVC prepared by prepolymer process with the variation of the NCO/OH ratio.

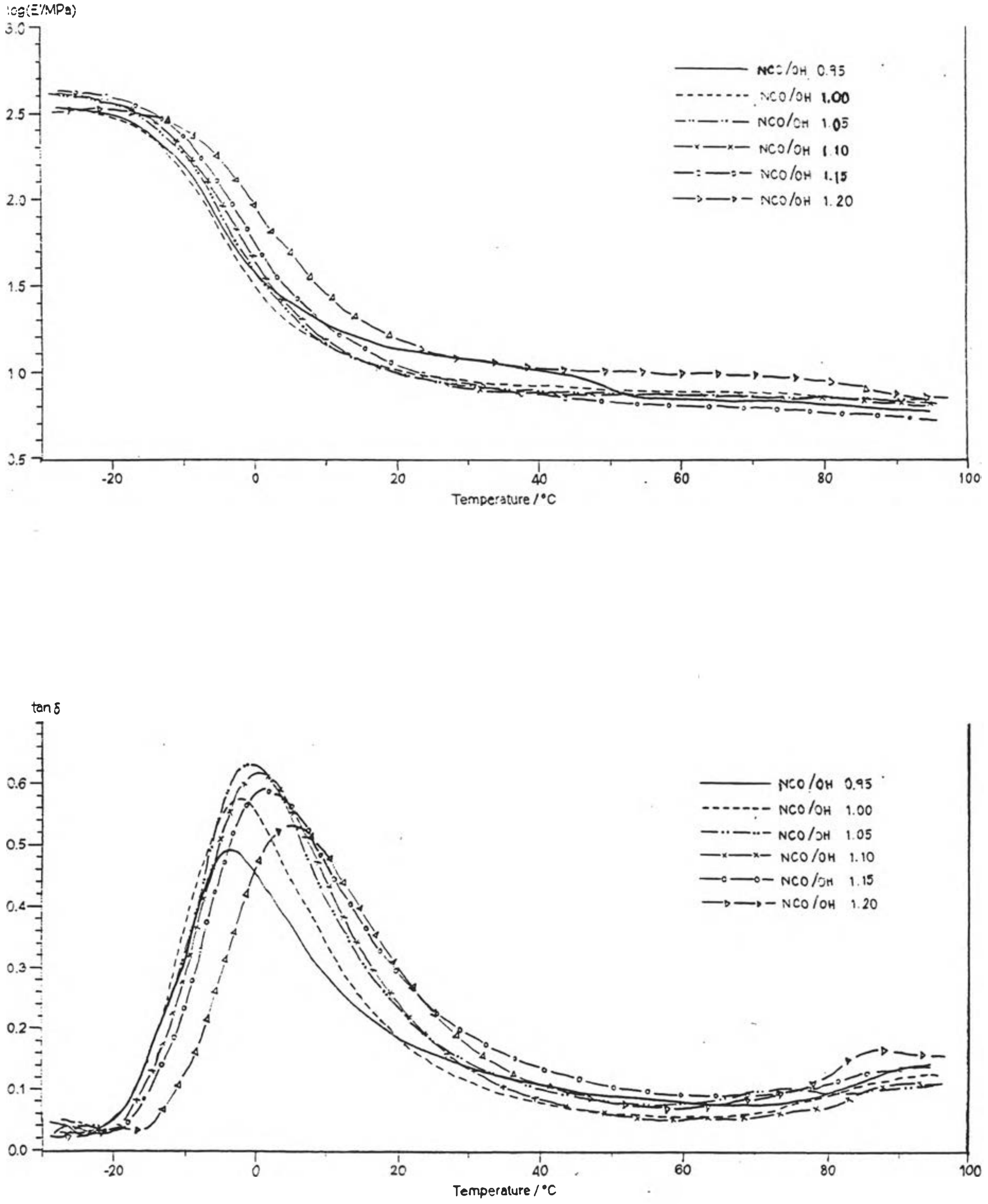
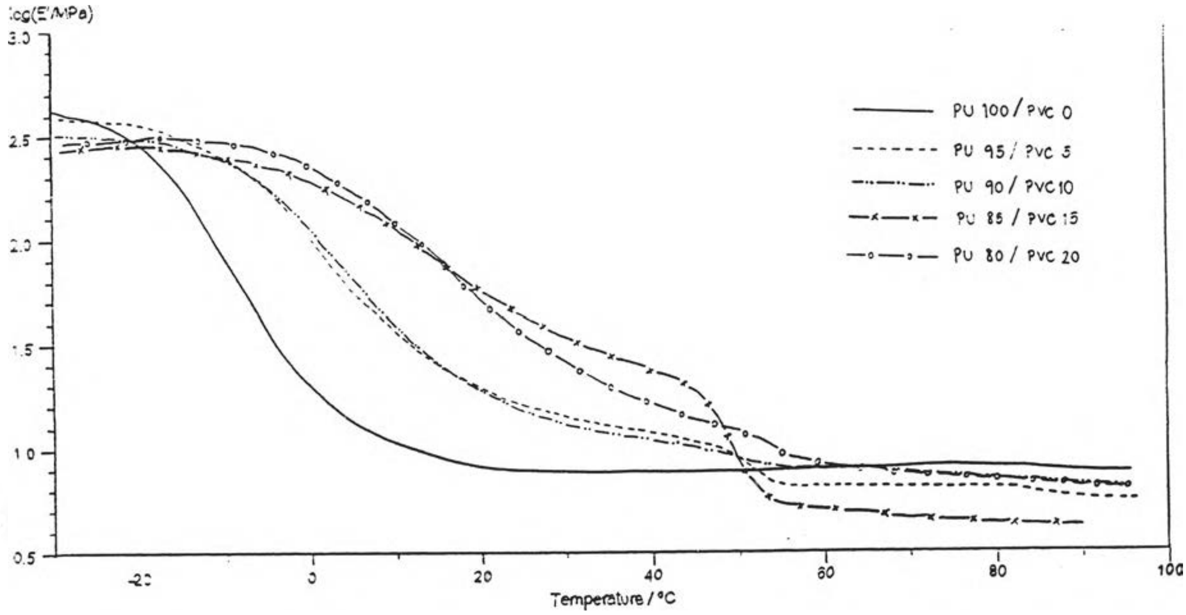


Figure 4.10 The plots of E' and tan δ against temperature of the semi-IPN of PU and PVC prepared by one-shot process with the variation of the amount of PVC.



