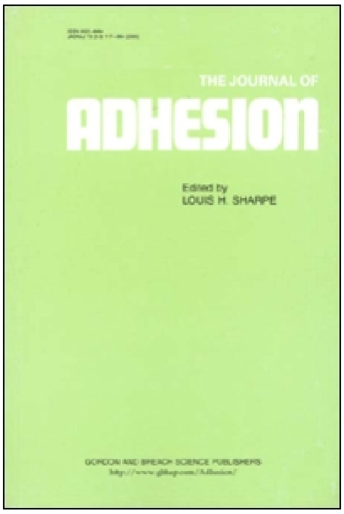

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Peel Adhesion of Poly(Vinyl Chloride) to Nitrile Rubbers

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In addition to molecular interaction and physical entanglement of the molecular chains across the interface in poly(vinyl chloride)-nitrile rubber joints, at high temperatures and long contact times interfacial chemical bonds may be formed which seem to couple the two adherends thereby resulting in cohesive failure of the rubber matrix on peeling. This is verified by performing the peel tests at high temperatures, low peel rates and under swollen conditions. Infrared spectroscopic studies of the PVC/NBR blend reveal the formation of chemical bonds at the contact temperatures studied. The peel fracture energy is found to depend on the acrylonitrile content and presence of carboxylic content in the NBR, and the presence of stabilizer and plasticizer in the PVC phase, in addition to the molding and testing conditions.

KEY WORDS adhesion; interface; diffusion; entanglements; crosslinks; rubber; PVC; peel testing; stabilizer; plasticizer; contact time and temperature; effects of swelling; IR spectroscopy.

INTRODUCTION

Commercial use of blends of nitrile rubber (NBR) and poly(vinyl chloride) (PVC) has been known for a long time.[1–4] Blends have been termed miscible, partially miscible and even heterogeneous depending on the acrylonitrile (ACN) content of the NBR, the blend composition and the blending method.[3–5] Recently it has been shown, on the basis of Monsanto rheometry, solvent swelling, infrared spectroscopy and dynamic mechanical analysis, that the PVC-NBR blend is crosslinked in the absence of any external crosslinking agents during high temperature molding.[6] The degree of crosslinking was found to be dependent on the ACN content of NBR, the presence of any PVC stabilizers and the molding conditions. The chemical interaction is believed to take place between the allylic chlorine in PVC and the amide/acid groups formed in NBR.[6] But a stabilizer such as tribasic lead sulfate (TBLS) prevented the chemical reaction.[6] Accordingly, it was thought that it would be interesting to study the effect of contact time, contact temperature, acrylonitrile (ACN) content of NBR, presence of stabilizer and plasticizer in PVC, and additional functional groups such as the carboxyl group (as in carboxylated nitrile rubber (XNBR))

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on the adhesion between PVC and nitrile rubber. The present paper reports the results of such studies on the adhesion between PVC and nitrile rubbers.

EXPERIMENTAL

Details of the materials used are given in Table I.

(a) Preparation of Test Samples

Light crosslinking of soft polymers, expected to reduce the possibility of viscous flow during testing, is known to be a cause of energy dissipation.[7] All of the rubber specimens were lightly crosslinked using sulphur and zinc diethyl dithiocarbamate (0.4 phr each). In this way, their characteristic interaction with any substrate can be preserved, yet they are prevented from flowing apart during establishment of contact at high temperatures, and on separation. The rubber sheets were prepared by compression molding the compounded rubber at 150°C for 10 min. between a Cellophane sheet and a piece of cotton fabric (0.02 mm thick), the latter to serve as the backing.

