

# Cellulose Nitrate–Poly(vinyl Chloride-co-Vinyl Acetate)–Polyurethane Ternary IPNs: FT-IR and Morphological Studies

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## SYNOPSIS

Ternary semi-IPNs of nitrocellulose, poly(vinyl chloride-co-vinyl acetate), and polyurethanes have been synthesized and characterized by FT-IR, SEM, and differential scanning calorimetry. Semi-IPNs of nitrocellulose–polyurethanes are found to be incompatible whereas the ternary system consisting of nitrocellulose–poly(vinyl chloride-co-vinyl acetate) and polyurethanes is partially compatible. Hydrogen bonding interactions are discussed based on the FT-IR analysis. The tensile strength and percent elongation are interpreted on the basis of the NCO/OH ratio and composition.

## INTRODUCTION

Interpenetrating polymer networks are a mixture of two or more distinctly crosslinked polymers which are mutually held together by permanent entanglements.<sup>1</sup> If one polymer is crosslinked and the other is linear, the resulting system is called a semi-IPN. IPNs of different types with wide range of properties have been reported elsewhere.<sup>2–6</sup> In our earlier work, we have reported the morphological and mechanical properties of ternary semi-IPNs based on nitrocellulose (NC), poly(vinyl chloride-co-vinyl acetate) (Vc-VAc) and polyurethanes (PU) derived from castor oil.<sup>7</sup>

Phase behavior of polyurethane semi-IPNs with vinyl acetate containing various amounts of poly(butyl methacrylate) has been reported.<sup>8</sup> Since the phase morphology of such combined systems is mainly due to the presence of specific interactions between the constituents, the study of the nature of such interactions is essential in order to understand the phase behavior of the system. In this paper we have discussed the FT-IR spectra of the ternary IPNs of NC, Vc-VAc, and polyurethanes and their morphological features by scanning electron microscopy.

Fourier transform infrared spectroscopy has become an effective technique in studying the specific interactions between two polymer systems. Extensive studies on hydrogen bonding in such binary systems have been done using FT-IR. Studies of polyurethane–ether<sup>9</sup> and poly(vinyl chloride)-segmented polyurethane<sup>10</sup> blends have shown interesting results regarding the interactions between them. It has been reported that the vibrational bands of polyester–nitrocellulose blends are significantly perturbed and the carbonyl stretching band in the blend broadens and shifts as a function of composition.

## EXPERIMENTAL

NC and Vc-VAc were dissolved in distilled methyl ethyl ketone and reprecipitated with petroleum ether. Hexamethylene diisocyanate of specific gravity 1.05 supplied by Fluka AG was used as received. Poly(propylene glycol) of molecular weight 1000 was used after degassing at 100°C under vacuum for 30 min. Dibutyltindilaurate catalyst was used as received. The IPNs were synthesized using the same method described in our earlier work.<sup>7</sup>

Thin films were cast from the IPN reaction mixture over a mercury pool for FT-IR studies. After complete drying, the films were taken out without

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distortion and mounted between the window cuts of a thick sheet. The spectra were recorded using a Nicolet 20-DXB FT-IR spectrophotometer. The scanning electron micrographs were taken by using an S-150 stereoscan model scanning electron microscope. Tensile strength measurements were carried out in an Instron universal testing machine, Model 4301. The specimens were prepared by using a dumbbell die of width 0.4 cm and length 2.2 cm in the narrow portion. Thickness of the specimens was measured after conditioning at  $27 \pm 2^\circ\text{C}$  for 4 h. The rate of separation of the crosshead was maintained at 200 mm/min. Glass transition temperatures for some IPNs were found out by using a Mettler TA 3000 system at a heating rate of 20 K/min from  $-100$  to  $+250^\circ\text{C}$ .