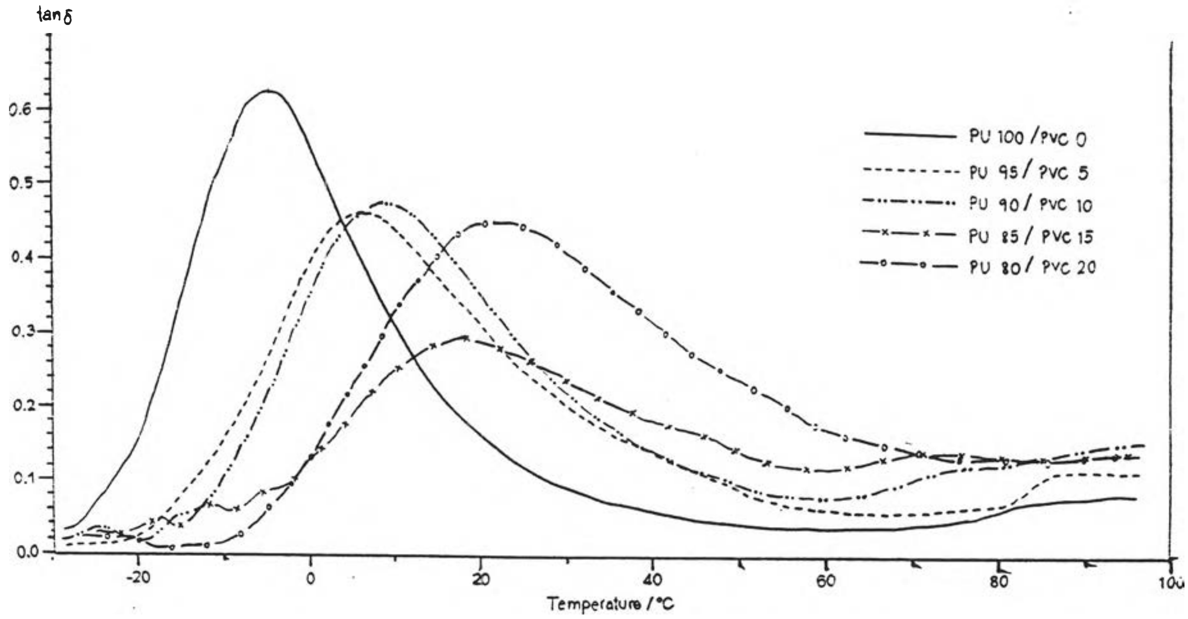
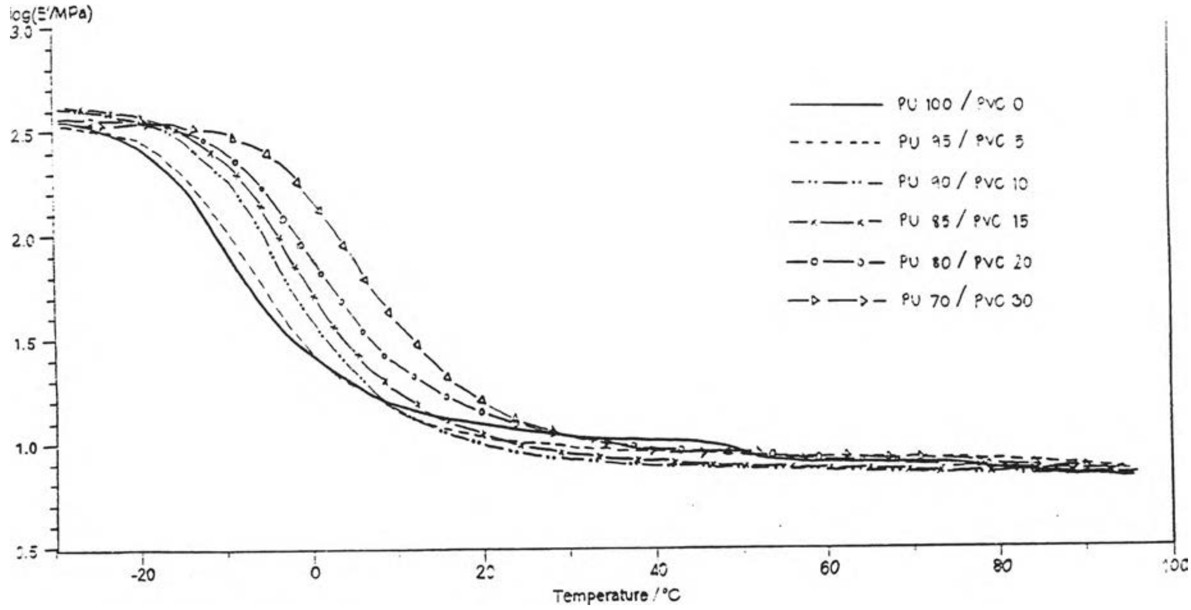
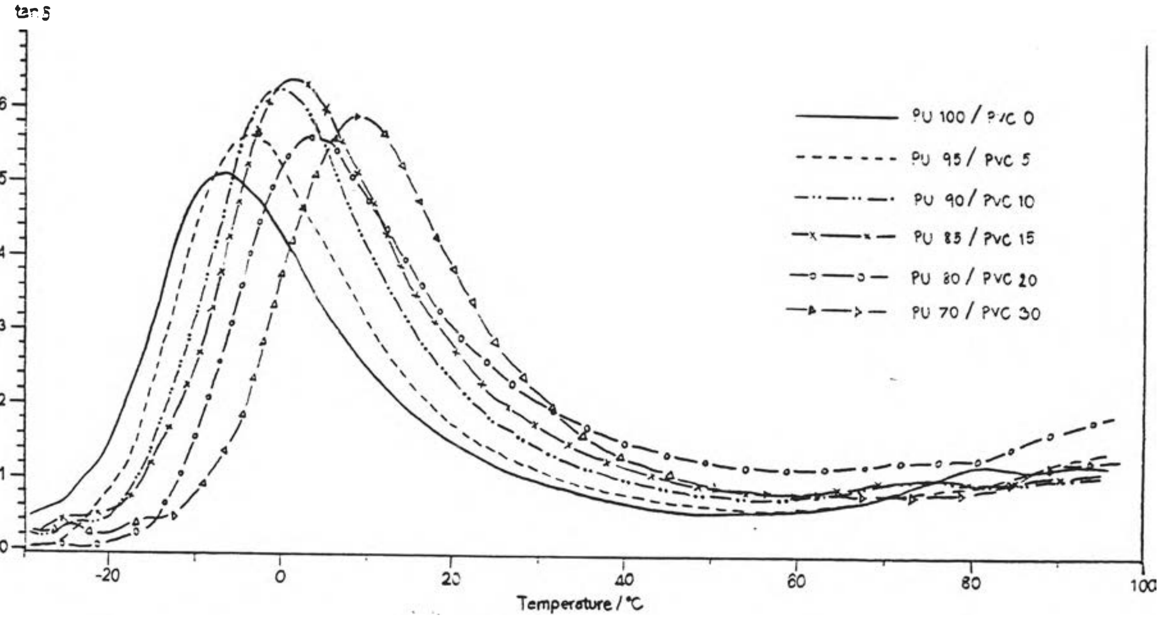


Figure 4.11 The plots of E’ and tan δ against temperature of the semi-IPN of PU and PVC prepared by prepolymer process with the variation of the amount of PVC.





4.4 Thermogravimetric Analysis (TGA) of PU and the Semi-IPN

TGA is usually employed to study materials compositions. When they are subjected to thermal treatment, at the certain temperature fractions of their molecules or atoms are destroyed, rendering weight reduction from the original mass. In these studies, one-shot and prepolymer PUs and semi-IPNs were subjected to the thermal treatment in a TGA furnace from 50-700°C, and their typical thermograms are shown in Figures 4.12-4.16.

The thermograms of the one shot and prepolymer PU (Figures 4.12 and 4.13) are of the same pattern of weight loss upon thermal treatment. There are two main weight losses at 300-430°C and at 430-480°C, which are associated to the soft segment and the crosslinking of PU, respectively. Figures 4.14 and 4.15 show the thermogram of the one-shot and the prepolymer semi-IPNs, which are also similar to each other. There are three steps of weight losses at 250-300°C, 300-430°C and 430-490°C, associated to the PVC, and soft segment and the crosslinking of PU in the resulting semi-IPNs, respectively. Figure 4.16 shows the thermogram of PVC, which the peak at 270-390°C should be the weight losses due to the decomposition of HCl and Cl_2.

Figure 4.12 TGA thermogram of PCL/MMDI/TEA-based PU (one-shot process , the NCO/OH ratio = 1.05 and PCL:MMDI:TEA = 1:3:2)

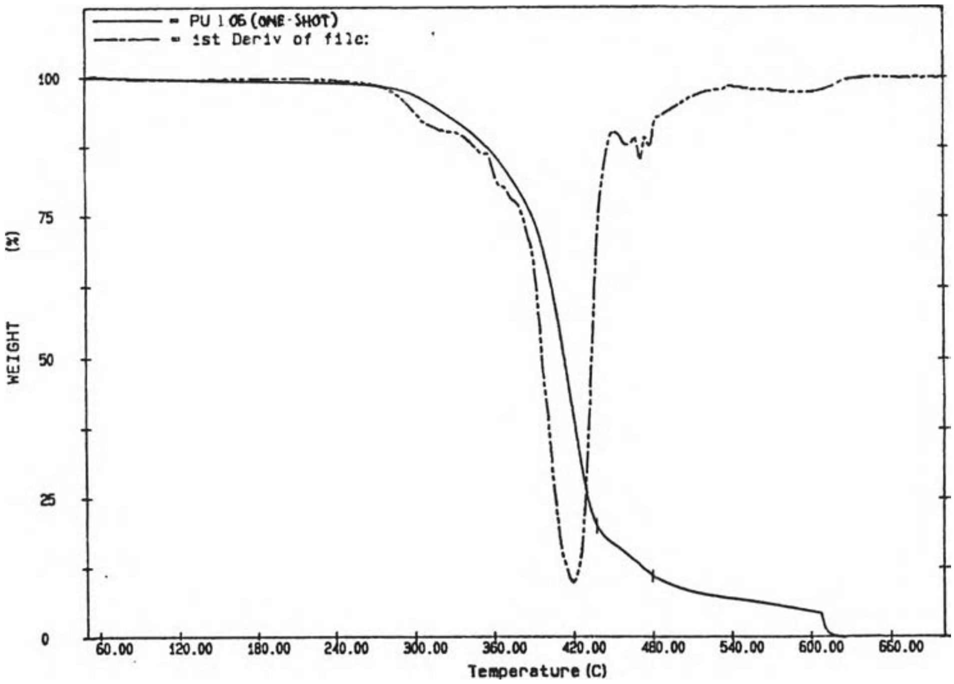


Figure 4.13 TGA thermogram of PCL/MMDI/TEA-based PU (prepolymer process, the NCO/OH ratio = 1.05 and PCL:MMDI:TEA = 1:3:2).

