Studies on a self-crosslinking blend system based on neoprene and polyacrylamide:
1. Mechanism and characterization

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The neoprene and polyacrylamide system was studied at various blend ratios. Infra-red studies indicate the reactive nature of neoprene, polyacrylamide and their blends. Inter-crosslinking between neoprene and polyacrylamide segments occurs by chemical reaction through the imide groups formed from polyacrylamide and the halogen atoms of neoprene. Studies with a differential scanning calorimeter and a dynamic mechanical analyser clearly indicate the apparent incompatible nature of the blend and show it to be a three-phase system. The third phase is a compatibilized interfacial zone of inter-crosslinked material. Preferential etching of the phases with solvents is possible. A scanning electron microscopy study also confirmed the multiple-phase structure of the cured blends.

(Keywords: self crosslinking: infra-red absorption; differential scanning calorimetry; dynamic mechanical analysis; scanning electron microscopy; morphology; glass transition temperature; six-membered ring imide; grafting; allenes; amido acids; diacyl amines)

INTRODUCTION

The possibility of a multitude of physical as well as chemical interactions between two functionalized polymeric species has variously been described as *in situ* compatibilization, toughening through reactive blending, physical or chemical compatibilization, etc.[1–3]. However, suitably functionalized elastomeric blend systems can lead to vulcanization. This was firmly established by De *et al.*[4] for the epoxidized natural rubber–carboxylated nitrile rubber (ENR–XNBR) blend system, and the idea was subsequently advanced to other rubber–rubber and rubber–plastic blend systems[5–7]. Suitable reaction schemes were also proposed for the systems.

In view of the need for environmental protection, the development of a water-degradable elastomer system (a preliminary step in environmental degradation) was attempted through blending as this offers tremendous flexibility for property manipulation. Blends normally suffer from cure imbalance and thus a self-crosslinking system based on neoprene and polyacrylamide was chosen. Neoprene is known to be chemically active due to its unsaturation and halogenated structure. Polyacrylamide was chosen as the other constituent owing to various chemical reactivities associated with the amide group. Also, the water resistance of polyacrylamide is poor and it slowly dissolves in water, but its resistance to other solvents is extremely high as its solubility parameter is considerably higher than normally encountered solvents. Thus neoprene is likely to offer rubberiness and water resistance to the blend and polyacrylamide will provide resistance to solvents like chloroform, toluene, etc. and also a convenient route for environmental degradation.

Moreover, characterization of the blends, specifically for establishing the chemical processes which lead to the crosslinking reaction, is difficult. Solid-phase polymer reactions may be diffusive in nature and hence various competitive reactions can take a dominating role and any simple sketching of the chemical changes fails to give the correct picture[8]. Isolation of functional groups from the network structure is not possible as any attempt to break down the network does not provide any guarantee for protecting the important chemical groups. A special i.r. technique developed at our laboratory by De and Roy[9] has been adopted to investigate the chemical processes which occur as a function of reaction time. The method seems to be very encouraging in terms of its ability to resolve the identities of various chemical groups.

EXPERIMENTAL

Materials

Neoprene was supplied by DuPont, USA, and polyacrylamide was supplied by BDH Chemicals Ltd, UK. The molecular weight of polyacrylamide was $>5\times10^6$, and its solution viscosity (0.5% aqueous solution at 25°C) was about 0.280 Pa s.

Sample preparation for d.s.c. and d.m.a. studies

Blending of polyacrylamide with neoprene was done in a Brabender Plasticorder PLE 330 at 180°C and at a rotor speed of 90 rev min^{-1} as per the composition of mix given in *Table 1*. First of all, the rotor speed was adjusted to 25 rev min^{-1} and the calculated amount of polyacrylamide was fed into the plasticorder. Neoprene was added in the form of thin strips after warming the polyacrylamide for 1 min. The rotor speed was then adjusted to 90 rev min^{-1}. After 2 min the mix was taken

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Table 1 Mixes and their compositions