Rigid PVC sheets were prepared by compression molding PVC powder between

TABLE I
Details of the materials used

Material	Designation	Characteristics	Source
Poly(vinyl chloride)	PVC	suspension polymerised PVC (NOCIL PVC 5 67-311) K value 66 to 69	National Organic Chemical Industries Ltd., Bombay, India.
Nitrile rubbers			
	NBR_1	Paracryl AJLT % ACN: 25.8–29.2 ML_{1+4}: 35–50	Uniroyal Chemical Company Inc., Connecticut, USA.
	NBR_2	Krynac 34.50 % ACN: 34 ML_{1+4}: 50	Polysar Ltd., Sarnia, Canada.
	NBR_3	Paracryl CJLT % ACN: 38.5–40.9 ML_{1+4}: 50±7	Uniroyal Chemical Company Inc., Connecticut, USA.
	XNBR	Krynac X7.50 % COOH: 7 % ACN: 34 ML_{1+4}: 50	Polysar Ltd., Sarnia, Canada.
cis-1,4-Polybutadiene	BR	Cisamer % cis-1,4: 96 ML_{1+4}: 42	Indian Petrochemicals Ltd., Baroda, India.
Dioctyl phthalate	DOP	PVC-plasticizer mol. wt: 390.57	Ranbaxy Laboratories Ltd., Punjab, India.
Tribasic lead sulfate	TBLS	PVC stabilizer sp.gr.: 6.5	Waldies Ltd., Calcutta, India.

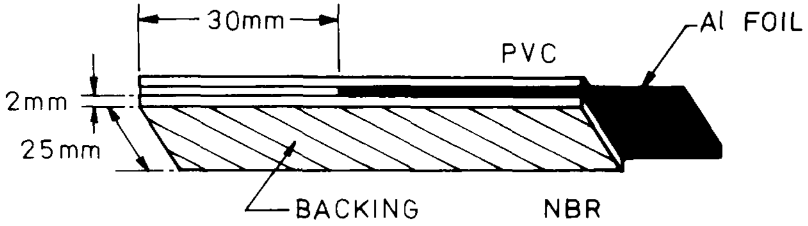

FIGURE 1 Geometry of the PVC-NBR joints.

aluminium foils at 180°C for 5 min. The PVC was plasticized using dioctyl phthalate (40 wt%) in a Brabender Plasticorder at 180°C for 6 minutes at 70 rpm. Whenever a stabilizer was used, it was thoroughly mixed with the PVC powder before the incorporation of the plasticizer. Plasticization allows easier handling of the specimens during molding and testing. The plasticized PVC sheets were also prepared by compression molding at 180°C for two minutes. Unless otherwise specified, PVC refers to the plasticized PVC.

All of the samples were stored at room temperature for 24 hr. before being cut into 25 mm wide pieces. The joints were prepared by combining the surfaces of PVC and the rubber specimens, at different contact times and temperatures under pressure (0.2 MPa) in a Labopress. A small piece of aluminium foil placed between the two sheets (Fig.1) during molding provides arms for the peel tests.

For infrared spectroscopic studies, a melt-mixed blend of PVC and NBR (50/50 by wt) was prepared in a Brabender Plasicorder at 180°C and 60 rpm for 4 min. Thin films for the analysis were prepared by compression molding the samples between aluminium foils at 150°C for 2 and 60 min.

(b) Measurement of Peel Adhesion

The peel strength as measured by a T-peel test in an Instron Universal Testing Machine, model 1195, is expressed as the peel fracture energy G,

$$G = 2F/\omega \qquad (1)$$

where F is average force to separate the joints and ω is the width of the specimen.[8] The fracture energy is the sum of the intrinsic work of adhesion or cohesion and the bulk energy dissipated in the stripping member.[8] The peel rates were 0.5, 5 and 50 mm/min.

A temperature cabinet was used to achieve higher temperatures. However, tests could not be carried out above 100°C, because the PVC phase became the locus of failure as it softens at high temperatures.

Five specimens were tested for each condition. A minimum of 25 mm of the joint was separated in each case and the average force was calculated as the median from the force-displacement traces. The reproducibility of the results may be expressed from the differences of the test values from the average. The 95% confidence level has been approximated to be 20% of the average measured force.

Infrared (IR) spectra were obtained in a Perkin Elmer IR spectrophotometer, model 843, on thin films at a resolution of 2.40 cm^{-1}.