## RESULTS AND DISCUSSION

**FT-IR.** Before starting the discussion on specific interactions in the semi-IPNs, we will discuss the infrared spectra of polyurethane which is shown in Figure 1. The N—H stretching vibration of urethane

occurs approximately at  $3350\text{ cm}^{-1}$  and the peak has split into two sharp bands. The primary intermolecular interactions occurring in urethanes is the hydrogen bonding between the urethane C=O group of one unit with the urethane N—H group of another. Hence chains of hydrogen-bonded urethane groups are formed and at the ends of these chains are two non-hydrogen-bonded groups, i.e., one C=O and one N—H. This is the reason why the N—H stretching vibration has split into two bands one corresponding to the hydrogen-bonded N—H and the other for nonbonded. Correspondingly there are two peaks in the carbonyl stretching observed at  $1725$  and  $1709\text{ cm}^{-1}$  with comparable intensities. This again indicates the presence of bonded and nonbonded carbonyl groups.

Introduction of nitrocellulose to the urethane has changed the N—H stretching vibration considerably. The spectrum of the polyurethane-nitrocellulose semi-IPN is shown in Figure 2. The addition of NC provides a further site which is capable of forming a hydrogen bond with the urethane N—H group. The broadening of N—H stretching in the semi-IPN indicates this possibility of interaction. The