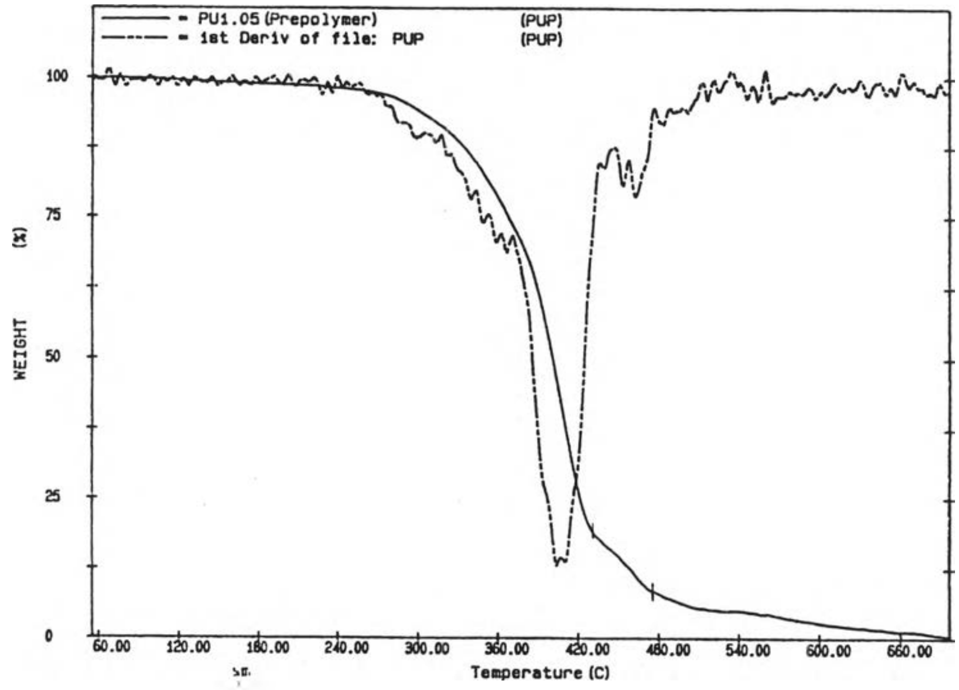


Figure 4.14 TGA thermogram of the semi-IPN PU/PVC (one-shot process, sample = SI05C15/06-0).

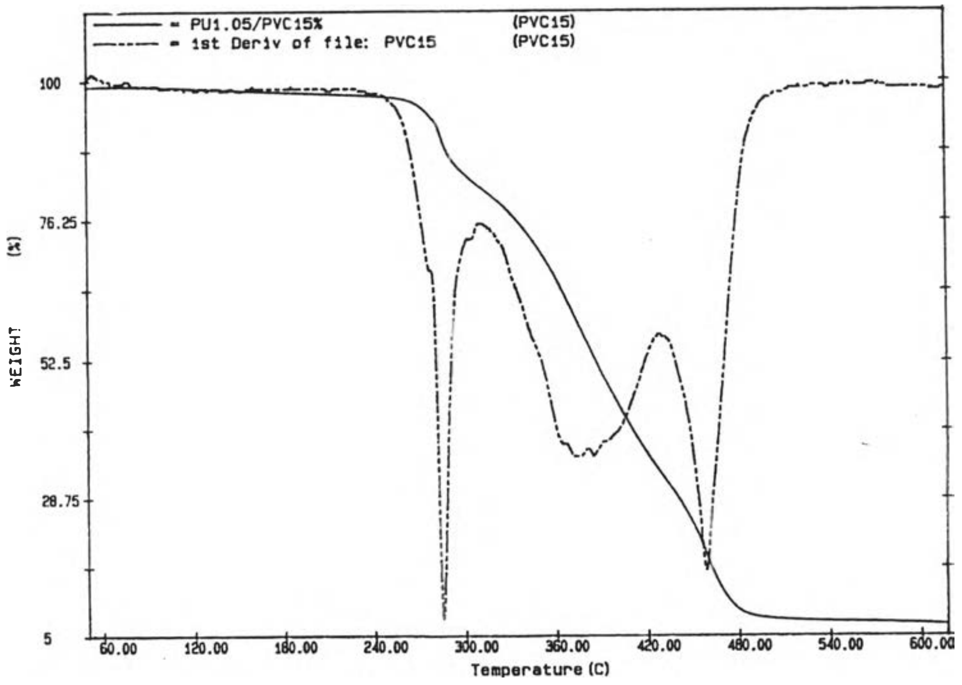


Figure 4.15 TGA thermogram of the semi-IPN PU/PVC (prepolymer process, sample = SI05C15/06-P).

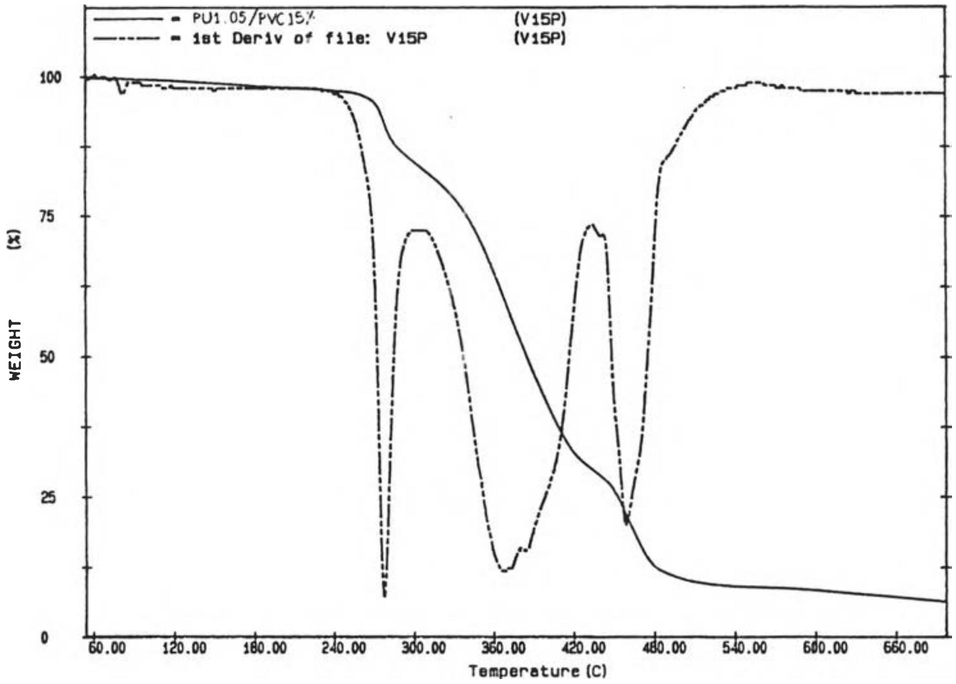
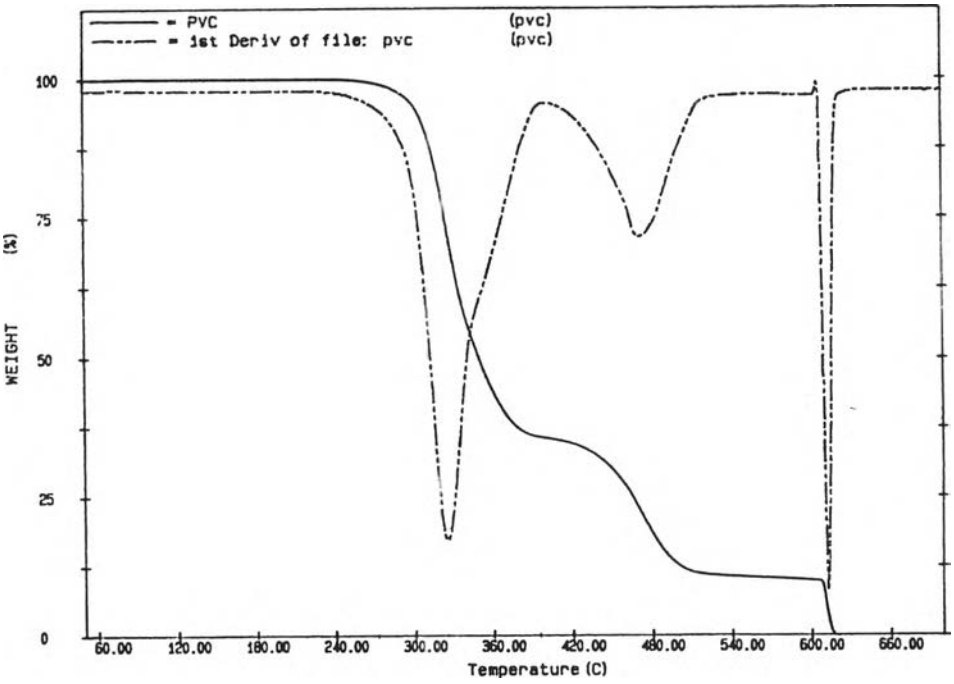


Figure 4.16 TGA thermogram of PVC resin(MW= 50,625 g/mol), supplied by TPC Co.,Ltd..



4.5 Mechanical Property of PU and the Semi-IPN

The mechanical properties of PUs and semi-PUs prepared in these studies were tensile property and hardness (shore A). The former includes the tensile strength and the elongation at break. The effect of equivalent ratios of NCO/OH and of PCL:MMDI:TEA used for the preparation of PUs and the semi-IPNs prepared either by one-shot or prepolymer processes on those mechanical properties are discussed subsequently.

4.5.1 Effect of the equivalent ratio of PCL:MMDI:TEA on the mechanical property of PU

Table 4.4 shows the values of the current mentioned mechanical properties of PUs and the semi-IPNs prepared by the one-shot or prepolymer processes as well as by various materials compositions.

Table 4.4 The tensile strength, the elongation at break and the Shore A hardness of PUs and the semi-IPNs prepared in these studies.