Mix	Neoprene (parts)	Polyacrylamide (parts)
A	100	0
B	75	25
C	50	50
D	25	75
E	0	100

out and passed through the roll mill. The blends were vulcanized at 140°C for 1 h in a hydraulic press (Labo Press, Toyoseiki) at a pressure of 5 MPa. The press was then cooled to room temperature by circulating cooling water. The pressure was released and the sheet was taken out of the mould. In the case of pure neoprene, it was first passed through a roll mill three or four times and then finally taken out as a thin sheet. Moulding was done as before. The specimen for the rheovibron study was cut into thin strips ($5 \times 0.7 \times 0.3$ cm). For the d.s.c. study, about 10 mg of material were taken from each of the moulded sheets. The d.s.c. study of polyacrylamide was done with the powder as supplied, whereas the d.m.a. sample of polyacrylamide was prepared by solution casting of an approximately 0.5% aqueous solution. Polyacrylamide was dissolved in warm water (70°C) with stirring over 5 h. The homogeneous solution was then poured into a clean Petri dish. The bulk of the water was allowed to evaporate at room temperature and the product was finally kept under vacuum for five days. The d.m.a. sample was prepared from this cast sheet.

Sample preparation for i.r. studies

The preparation of samples for i.r. study is very tricky. Thin films made by pressing in a Labo press at a pressure of 5 MPa were found to be opaque to i.r. in the characteristic zones. Therefore, a method developed in our laboratory by De and Roy[9] was adopted. In this method, 50 g of LDPE were fed to the plasticorder at 180°C and melted. Then 10 g of the required material were added to the plasticorder. Mixing was done for 4 min at a rotor speed of 60 rev min^{-1}. The stock was then removed from the mixer, passed through a roll mill and taken out as a sheet. It was again fed to the plasticorder in thin strips and mixing was continued for 2 min, after which the stock was taken out and passed through a roll mill.

About 0.6 g of the above stock was taken and pressed between two aluminium foils in a Labo press at 190°C and at a pressure of 50 MPa for various periods, e.g. 4, 20 and 40 min. In each case, the film was taken out after cooling the mould with cold water. The samples prepared by this method included neoprene, polyacrylamide and blends of these with the compositions (neoprene:polyacrylamide) 75:25, 50:50 and 25:75.

Etching with solvents

Solvent etching of the vulcanized blends was performed at room temperature using chloroform and water independently to extract neoprene and polyacrylamide, respectively. In each case nearly 1 g of the sample was immersed in about 50 ml of solvent and the solvent was replaced by a fresh 50 ml every alternate day. After two weeks the specimens were taken out of the solvent and dried in a vacuum oven at 70°C for 24 h.

I.r. study

The i.r. study was carried out using the films prepared as described above in the wavenumber range from 4000 to 200 cm^{-1} using a Perkin–Elmer 843 infra-red spectrophotometer.

D.s.c. study

The d.s.c. study was carried out in the temperature range from -50 to 150°C in a nitrogen atmosphere with a temperature rise of 20°C min^{-1}. The lower temperatures were attained through the use of liquid nitrogen. The instrument used was a DuPont 910 differential scanning calorimeter attached to a DuPont 9000 thermal analyser system.

D.m.a. study

The dynamic properties were measured in a rheovibron (model DDV-III-EP, Orientec Corporation, Japan) in the temperature range from -150 to 150°C, with a heating rate of 2°C min^{-1} and at a frequency of 3.5 Hz. Liquid nitrogen was used to achieve low temperatures.

Scanning electron microscopy study

An SEM study was performed for both etched and unetched specimens. Samples embrittled in liquid nitrogen were broken by bending and the fractured surfaces were studied for morphology in a Cam Scan Series II scanning electron microscope after coating the surfaces with gold in a sputter machine.

RESULTS AND DISCUSSION

Analysis of i.r. spectrographs

In the present investigation, instead of a thorough analysis of the spectrographs, we have concentrated more on the possible ongoing changes with curing time in the individual polymers and also in the blend systems. In view of the disappearance of some of the peaks and appearance of some new peaks, it is very clear that the individual systems and the blends are very reactive, and the blends undergo even more chemical reactions than the individual components.