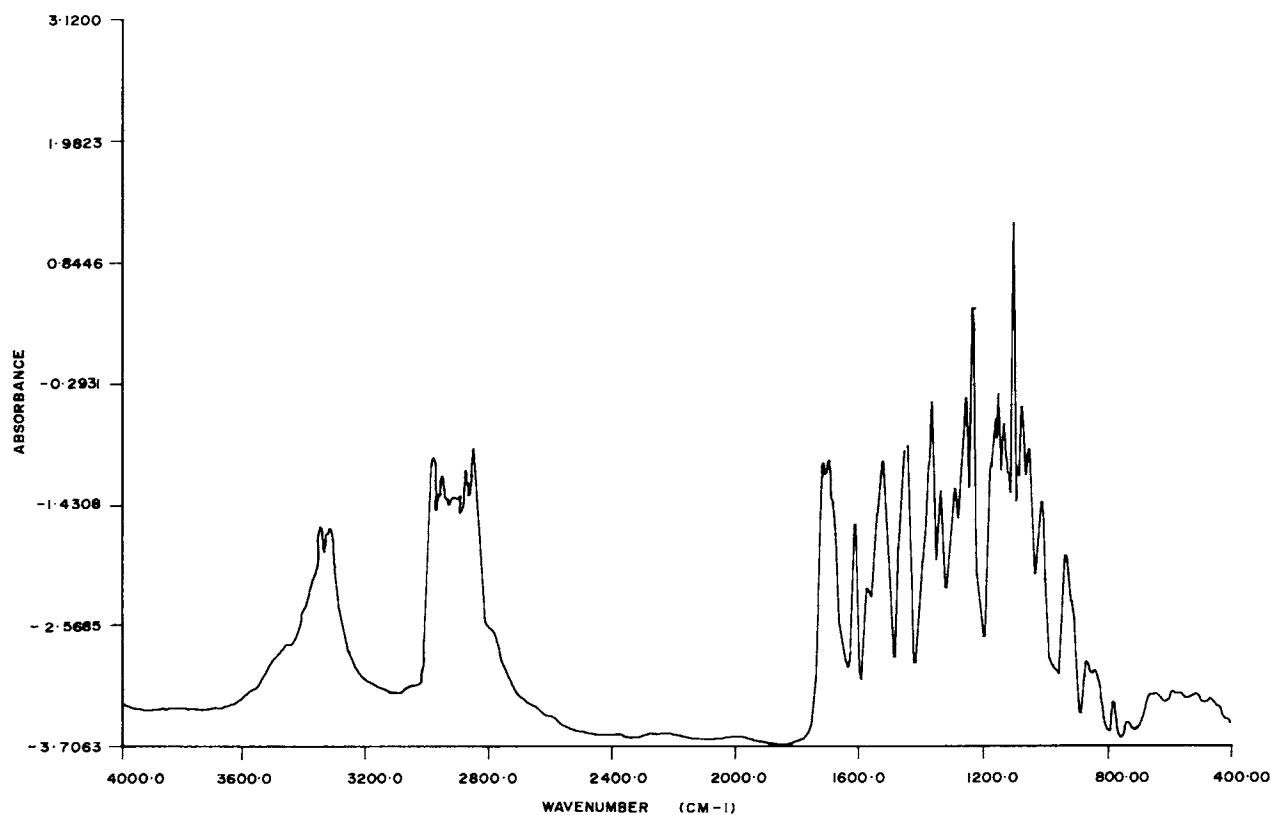


Figure 1 FTIR spectra of polyurethane.