Sample	Tensile strength (N/mm^2)	Elongation at break (%)	Hardness (shore A)
PU05A00/02-O	1.31	451.3	46.4
PU05B00/04-O	1.81	322.1	50.8
PU05C00/06-O	3.77	329.2	66.7
PU95C00/07-O	1.16	203.5	65.8
PU00C00/07-O	1.57	231.3	66.2
PU05C00/07-O	3.77	329.2	66.7
PU10C00/06-O	4.42	329.1	66.8
PU15C00/06-O	4.25	298.9	67.0
PU20C00/06-O	5.17	327.6	68.0
SI95C10/07-O	2.01	127.9	70.0
SI95C10/07-P	2.09	292.4	59.3
SI00C10/07-O	2.13	146.4	70.2
SI00C10/07-P	2.29	454.8	59.4
SI05C10/07-O	2.63	216.7	70.7
SI05C10/07-P	3.80	416.1	59.5
SI10C10/06-O	2.76	244.1	67.8
SI10C10/06-P	3.48	404.5	59.4
SI15C10/06-O	3.12	245.7	68.8
SI15C10/06-P	2.80	393.3	58.2
SI20C10/06-O	2.91	197.0	70.4
SI20C10/06-P	3.79	436.1	63.4

Table 4.4 The tensile strength, the elongation at break and the Shore A hardness of PUs and the semi-IPNs prepared in these studies.(continue)

Sample	Tensile strength (N/mm^2)	Elongation at break (%)	Hardness (shore A)
PU05C00/06-O	3.77	329.2	66.7
PU05C00/06-P	3.45	323.3	69.1
SI05C05/06-O	2.48	199.2	68.2
SI05C05/06-P	3.46	385.4	64.3
SI05C10/06-O	2.63	216.7	70.7
SI05C10/06-P	3.80	416.1	59.5
SI05C15/06-O	3.78	235.6	79.6
SI05C15/06-P	3.72	557.3	59.6
SI05C20/06-O	4.99	310.4	80.4
SI05C20/06-P	4.62	536.1	60.4
SI05C30/06-P	6.10	545.4	61.6

Three differnt equivalent ratios of PCL:MMDI:TEA were used to prepare PUs having different amount of crosslinking and soft segments, the relevant samples are PU05A00/02-O, PU05B00/04-O and PU05C00/07-O. Figures 4.17-4.19 show that when increasing of the number of crosslinking, tensile strength and hardness of PUs increase while elongation at break decrease. This trend is expected since the synthesized PUs contain more crosslinked linkages.

The best properties of hardness and tensile strength obtained in these studies are the sample PU05C00/07-O. It was the easiest to hand-cast than the others, so that the equivalent ratio of PCL:MMDI:TEA equal to 1:3:2 was dedicated for the preparation of PUs and the semi-IPNs.

Figure 4.17 Effect of the amount of crosslinking on the tensile strength of PUs : the equivalent ratio of NCO/OH was constant at 1.05, and PUs were prepared by the one-shot process.

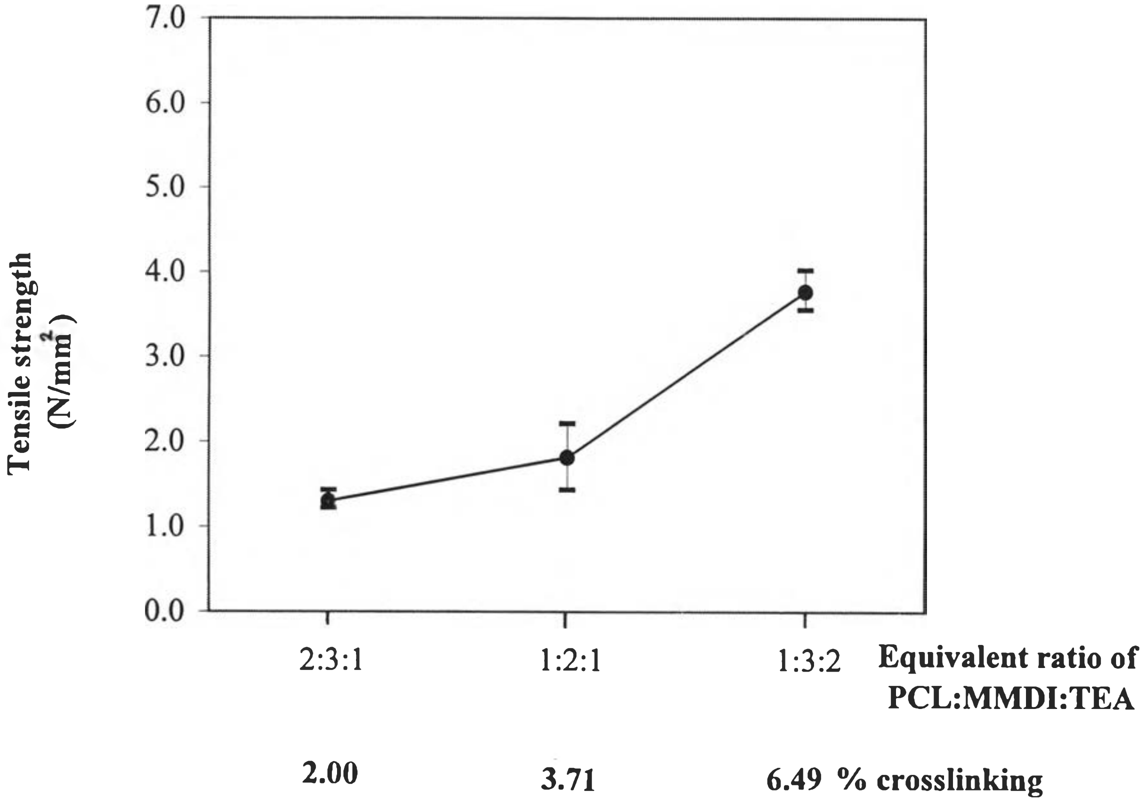


Figure 4.18 Effect of the amount of crosslinking on the Shore A hardness of PUs : the equivalent ratio of NCO/OH was constant at 1.05, and PUs were prepared by the one-shot process.

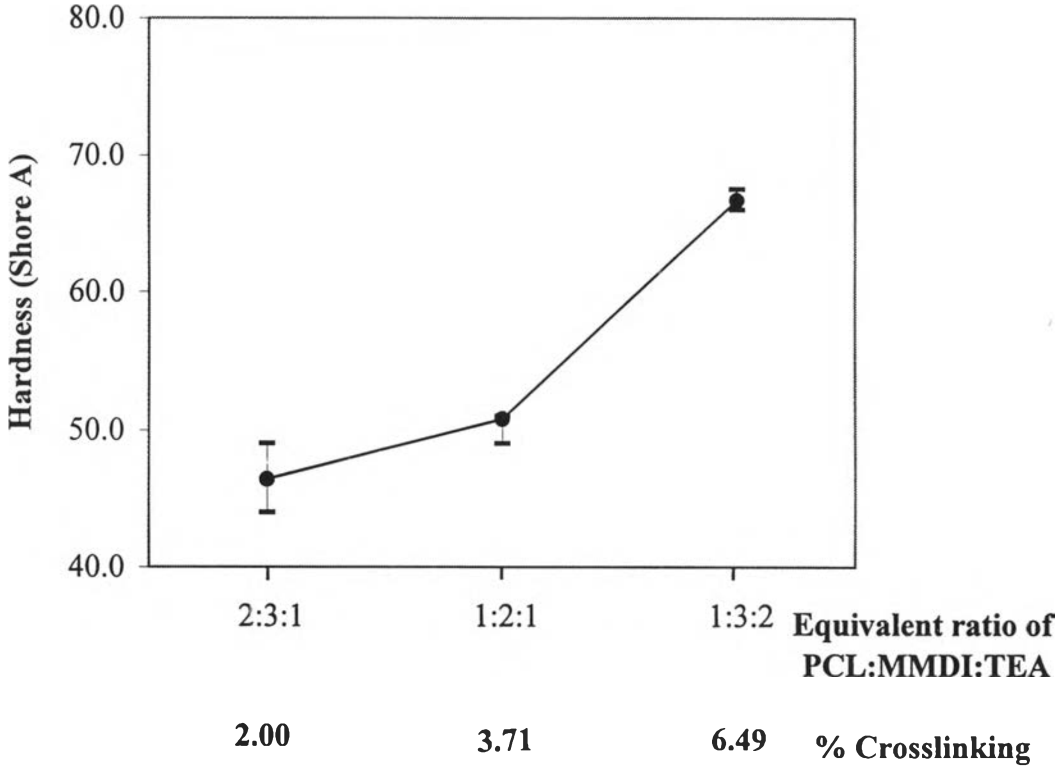
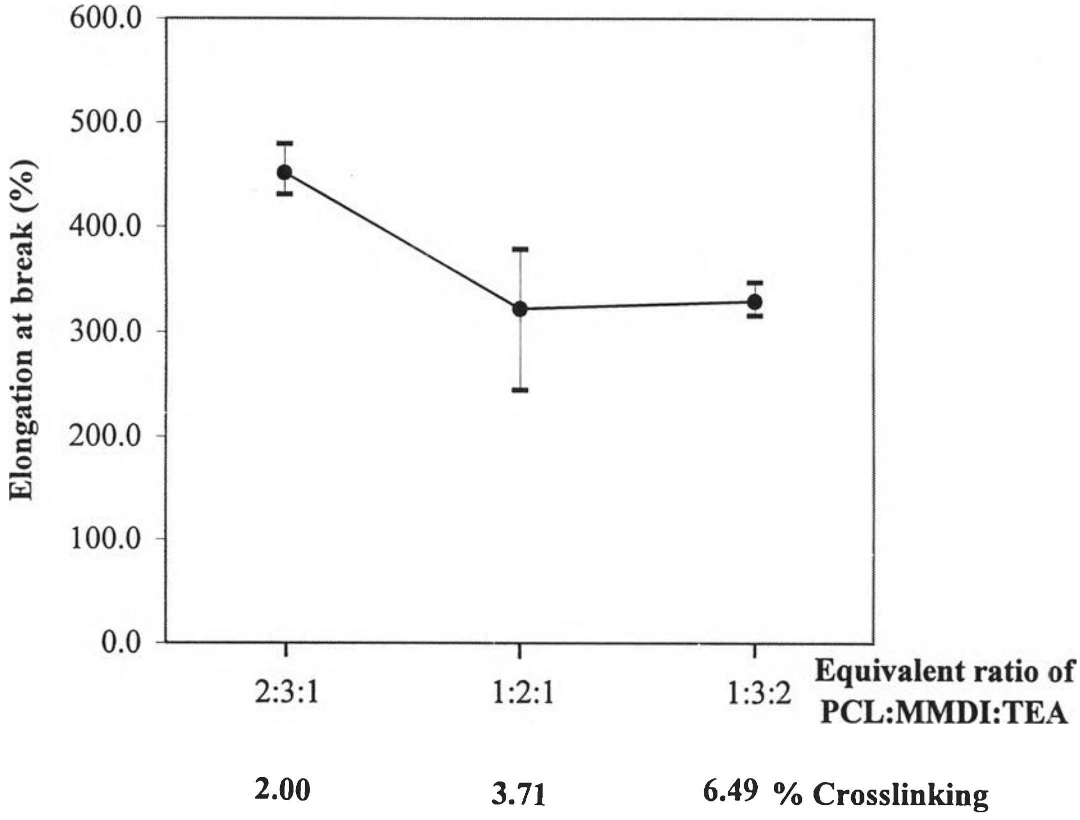