RESULTS AND DISCUSSION

(a) Effect of ACN Content and Carboxyl Group in NBR

Table II gives the peel fracture energy of the different PVC-rubber joints, tested at a peel rate of 50 mm/min at 25°C. The peel fracture energy of the PVC-polybutadiene rubber (BR) joints is quite low, of the order of 0.01–0.02 KJ/m^2 (0.25–0.5 N/25mm), as compared with the 0.5–2 KJ/m^2 (12.5–50 N/25mm) of the PVC-NBR joints. This may be attributed to the compatibility of the PVC-NBR system and to the existence of strong dipole interactions due to the polar ACN group.[3–5] The compatibility leads to intermolecular diffusion across the interface, as suggested by Voyutskii.[9] When XNBR was the adherend, the peel fracture energy increased further. The presence of carboxyl groups in adherends is known to improve the joint strength because of strong intermolecular interaction.[10,11]

(b) Effect of Stabilizer and Plasticizer in PVC

In the presence of a stabilizer such as TBLS in PVC, there was a slight decrease in the peel fracture energy as shown in Table II. The stabilizer is thought to block the reactive sites in PVC,[12] which could reduce the chances of dipolar interactions in the PVC-NBR system.

The flexibility of the adherend is an important factor in the attainment of molecular level contact, which is a necessary condition for good adhesion. This is shown in the marked decrease in the peel fracture energy of rigid PVC-NBR joints (Table

TABLE II
Peel fracture energy of different PVC-rubber joints.
Contact time: 5 min., Peel rate: 50 mm/min, at 25°C

	Contact temperature (°C)			
	35	50	100	150
Joint	Peel fracture energy (kJ/m^2)			
PVC-BR	0.01	—	0.02	—
PVC-NBR_1	0.52	0.48	1.10	3.15*
PVC-NBR_2	0.57	0.59	1.56	3.54*
PVC-NBR_3	0.78	0.71	1.81	3.98*
PVC-XNBR	3.12	3.08	9.26*	9.84*
†PVC_s-NBR_2	0.51	0.57	1.26	3.78*
‡PVC_r-NBR_2	0.20	0.30	0.94	1.01

*cohesive failure.
†denotes PVC phase that is plasticized and stabilized.
‡denotes rigid PVC phase.

II). Plasticized PVC can easily deform at low temperatures so as to adjust the microirregularities on the surface, while rigid PVC requires a high temperature for the same.

(c) Effect of Contact Time and Temperature

The dependence of peel fracture energy on contact time and temperature is shown in Table III, for PVC-NBR_2 joints. The fracture energy was found to be independent of the contact time. This may be attributed to the compatibility of the system, which imparts substantial interpenetration within a few seconds of contact.[13]

The peel fracture energy increases progressively with increase in contact temperature. At low contact temperatures (35°, 50°, 100°C), the joints failed (visually) at the interface, *i.e.*, clean separation of the two adherends as shown in Figure 3a. However, at higher temperature of contact (150°C), the rubber phase became the locus of failure, indicating a strong interface (Fig. 3b). The formation of various topological coupling forms (entanglements, local kinks and entwining, and long range loops) by similar or dissimilar polymer chains across an interface has been established.[14,15] Thus the transition to cohesive failure may be due to a strong entanglement network formed across the interface at higher temperatures. Alternatively, there may be the formation of chemical bonds across the interface at high contact temperatures and time, as shown in the case of PVC-NBR blends.[6] To establish this, experiments were done on PVC-NBR_2 joints at different peel rates, temperatures and also after swelling the joints in toluene.

(d) Effect of Peel and Test Temperature

Table IV shows the variation of peel fracture energy with peel rate and test temperature for PVC-NBR_2 joints. As the peel rate is reduced, the mode of failure changes from cohesive (Fig. 2b and 3ii) to interfacial (Fig. 2a and 3i) (visually determined) for all samples except those molded at 150°C for 60 minutes. Such a transition from cohesive to interfacial failure has earlier been observed. It was attributed to the difference in the peel rate and the time interval required for disentanglement of interdiffused chains.[16,17]

TABLE III
Effect of contact time and temperature on the peel fracture energy of PVC-NBR_2 joints. Peel rate: 50 mm/min. at 25°C

Contact temperature	Contact time (min.)			
	5	30	60	120
(°C)	Peel fracture energy (kJ/m^2)			
35	0.57	0.57	0.53	0.55
50	0.59	0.65	0.67	0.65
100	1.56	1.48	3.98*	3.98*
150	3.98*	3.98*	3.98*	3.98*

*cohesive failure.