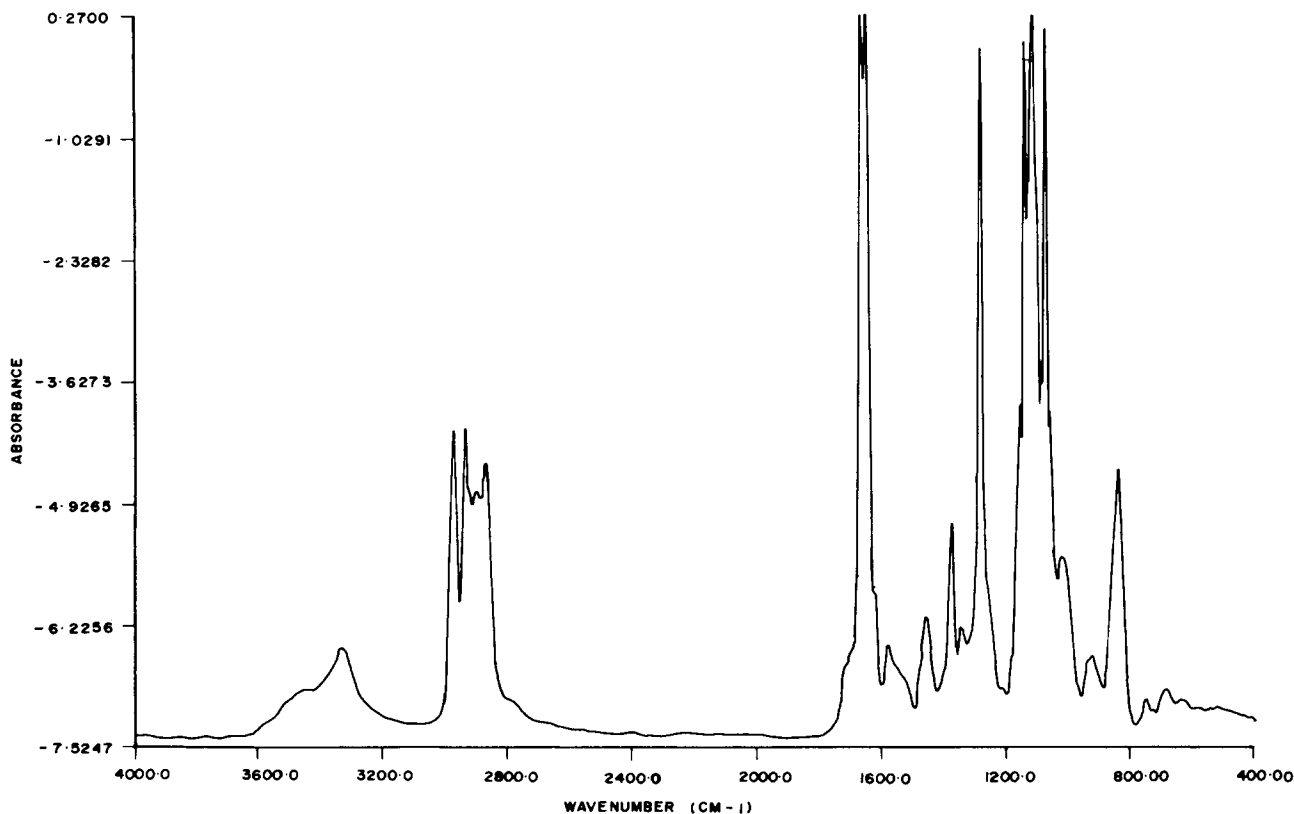


Figure 2 FTIR spectra of cellulose nitrate-polyurethane semi-IPNs.

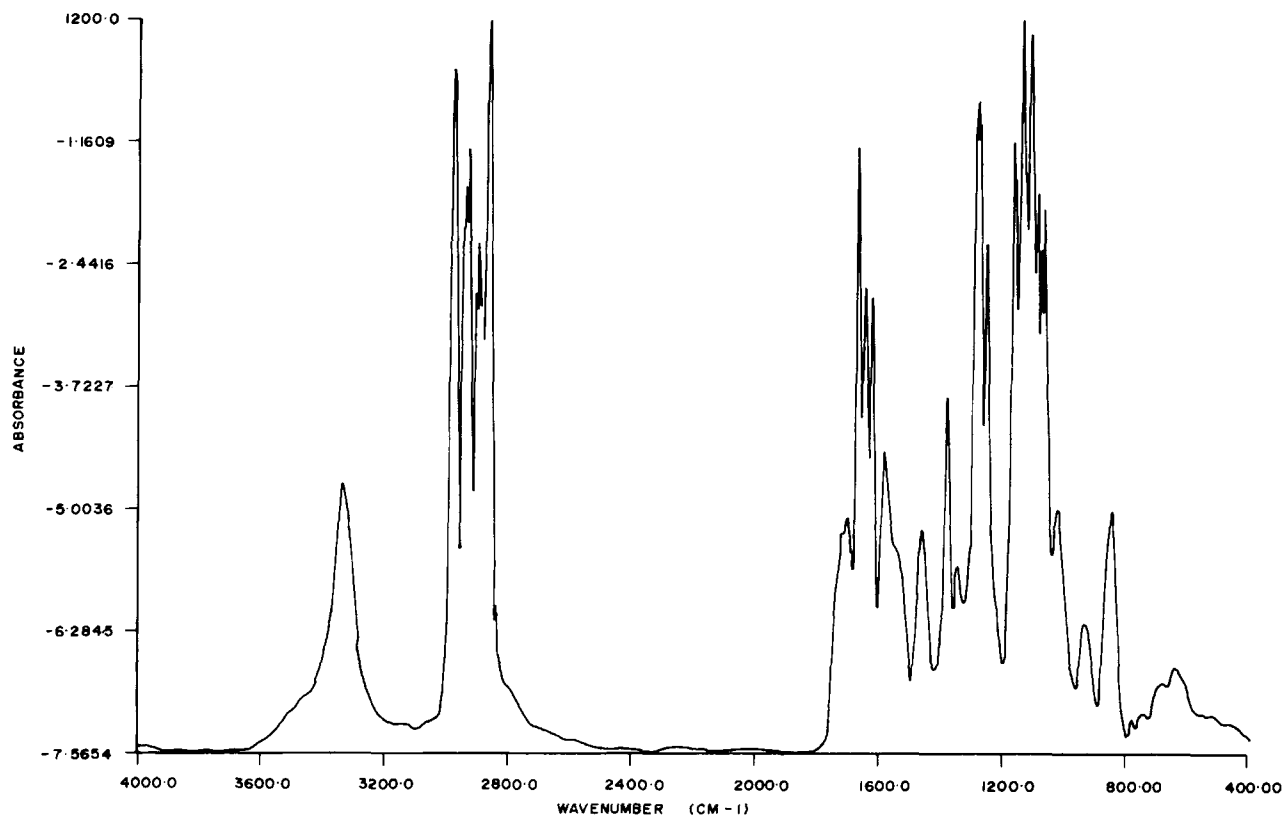
carbonyl stretchings in the pure urethane at 1725 and 1709  $\text{cm}^{-1}$  have disappeared in the semi-IPN spectrum. However, these vibrations seem to have overlapped with the asymmetric stretching of the O—NO<sub>2</sub> groups of nitrocellulose. For pure NC this asymmetric stretching of O—NO<sub>2</sub> occurs strongly at 1660  $\text{cm}^{-1}$  but in the IPN these vibrations have split into two new bands at 1666 and 1648  $\text{cm}^{-1}$ , indicating the presence of free and perturbed O—NO<sub>2</sub> groups. From these observations we may conclude the existence of hydrogen bonds between the —O—NO<sub>2</sub> of nitrocellulose and the urethane N—H groups. A further evidence for this is the disappearance of strong N—H bending vibration at 1620  $\text{cm}^{-1}$  in the semi IPN.