Figure 4.19 Effect of the amount of crosslinking on the elongation at break of PUs : the equivalent ratio of NCO/OH was constant at 1.05, and PUs were prepared by the one-shot process.



4.5.2 Effect of the equivalent ratio of NCO/OH on the mechanical property of PU.

The NCO/OH equivalent ratio was varied from 0.95 to 1.20 at the constant equivalent ratio of PCL:MMDI:TEA at 1:3:2, which means that the number of crosslinking and the soft segment of PUs are more or less the same. The amount of NCO was excess when the ratio was greater than 1 and that of OH was excess when the ratio was less than 1. The stoichiometric reaction of NCO with OH achieves when using the equal ratio of NCO to OH. The samples PU95C00/07-O, PU00C00/07-O, PU05C00/07-O, PU10C00/06-O, PU15C00/06-O, and PU20C00/06-O are relevant to these studies.

Figures 4.20-4.22 shows that the tensile strength of the resulting PUs is significantly improved for the higher NCO/OH equivalent ratio, while the elongation at break and hardness are not greatly different. However, a significantly improvement of the elongation at break of the solid PUs acheives when the NCO/OH equivalent ratio increases from 0.95 to 1.05.

When the equivalent ratio of NCO/OH is equal to one, there are presumably no secondary reaction between the isocyanate compound with carbamate groups of the resulting PUs. When this ratio is less than 1, i.e., lesser the isocyanate equivalence than the hydroxy one, there would be some PCL or TEA left in the resulting PUs. Since these compounds are low molecular weight viscous liquid, it may not be compatible totally to the solid resulting PU. The poorest mechanical properties are therefore expected. When the equivalent ratio of NCO/OH is greater than one, the excess isocyanate reacts with the carbamate linkages of the resulting PUs to obtain allophanate crosslinking linkages. These reactions are thermodynamically reversible. The linkages will definitely improve the mechanical properties of the resulting PUs. It is generally recommended to use the equivalent ratio of NCO/OH greater than one, i.e., 1.02-1.05, in order for the excess isocyanate compound to react with a trace of moisture presented in the polyol or crosslinking agent, resulting in substituted carbamic diacid which is then decomposed to give carbon dioxide and diamine. Micro bubbles due to the carbon dioxide gas may be the point that fracture causing to the mechanical failure of the resulting PU. The trace amount of diamine compound resulting from the reaction of water and diisocynate can definitely react with the excess diisocynate to give urea linkage, which may also react with the excess isocyanate to yield biuret crosslinking linkage, also improving the mechnical properties of the resulting PUs. However since the trace moisture remained in the diol compounds, the secondary reaction to form biuret linkages is unlikely to occur.

Figure 4.20 Effect of the equivalent ratio of NCO/OH on the tensile strength of PUs : the equivalent ratio of PCL:MMDI:TEA = 1:3:2, and PUs were prepared by the one-shot process.

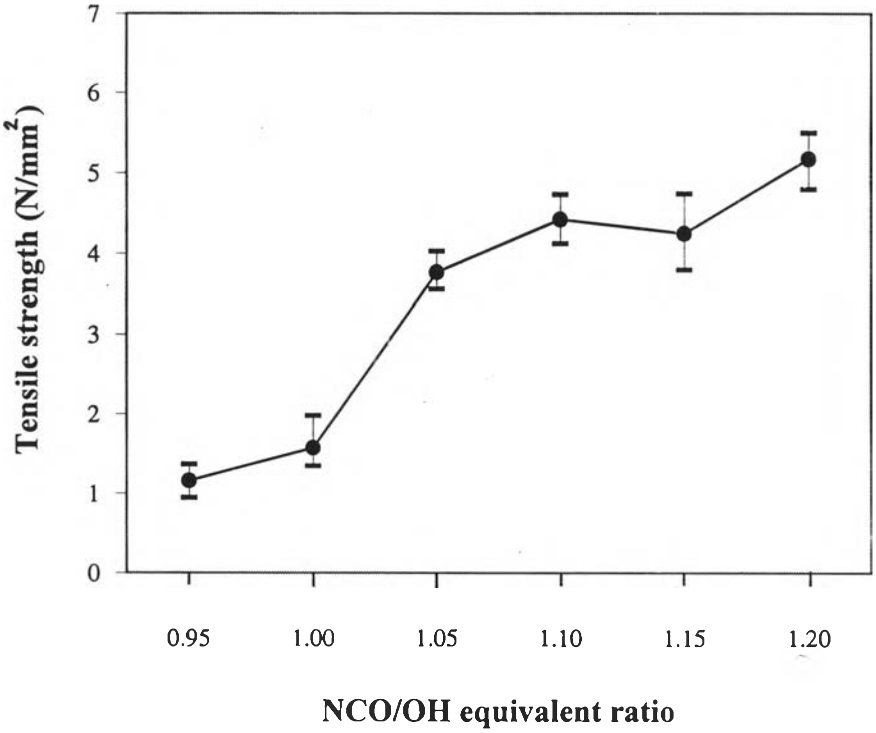


Figure 4.21 Effect of the equivalent ratio of NCO/OH on the Shore A hardness of PUs : the equivalent ratio of PCL: MMDI:TEA = 1: 3: 2, and PUs were prepared by the one-shot process.