The major peaks observed with polyacrylamide are at 1852, 1804, 1740, 1678 and 618 cm^{-1}. Apart from these, one peak at 1632 cm^{-1} gradually vanishes and another at 1622 cm^{-1} gradually becomes more and more prominent with moulding time (*Figure 1a*). The peak at 1632 cm^{-1} seems to be due to the combined motion of N–H bending and C–N stretching in the –CO–NH– group in its *trans* form (amide II band), and the band at 1622 cm^{-1} is due to C=O stretching of amido acids[10].

The sharpening of a peak at 1740 cm^{-1} may be due to N–H stretching of a *trans–trans*-type imide[11]. In fact, the development of a small peak at 1710 cm^{-1} indicates the generation of a six-membered cyclic imide structure[11].

Other major changes in the spectrographs of polyacrylamide are as follows.

(i) A peak at 1588 cm^{-1} gradually attenuates and a small peak appears at 1580 cm^{-1}.
(ii) The peak at 1800 cm^{-1} diminishes and the peak at 1786 cm^{-1} becomes more prominent.
(iii) The peak at 618 cm^{-1} disappears and one appears at 1176 cm^{-1}.

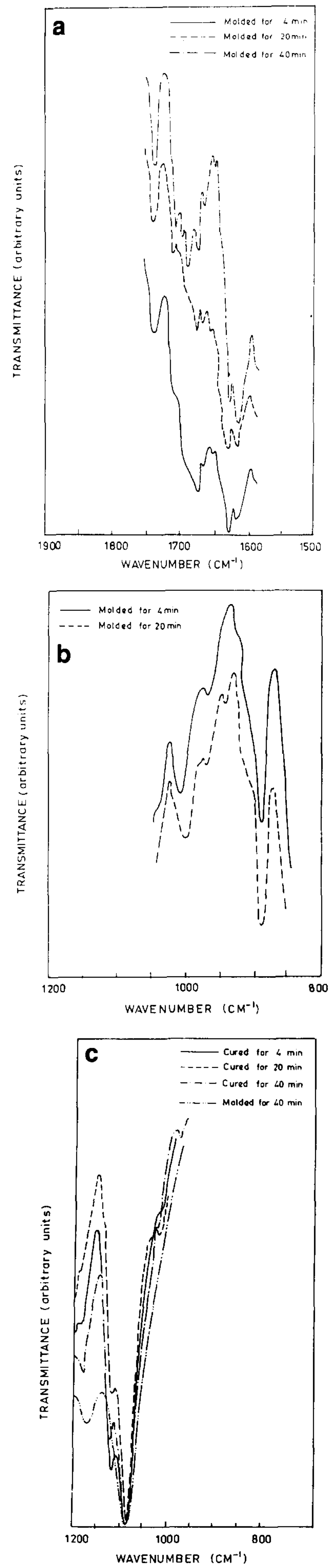


Figure 1 I.r. spectra of: (a) polyacrylamide at different moulding times; (b) neoprene at different moulding times; and (c) the 50:50 blend cured for 4, 20 and 40 min and polyacrylamide moulded for 40 min

(iv) A small peak at 900 cm^{-1} disappears, and one appears at 890 cm^{-1}, only to disappear with the progress of time.

Neoprene is found to contain prominent peaks at 1657, 1697, 1082, 1115, 650 and 609 cm^{-1}. On curing at 190°C, two peaks are formed at 532 and 420 cm^{-1} and a peak at 500 cm^{-1} disappears.

A very small peak is formed at 940 cm^{-1} and this could be due to an acetylenic C–C stretching vibration[12] (*Figure 1b*). It does not show the bands due to an H–C–C bending vibration. Therefore, the acetylenic structure is generated in the main chain, rather than in the pendant group where a terminal acetylene can form[12].

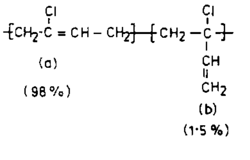
On curing the blends, two peaks are generated prominently, one at 1176 cm^{-1} and the other at 302 cm^{-1}. The first peak tends to shift to higher wavenumbers as curing proceeds (*Figure 1c*).