Incorporation of Vc-VAc copolymer gives a ternary IPN and its spectrum is given in Figure 3. The carbonyl stretching vibration of the copolymer has broadened and appears as a shoulder in the ternary system. The intensity of O—NO<sub>2</sub> asymmetric stretching has decreased and thereby the priority for hydrogen bonding between O—NO<sub>2</sub> and the N—H decreases. On the other hand, the N—H stretching vibration gives a single strong peak, which in

turn indicates the possibility of hydrogen bonding between the urethane N—H group and the carbonyl group of the copolymer.

**Morphology.** Morphological features of the semi-IPNs are shown in the scanning electron micrographs. The criteria for complete miscibility is a single homogeneous phase of the combined system in the scanning electron micrograph. However, such a system could only be formed when there are specific functional groups in each of the constituents which are capable of interacting strongly with each other.

From the Figure 4 (a) it can be seen that the polyurethane-NC IPNs show poor compatibility. In our previous paper we had discussed the morphology of polyurethane-NC IPNs wherein the PU was based on castor oil.<sup>7</sup> In that case we reported the partial miscibility of NC-PU with composition 30 : 70. For the same composition the present system shows poor miscibility, which may be due to the decreased functionality of the diol [poly(propylene glycol)] when compared to castor oil. When Vc-VAc copolymer is introduced to this semi-IPN, the resulting ternary system shows enhanced phase

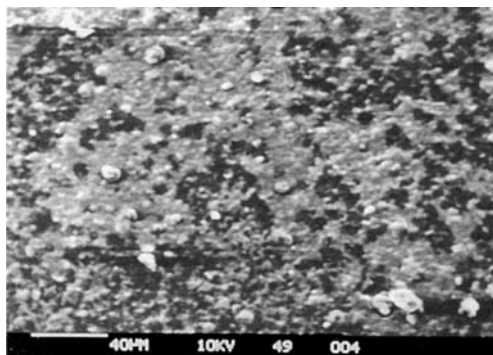


**Figure 3** FTIR spectra of cellulose nitrate-poly(vinyl chloride-co-vinyl acetate) polyurethane ternary semi-IPNs.

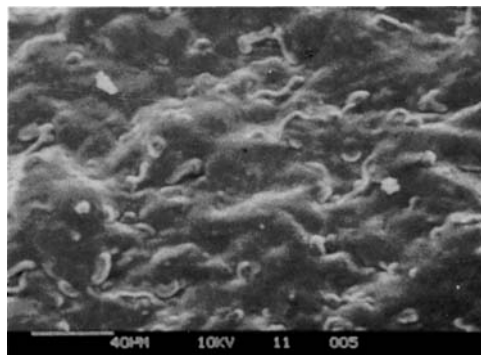
mixing as can be seen from the Figure 4(b). For the same ternary system, an increase in NCO/OH ratio increases the crosslink density of the system thereby giving a more homogeneous phase (Figure 4(c)). Keeping the NC/Vc-VAc ratio constant, decrease in the polyurethane content in the ternary system again gives a poor compatible system (Figure 4(d)) but more compatible than the IPN based on NC-PU alone.