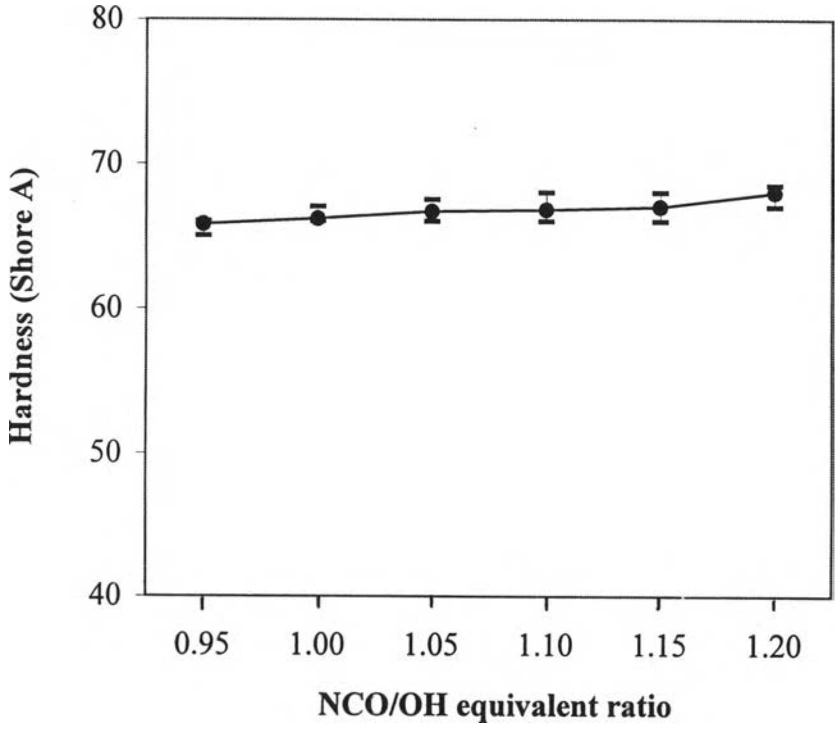
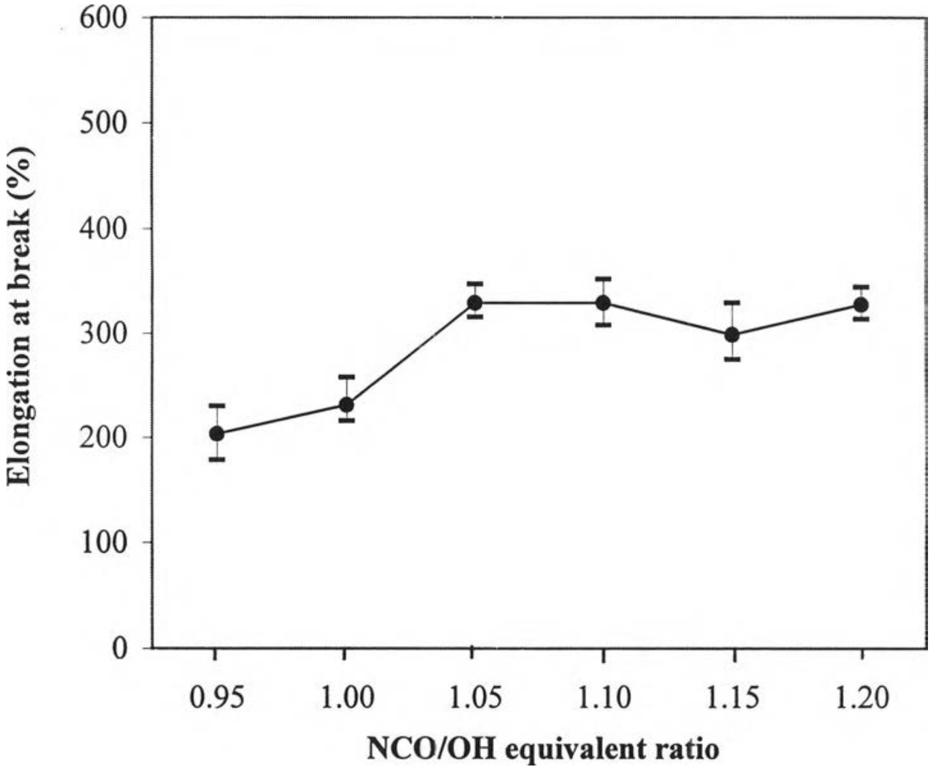


Figure 4.22 Effect of the equivalent ratio of NCO/OH on the elongation at break of PUs : the equivalent ratio of PCL : MMDI : TEA = 1: 3: 2, and PUs were prepared by the one-shot process.



4.5.3 Effect of the equivalent ratio of NCO/OH on the mechanical property of the semi-IPN.

The semi-IPNs prepared by either one-shot or prepolymer processes were prepared by variation of the equivalent ratio of NCO/OH from 0.95 to 1.20, while the weight percentage ratio of PU/PVC was constant at 90/10. The tensile strength, elongation at break and Shore A hardness of the resulting semi-IPNs are graphically shown in Figures 4.23-4.25 (solid line (——)for the prepolymer and broken line (----)for the one-shot processes). The samples SI95C10/07-O, SI00C10/07-O, SI05C10/07-O, SI10C10/06-O, SI15C10/06-O and SI20C10/06-O were prepared by the one-shot process, and the samples SI95C10/07-P, SI00C10/07-P, SI05C10/07-P, SI10C10/06-P, SI15C10/06-P and SI20C10/06-P were by the prepolymer one.

The prepolymer process allowed to obtain the transparent semi-IPN of PU/PVC, which indicated that the compatibility between PU and PVC phases was acheived. The compatibility is derived from the strong H-bondings between the PU and PVC carbonyls with the α-H of PVC. It is apparently that the number of crosslinking in those samples and the amount of PVC were fixed constantly. This indicates that the differences in the mechanical properties of the resulting semi-IPNs should be due to the effect of secondary reactions to give addition crosslinkings.

For the one-shot process, the tensile strength and elongation at break are optimum when the NCO/OH equivalent ratio is 1.15, while the hardness do not differ much. It is worth to note that the general trend of the mechanical properties are more or less like those of PUs discussed previously.

For the prepolymer process, the tensile strength is optimum at the NCO/OH equivalent ratio of 1.05, and then it drops until the NCO/OH equivalent ratio is 1.20. The elongation at break shows the similar behaviour to the tensile strength. It is noted that the maximum value obtained when the NCO/OH equivalent ratio is 1.00. The hardness has the maximum value when the NCO/OH equivalent ratio is 1.20, and at the other equivalent ratios of NCO/OH their hardness values are not much differnt from one another. The overall picture of the mechanical properties of the semi-IPNs from this process is better than those prepared by the one-shot process. The superior properties obtained are due to the compatibility between PU and PVC.

For the fact that PVC is miscible with PCL because of the interaction between the carbonyl group of PCL and the α-hydrogen of PVC. However, this semi-IPN prepared from one-shot process was turbid, and ones can observe imperfect compatibility between PU matrix and the dispersed PVC phase. The evidence occured due to the incompleted mechanical blending of these two phases resulting in an aggromerated PVC dispersed in the continuous PU matrix, which ones could observed by necked-eyes.

Figure 4.23 Effect of the equivalent ratio of NCO/OH on the tensile strength of the semi-IPNs : the equivalent ratio of PCL: MMDI: TEA of PUs was constant at 1: 3: 2, and the weight percentage of PVC in the resulting polymer was fixed at 10% ; (—■—)the prepolymer and (---●---) the one-shot processes.

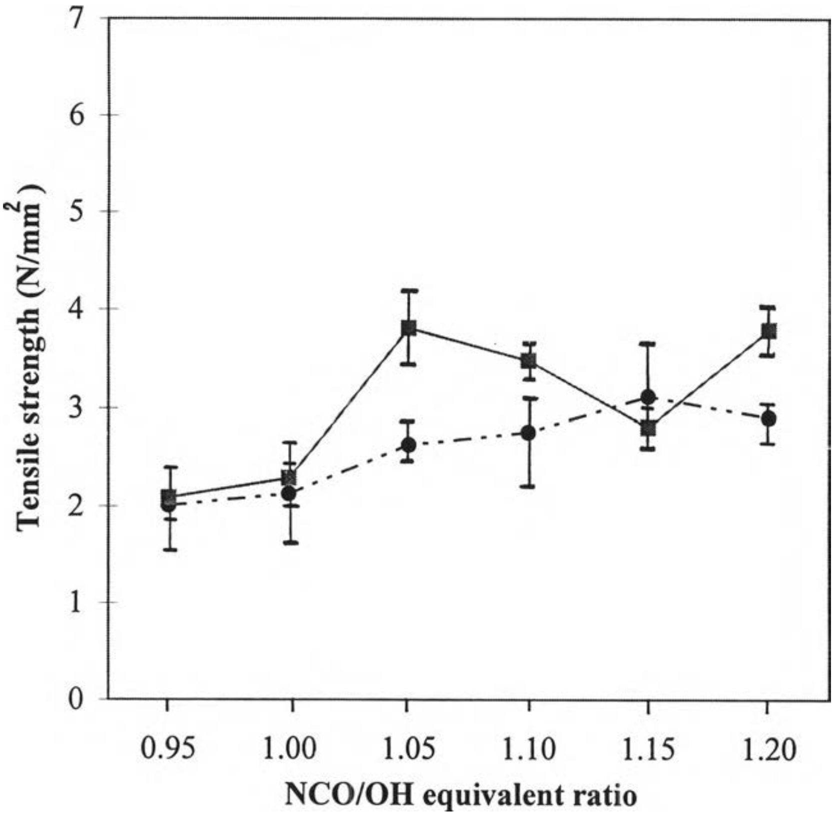


Figure 4.24 Effect of the equivalent ratio of NCO/OH on the elongation at break of the semi-IPNs : the equivalent ratio of PCL: MMDI: TEA of PUs was constant at 1: 3: 2, and the weight percentage of PVC in the resulting polymer was fixed at 10% ; (—■—)the prepolymer and (-- —●- —-) the one-shot processes.