Based on the observations in the i.r. study of neoprene, polyacrylamide and their blends, we deduce some interesting phenomena. It is already known that HCl elimination from neoprene can be followed by cyclization, rearrangement and many other side reactions[13]. Additionally, here we observe the formation of an acetylenic structure. Polyacrylamide shows indications of amido acid formation as a peak at 1622 cm^{-1} is broadened. Imide formation is also confirmed on the basis of an absorption peak at 1710 cm^{-1} and also by the appearance of a new peak at 1185 cm^{-1}. Further, a band at 3400 cm^{-1} shifts to 3300 cm^{-1} which is very close to the imide band. The band observed at 1175 cm^{-1} after 40 min moulding time is likely to be an amide III band arising from the imides[11]. This band also appears in the blends with curing and shifts by 10 cm^{-1} towards a higher wavenumber (*Figure 1c*), and it possibly indicates some chemical interaction maintaining the basic structure of the imide.

Finally, a scheme of reactions has been proposed that conforms to the observations in the i.r. studies and also to the basic principles of organic chemistry.

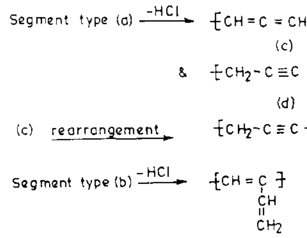
Neoprene

The microstructure of neoprene can be represented as[14]



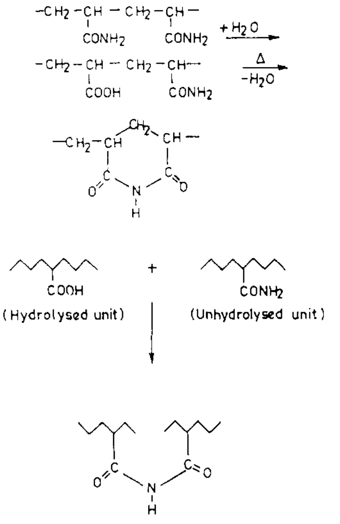
$$\underset{(98\%)}{\underset{(a)}{\left[CH_2-\overset{Cl}{C}=CH-CH_2\right]}}\;\underset{(1\cdot 5\%)}{\underset{(b)}{\left[CH_2-\underset{\underset{CH_2}{\overset{\|}{CH}}}{\overset{Cl}{C}}\right]}}$$

HCl elimination will further introduce some more unsaturation into the already existing olefinic structure. Thermodynamically, whenever a mechanism is available, the formation of a conjugated diene will be favoured[15]. In other cases, formation of allenes can compete well with that of acetylenes[16]. In fact, allenes formed will tend to rearrange to acetylenes[17]. Thus, the following scheme for neoprene degradation has been proposed



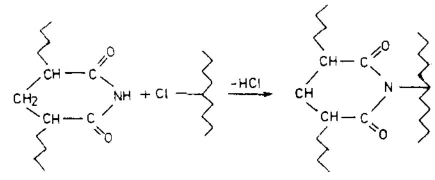
Polyacrylamide

Amide groups are hydrolysable and the process is accelerated by acids. Amido acids offer a convenient route to cyclic six-membered ring imides[15]. The possibility of acyclic imides (diacylamines) cannot be ruled out. Thus, the scheme can be represented as



Blends

In the blends, HCl eliminated from neoprene will accelerate amide hydrolysis which is the preliminary step for imide formation and NH_4Cl will be formed as a by-product of the hydrolysis reaction. The imides are capable of reacting with alkyl and allyl halides[18]. This will result in grafting of neoprene with polyacrylamide. At a higher level of grafting an inter-crosslinked product will be formed. This possibly explains the shift of the amide III band at 1175 cm^{-1} to a higher wavenumber in the vulcanized blends (*Figure 1c*).



D.s.c. studies

Figure 2 shows the d.s.c. thermograms of neoprene, polyacrylamide and their blends. Neoprene shows one sharp transition at −39°C and polyacrylamide shows a transition at 125°C.