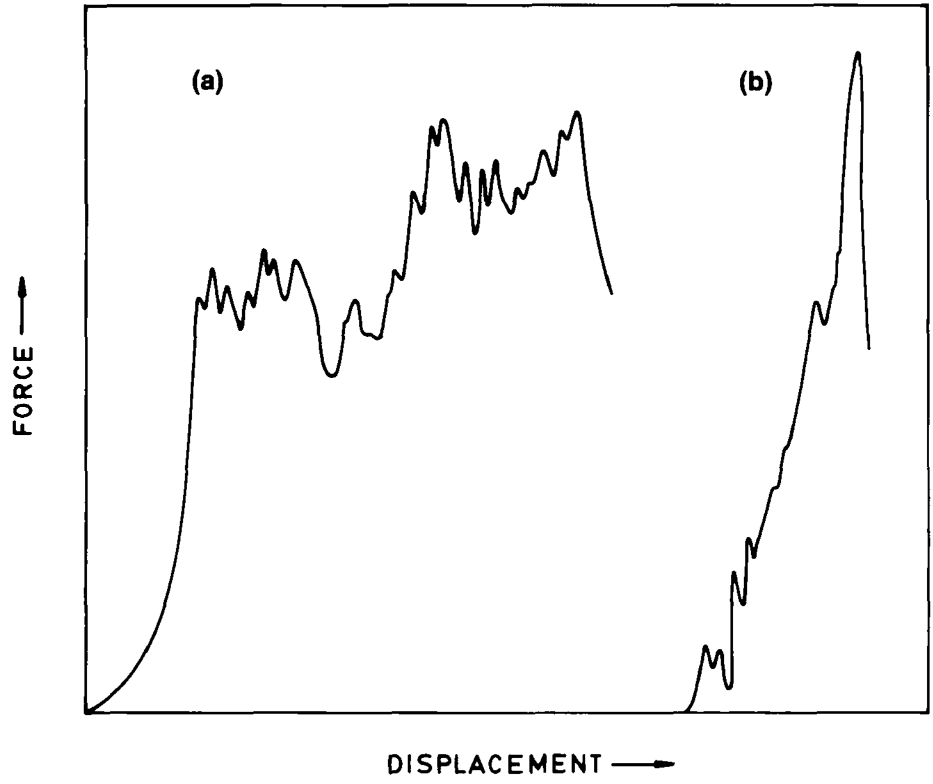

FIGURE 2 Typical peel patterns of PVC-NBR joints: (a) interfacial and (b) cohesive type.

TABLE IV
Effect of peel rate and test temperature on the peel fracture energy of PVC-NBR$_2$ joints. Contact time: 5 and 60 min. (data in parentheses correspond to 60 min.)

Contact temperature (°C)	Peel rate (mm/min)	Test temperature (°C) 25	50	75	100
		Peel fracture energy (kJ/m^2)			
35	50	0.57 (0.53)	0.22 (0.22)	0.21 (0.12)	0.18 (0.11)
	5	0.20 (0.15)	0.11 (0.08)	0.10 (0.05)	0.06 (0.04)
	0.5	0.09 (0.07)	0.07 (0.04)	0.03 (0.02)	0.03 (0.02)
100	50	1.56 (3.98*)	0.70 (0.76)	0.41 (0.28)	0.38 (0.20)
	5	0.41 (0.68)	0.36 (0.32)	0.22 (0.12)	0.21 (0.08)
	0.5	0.20 (0.55)	0.17 (0.14)	0.16 (0.08)	0.13 (0.06)

*cohesive failure.