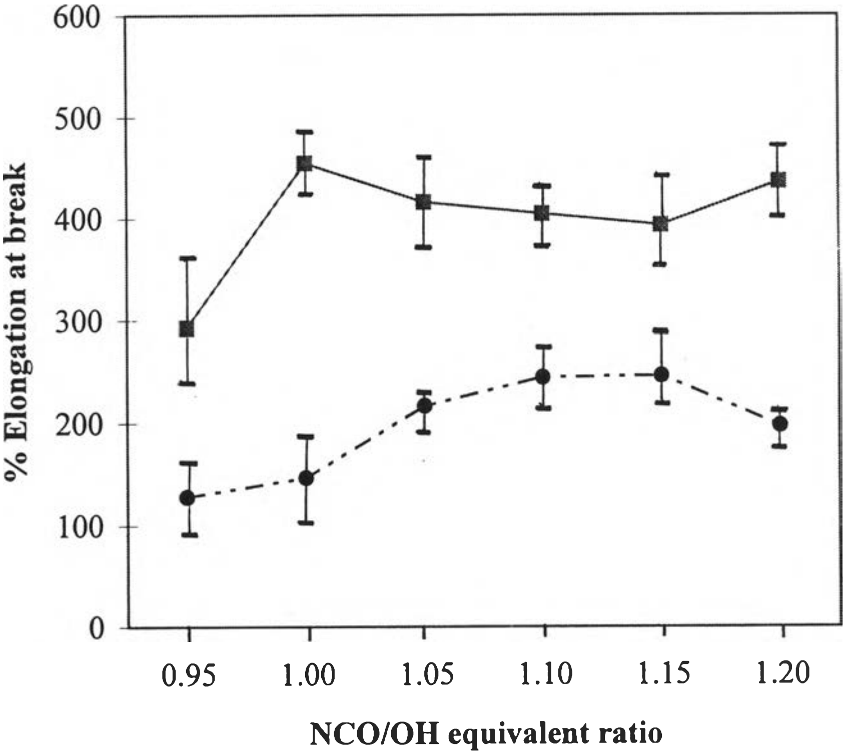
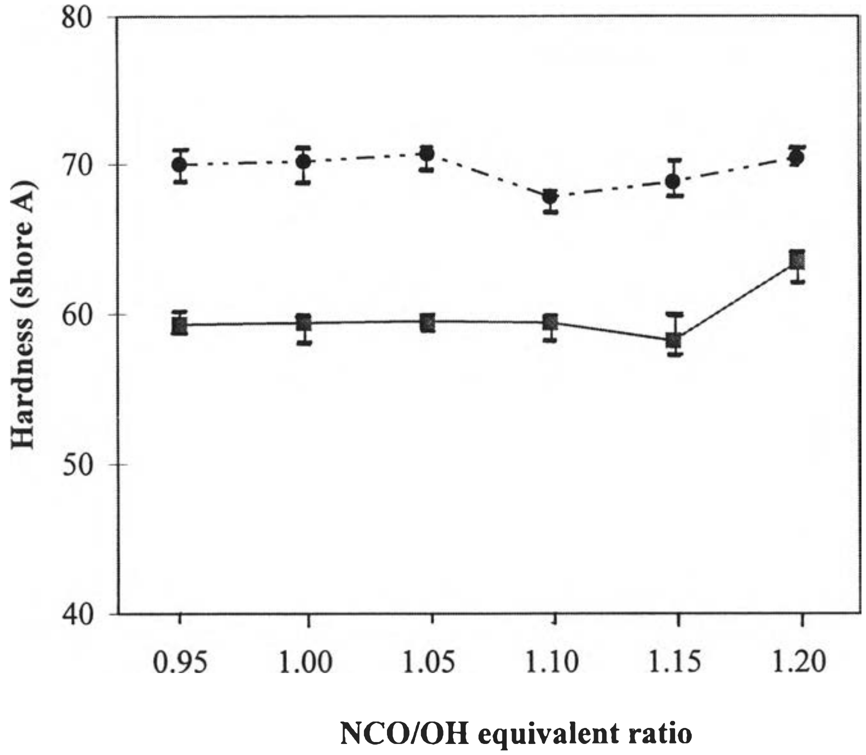


Figure 4.25 Effect of the equivalent ratio of NCO/OH on the Shore A hardness of the semi-IPNs : the equivalent ratio of PCL: MMDI: TEA of PUs was constant at 1: 3: 2, and the weight percentage of PVC in the resulting polymer was fixed at 10% ; (—■—)the prepolymer and (---●--) the one-shot processes.



4.5.4 Effect of the amount of PVC dispersed phase on the mechanical property of the semi-IPN.

The semi-IPNs were prepared by either the one-shot or the prepolymer processes in order to investigate the effect of variation of the weight percentage of PVC in the resulting semi-IPNs on their mechanical properties.

In these studies, the NCO/OH equivalent ratio was fixed at 1.05 and the equivalent ratio of PCL:MMDI:TEA was also kept constant at 1:3:2. The samples SI05C00/07-O, SI05C05/06-O, SI05C10/06-O, SI05C15/06-O, SI05C20/05-O were prepared by the one-shot process, and those SI05C00/07-P, SI05C05/06-P, SI05C10/06-P, SI05C15/06-P, SI05C20/05-P and SI05C30/05-P were by the prepolymer one.

Figure 4.26-4.28 show the results of effect of the PVC content in the resulting semi-IPNs on their mechanical properties, including the tensile strength, the elongation at break and the shore A hardness.

For the one-shot process, PU containing no PVC, i.e. PU05C00/07-O, shows better tensile strength than the semi-IPNs containing 5 and 10% PVC. The same trend can also be observed for the elongation at break, and even the amount of PVC increases upto 20%, this property is not better than that of PU containing no PVC. These evidencies illustrate the effect of incompatibility of the dispersed PVC phase with the PU matrix. However when the amount of PVC was upto 15-30%, the tensile strength of the semi-IPN was resumed equivalent to or better than the PVC-free PU. As discussed earlier, this is due to the partial compatible of PVC in the continuous matrix of PU as observed by SEM (see section 4.3).

In contrast to the one-shot process, the prepolymer method gave the compatible semi-IPNs having better tensile strength and elongation at break than the PVC-free PUs. These properties improve proportional to the increment of the amount of PVC dispersed phase in the resulting semi-IPNs.

The shore A hardness of the semi-IPNs prepared by the one-shot and the prepolymer processes is not in the same pattern, by which the former gives the better hardness upon increment of the PVC content in the resulting polymer. The latter gives poorer hardness when the amount of PVC increases from 5 to 10% and seems to be constant or slightly improvement when the PVC content increases from 15 to 30%. This evident suggusts that, for the compatible semi-IPNs, PVC exhibits itself as a plasticizer in the resulting polymers to have the softer and more flexible properties.

Figure 4.26 Effect of the PVC content in the resulting semi-IPNs on the tensile strength : the equivalent ratios of NCO/OH = 1.05 and of PCL: MMDI: TEA = 1: 3: 2 ; (—■—) the prepolymer and (-··-●-—-) the one-shot processes.

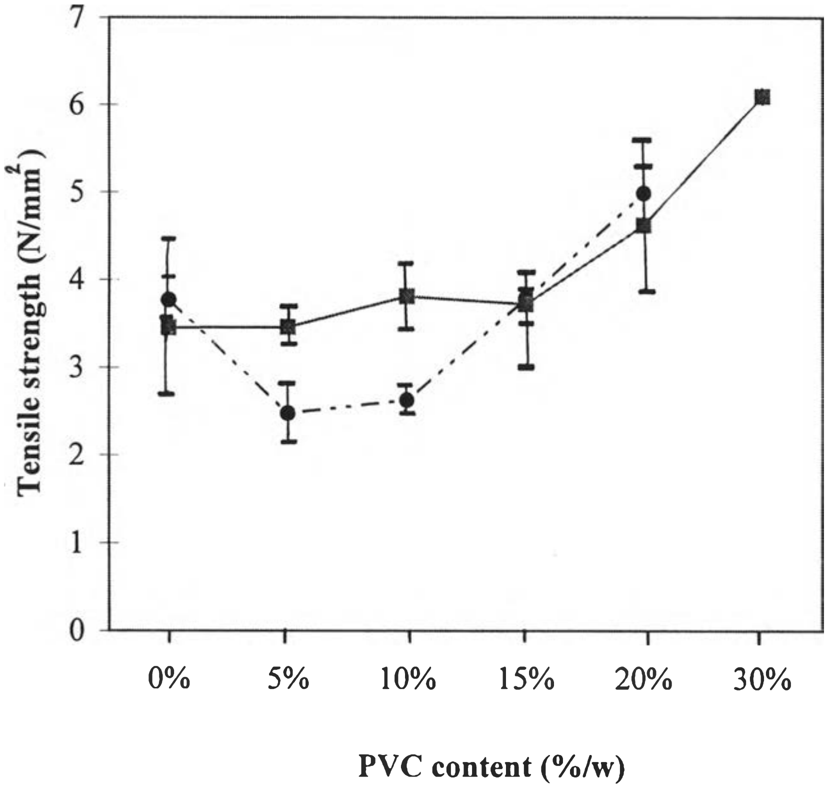


Figure 4.27 Effect of the PVC content in the resulting semi-IPNs on the elongation at break : the equivalent ratios of NCO/OH = 1.05 and of PCL: MMDI: TEA = 1: 3: 2 ; (—■—) the prepolymer and (- - -●- - -) the one-shot processes.