Incorporation of polyacrylamide into neoprene causes a shift in the glass transition temperature of neoprene to a higher temperature (*Figure 2a*). This could be due to a structural rearrangement of neoprene during curing. The high-temperature transition zone in the blends is broadened tremendously and the effect is very prominent with the 50:50 blend. The broad transition with the 50:50 blend seems to comprise two transitions. In line with the i.r. observations, the initial portion of this zone can be interpreted as the result of a compatible interfacial layer formed by inter-crosslinking reactions between the two components. The later portion is attributed to polyacrylamide transition. Thus, d.s.c. studies show that, while the components maintain their own individual characters, some portion undergoes reactive compatibilization through a self-crosslinking reaction. The transition behaviour of the polyacrylamide component is found to depend on the gross composition of the blend. The apparent gross composition dependent transition temperature of the polyacrylamide component in the blends can be rationalized if care is taken in the plasticizing action of small-molecule additives either formed by chemical reaction or from the residual absorbed moisture after chemical reaction. This explanation is supported by the recent theoretical developments and experimental findings of Ellis[19].

D.m.a. study

Figure 3a shows the loss tangent curves of neoprene and the blends containing neoprene and *Figure 3b* shows the loss tangent curve for polyacrylamide. The loss

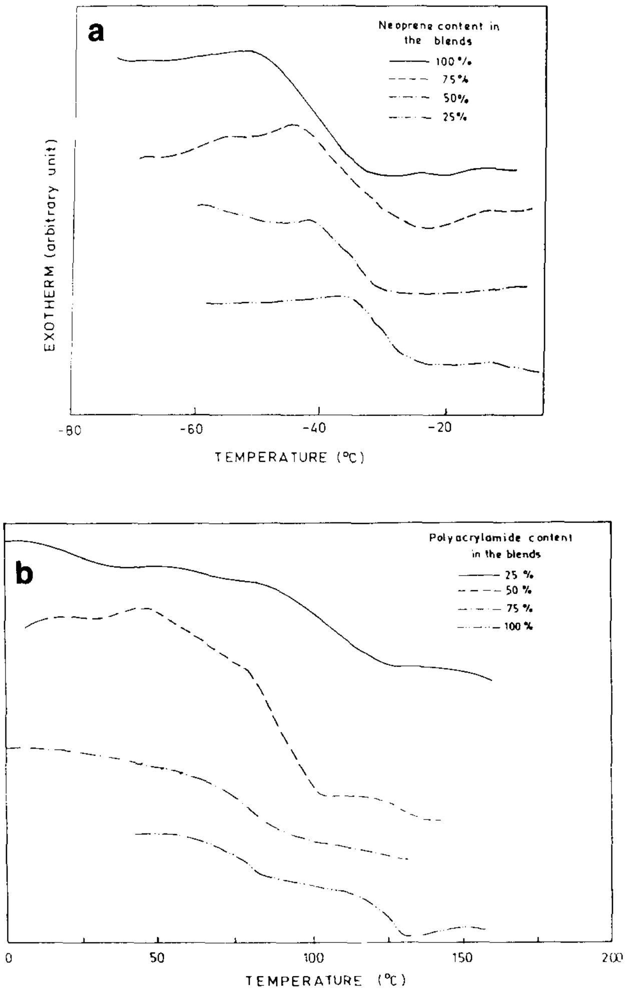


Figure 2 D.s.c. studies of (a) neoprene and its blends with polyacrylamide and (b) polyacrylamide and its blends with neoprene