**Tensile Strength.** In general, these IPNs are very soft and weak when compared to those based on castor oil. This is due to the difunctionality and soft nature of the poly(propylene glycol) than the castor oil. Semi-IPNs derived from NC and PU were flexible whereas those based on Vc-VAc and PU were brittle and tensile tests could not be performed for the latter system. The tensile strength values are given in Table I. It can be seen from the table that an increase in NCO/OH ratio increases the tensile strength as the crosslink density increases. Similarly for a constant NCO/OH ratio, increase in proportion of NC and Vc-VAc copolymer in the ternary systems shows an increase in tensile strength (Table II).

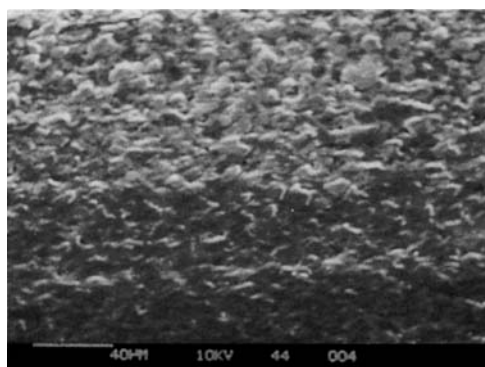
**Differential Scanning Calorimetry.** DSC curves of the semi-IPNs are given in Figure 5. The endothermic transition in curve A at  $-37^{\circ}\text{C}$  corresponds to the polyurethane soft segment in the NC-PU semi-IPNs. Keeping the urethane content constant, partial replacement of nitrocellulose with Vc-VAc copolymer imparts flexibility to the ternary system as can be seen from the reduction of  $T_g$  ( $-48^{\circ}\text{C}$ ) in curve B. This is further manifested from the fact that IPNs containing only copolymer and polyurethanes could not be prepared for tensile testing. Curve C shows the increase of  $T_g$  from  $-48$  to  $-33^{\circ}\text{C}$  when NC and Vc-VAc contents were increased from 15 to 20%, which again indicates the rigidity imparted to the system by nitrocellulose and the copolymer. For system containing 15% NC, 15% Vc-VAc, and 70% polyurethane increase in NCO/OH ratio from 1.05 to 1.35 increases the  $T_g$  from  $-48$  to  $-26^{\circ}\text{C}$  (curve D). This system shows a relatively homogeneous phase when compared to the other systems, as can be seen from the SEM micrograph 3. In all the ternary semi-IPNs an endotherm around  $80^{\circ}\text{C}$  shows the  $T_g$  of the Vc-VAc copolymer



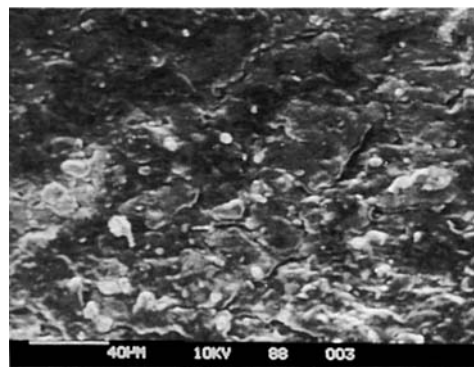
(a) SE Micrograph: 1  
NC/PU 30/70  
NCO/OH 1.05



(b) SE Micrograph: 2  
NC/Vc-VAc/PU 15/15/70  
NCO/OH 1.05



(c) SE Micrograph: 3  
NC/Vc-VAc/PU 15/15/70  
NCO/OH 1.35



(d) SE Micrograph: 4  
NC/Vc-VAc/PU 30/30/60  
NCO/OH 1.05.