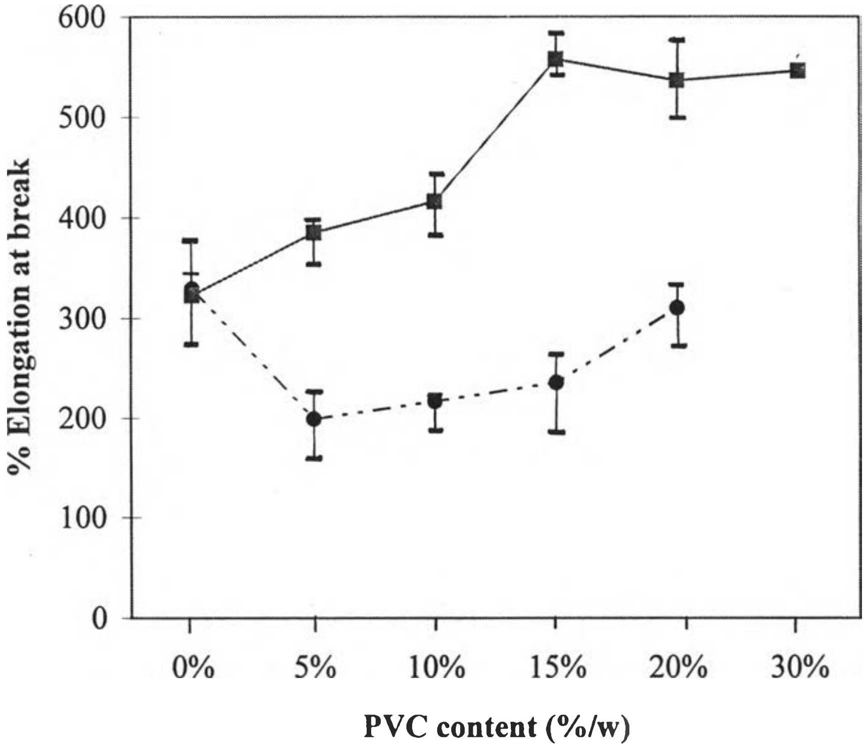
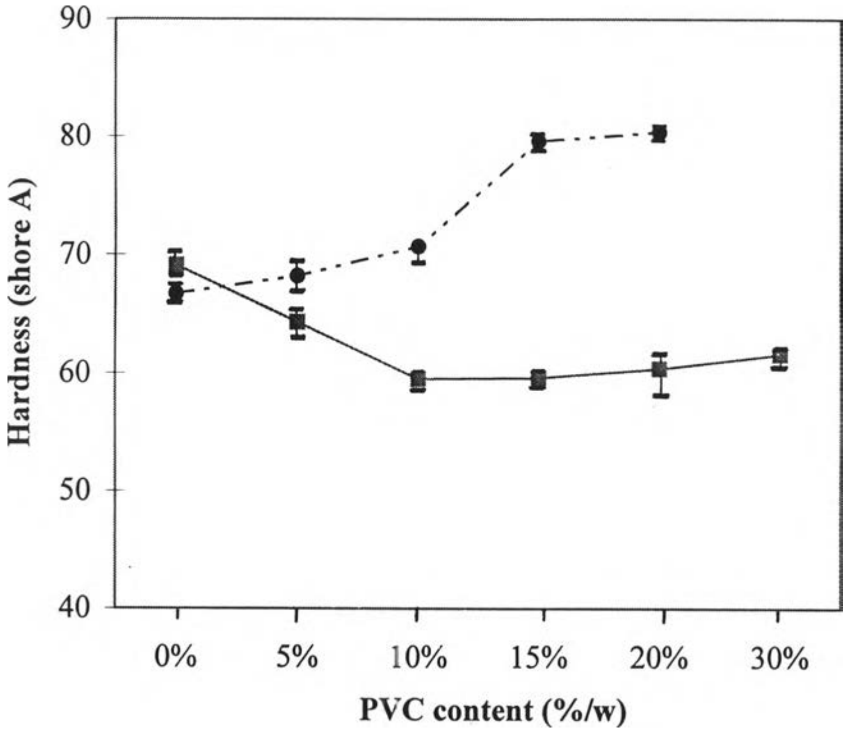
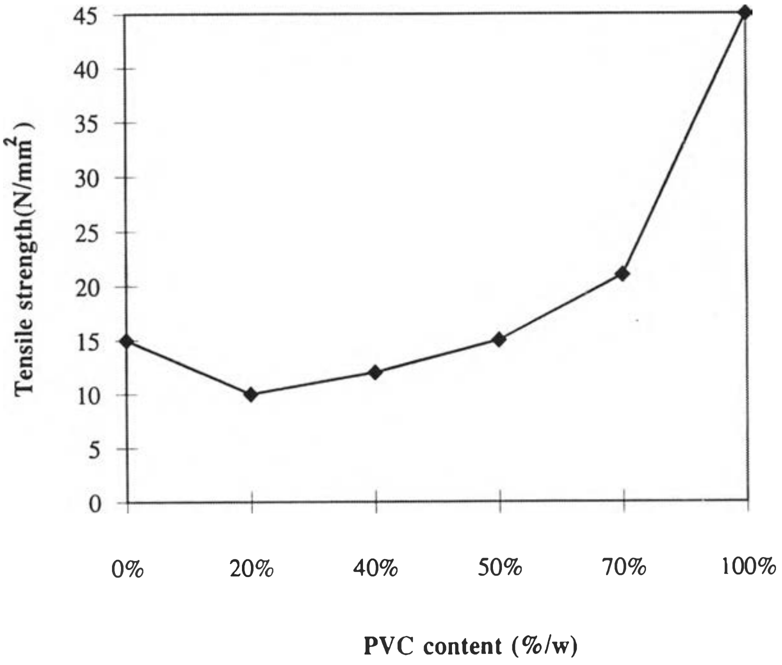


Figure 4.28 Effect of the PVC content in the resulting semi-IPNs on the Shore A hardness : the equivalent ratios of NCO/OH = 1.05 and of PCL: MMDI: TEA = 1: 3: 2 ; (—■—) the prepolymer and (- - - ● - -) the one-shot processes.



Bandyopadhyay and Shaw studied the tensile strength and elongation at break properties of PVC plasticized with PCL/MMDI/TEA-based PU. They found that the tensile strength increased while the elongation at break decreased, when the amount of PU decreased (see Figure 4.29). Their findings were contrast to the results of these studies, a lesser amount of PU acted as a plasticizer in a larger amount of PVC, it is therefore suggested to make a conclusion in these studies that the small portion of PVC dispersed phase is plasticized the larger portion of PU continuous matrix. Figure 4.30 supports the current conclusion. An investigation on an increment of the amount of PVC higher than 30% affects on the mechanical properties of the resulting semi-IPNs should be carried out further.

Figure 4.29 The tensile strength and elongation at break of PCL/MDI/TEA-based PU blended with various amount of PVC. (Bandyopadhyay and Shaw, 1982)



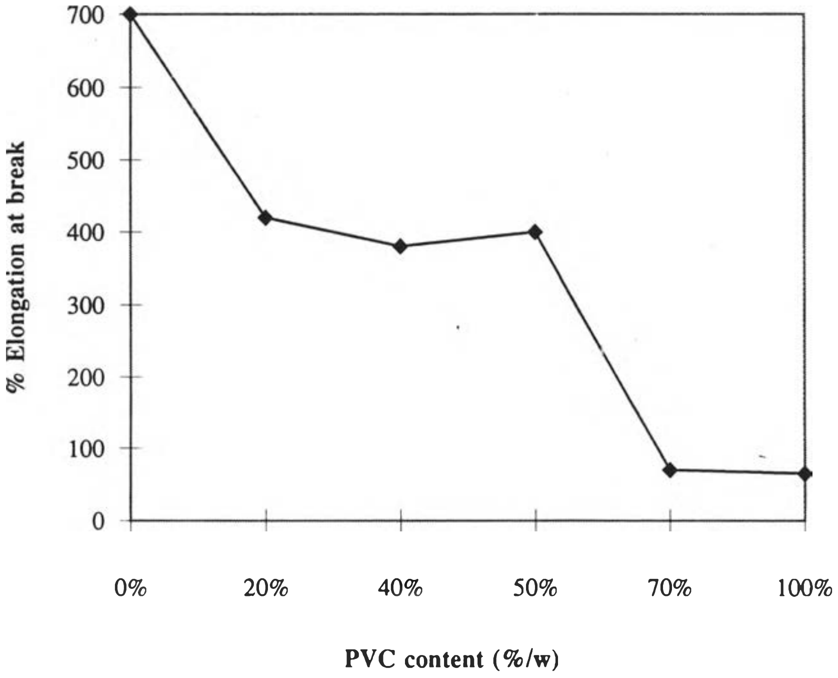


Figure 4.30 The tensile strength and elongation at break of polyblend of PCL/MDI/TEA-based PU with PVC prepared by Bandyopadhyay (——) and Shaw and of the semi-IPNs prepared in these studied (- - - - -).