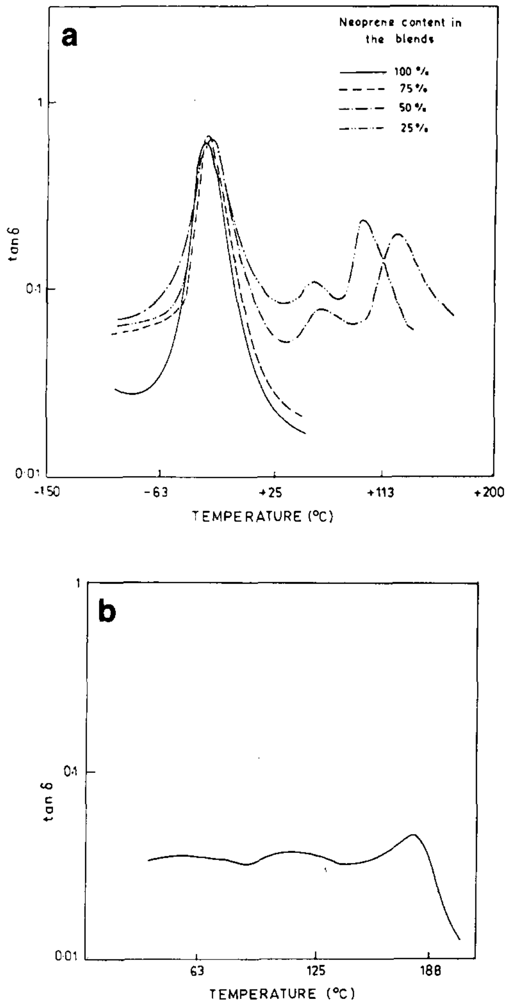


Figure 3 Loss tangent curves of (a) neoprene and its blends with polyacrylamide and (b) polyacrylamide

tangent curve of neoprene shows a fairly broad maximum at −29°C. This peak is due to glass transition and is, as expected, 10°C higher than the glass transition temperature obtained from d.s.c. Polyacrylamide does not show a smooth loss tangent curve. A fairly moderate peak can be identified at 170°C. The high value for the transition temperature from d.m.a. measurements can be explained by the fact that the dynamic measurements are done at a considerably lower rate of temperature scan than for the d.s.c. measurements. This provides ample scope for the specimens to lose moisture at temperatures around 100°C and above. Thus, the specimen will undergo continuous changes in properties and will stiffen due to the lack of the plasticizing action of moisture.

In the blends the neoprene peak is shifted by 2–4°C towards higher temperature. The 75:25 blend of neoprene and polyacrylamide does not show any loss tangent peak due to polyacrylamide. Surprisingly, the 50:50 and 25:75 blends of neoprene:polyacrylamide show two extra peaks, with one at about 55°C. The i.r. interpretations of the previous section confirm the formation of a grafted or inter-crosslinked structure between neoprene and polyacrylamide. In the inter-crosslinked zone, the mobility of one type of segment will tend to influence the mobility of the other type of segment and this mutual interaction will result in a mobility of intermediate type – hence the intermediate transition temperature.

The high-temperature peak due to polyacrylamide varies with blend composition and the observations are in line with those from d.s.c.

SEM study

The fractured surface of neoprene (*Figure 4a*) shows a network-type fibrillar structure represented by zone X, whereas the SEM photomicrograph of polyacrylamide (*Figure 4b*) shows clearly a plate-like lamellar structure (zone Y). A new zone (Z) appears in *Figure 4c* (the SEM photomicrograph of the 75:25 blend of CR:PAA) in addition to the X and Y zones and it shows the entanglement of the fibrillar structure with a thin layer of polyacrylamide. Since the neoprene content is greater in this blend, the interfacial zones are prominent. The SEM photomicrograph of the chloroform-etched specimen of the 25:75 blend of CR:PAA (*Figure 4d*) shows more plate-like structure and less interfacial zone. This is due to the low neoprene content of this blend. *Figures 4e* and *4f* (water-etched specimen of the 25:75 blend of CR:PAA) show that the polyacrylamide phase has been removed and vacuoles are formed. These observations suggest that the apparently incompatible phases are strongly bonded by an interfacial zone formed by chemical reaction between the two phases. This interfacial layer cannot be etched by chloroform, although the uncrosslinked portion can be removed by etching with a suitable solvent. Thus the SEM observations are in concordance with the observations obtained from the i.r., d.s.c. and d.m.a. studies.

CONCLUSIONS

Neoprene–polyacrylamide is found to form a self-crosslinkable blend system according to the following observations.

(i) The d.s.c. and d.m.a. studies indicate the apparent incompatible nature of neoprene and polyacrylamide, and also the formation of a compatible zone. The compatible interfacial zone is attributed to the inter-crosslinked product between neoprene and polyacrylamide.

(ii) SEM studies of cryogenically fractured surfaces confirm that the individual components are strongly held by an interfacial zone, which is concordant with the apparent incompatible nature of the blend. Lack of complete extraction of the phases after prolonged etching also suggests that the two phases are chemically bonded.

(iii) Finally, the i.r. study establishes that alkyl-substituted imide structures are responsible for the self crosslinking in the neoprene and polyacrylamide system.