**Figure 4** SE micrographs: (a) NC/PU, 30/70; NCO/OH, 1.05; (b) NC/Vc-VAc/PU, 15/15/70; NCO/OH, 1.05; (c) NC/Vc-VAc/PU, 15/15/70; NCO/OH, 1.35; (d) NC/Vc-VAc/PU, 30/30/60; NCO/OH, 1.05.

and the exotherm in the range of 180–200°C corresponds to the oxidation of cellulose nitrate.

### CONCLUSION

Semi-IPNs of nitrocellulose and polyurethanes based on polypropylene glycol are found to be in-

compatible but partial replacement of nitrocellulose with the poly(vinyl chloride-co-vinyl acetate) showed improved compatibility. FT-IR studies indicate hydrogen bonding between urethane groups and carbonyl groups of the copolymer. SEM and DSC results indicate improved compatibility for the

**Table I** Effect of NCO/OH Ratio on Tensile Strength of the IPNs

NCO/OH Ratio	Tensile Strength (kg/cm <sup>2</sup> )	Elongation at Break (%)
1.05	15.08	50
1.15	46.82	40
1.25	50.54	48
1.35	53.75	27
1.45	56.16	27

**Table II** Effect of Composition at Tensile Strength of the IPNs

Composition NC/Vc-VAc/PU	Tensile Strength (kg/cm <sup>2</sup> )	Elongation at Break (%)
30/0/70	52.55	13
0/30/70	Brittle	—
10/10/80	20.39	13
20/20/60	58.50	49
25/25/50	94.85	82
30/30/40	148.00	60

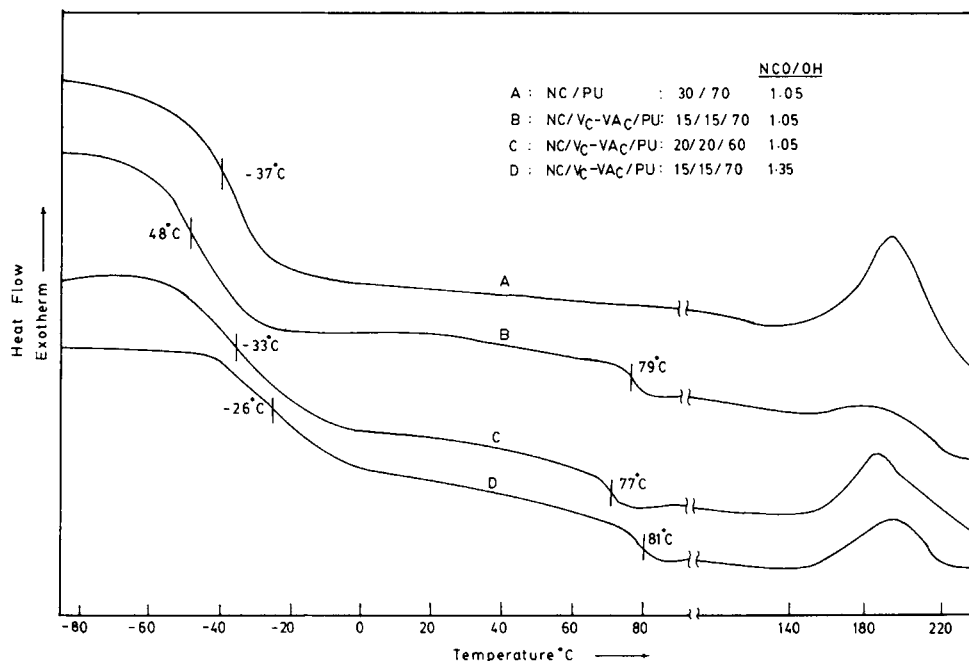


Figure 5 DSC traces of semi-IPNs.

ternary system. The IPNs are found to be very soft and weak in their mechanical properties.

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