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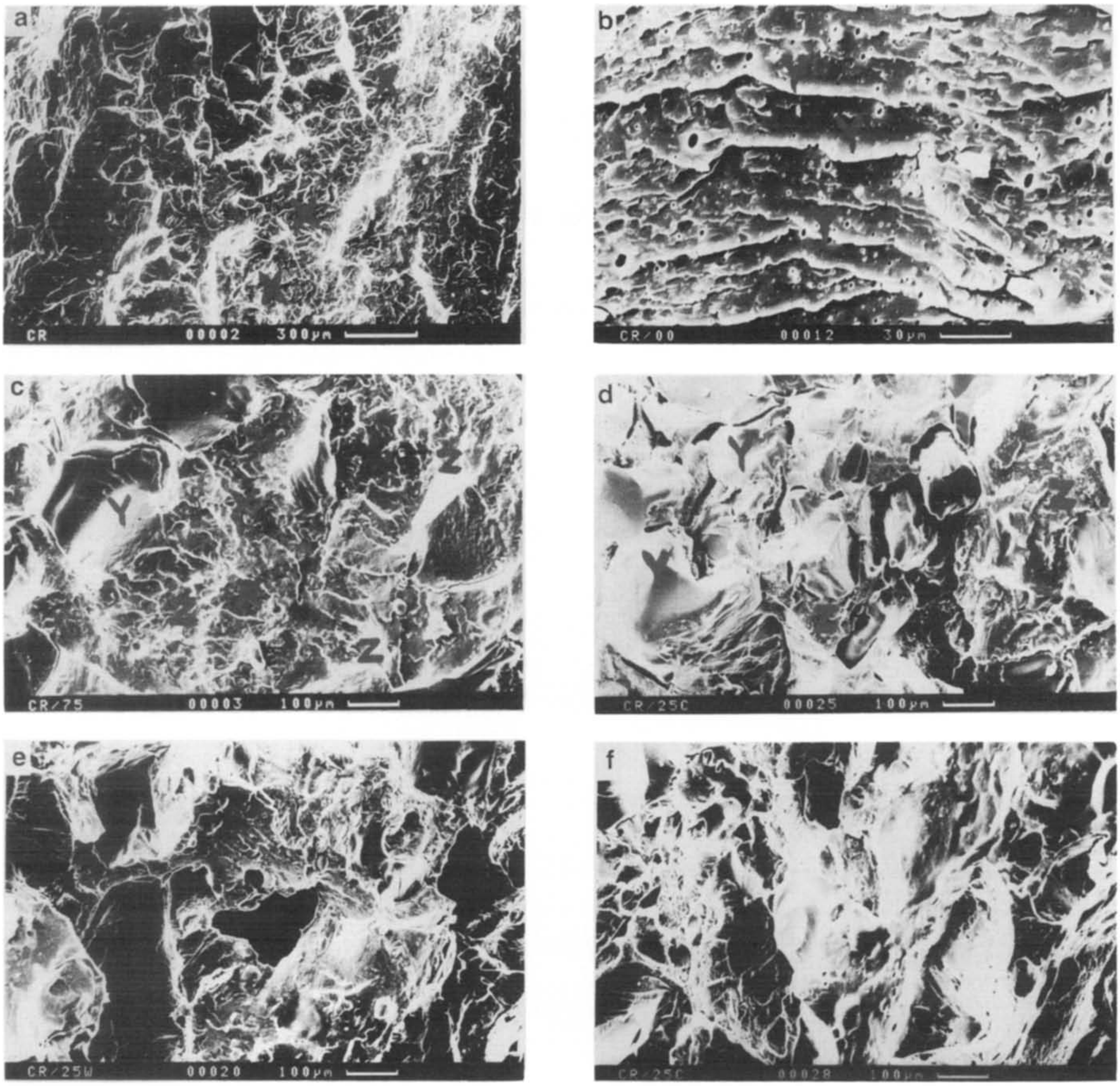

Figure 4 SEM micrographs of cryogenically fractured surfaces of: (a) neoprene; (b) polyacrylamide; (c) the 75:25 vulcanized blend of CR:PAA; (d) the chloroform-etched 25:75 vulcanized blend of CR:PAA; (e) the water-etched 50:50 vulcanized blend of CR:PAA; and (f) the water-etched 25:75 vulcanized blend of CR:PAA

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