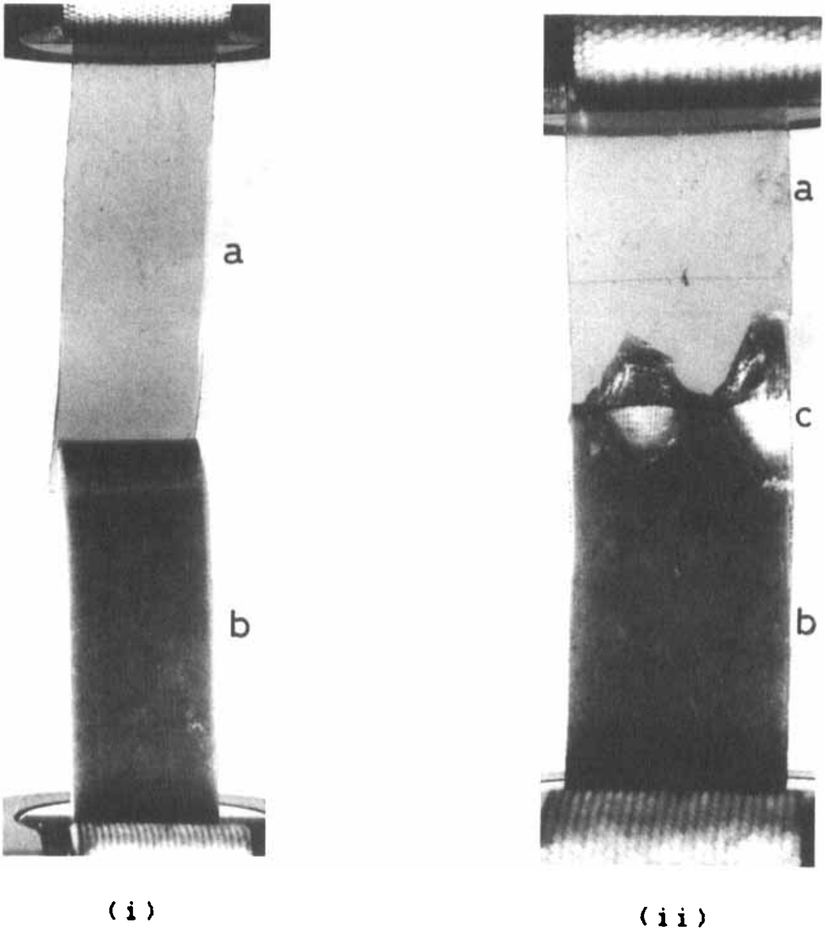

FIGURE 3 Photographs showing (i) interfacial failure and (ii) cohesive failure, of PVC-NBR joints. a) PVC, b) NBR and c) fabric backing.

As the testing temperature is increased, the peel fracture energy is found to decrease (as with decreasing peel rates). This is due to the enhancement of the chain mobility at higher temperature which minimizes the effect of entanglements as the so-called threshold condition is approached.[8] However, even at 100°C and 0.5 mm/min., the specimens molded at 150°C for 60 min. underwent cohesive failure.

(e) Effect of Swelling

Swelling of the joints is expected to nullify the effect of all types of physical entanglements; however, not that of chemical bonds, if any, at the interface. Hence, the

TABLE V
Effect of swelling (in toluene for 48 hr.) on the peel fracture energy of PVC-NBR$_2$ joints. Contact time: 60 min.

Adherend	Contact temperature (°C)	Before swelling		After swelling	
		Peel fracture energy (kJ/m^2)			
		0.5 mm/min	50 mm/min	0.5 mm/min	50 mm/min
PVC-NBR$_2$	35	0.07	0.53	0.03	0.07
	100	0.55	3.98*	0.12	0.62
	150	1.32*	3.98*	0.98*	3.62*
†PVC$_s$-NBR$_2$	150	1.32*	3.78*	0.28	0.78

*cohesive failure.
†denotes PVC that is plasticized and stabilized.

PVC-NBR$_2$ joints were kept immersed in toluene for 48 hours at 35°C, with fresh solvent replacement at every 12 hours. The joints were taken out and tested immediately. The results are summarized in Table V. The joints after swelling show a sharp reduction in the fracture energy, as the contribution from the bulk energy dissipation and the effect of entanglements become negligible. However, the joints made a 150°C and 60 min. fractured cohesively, though at a lower fracture energy than before swelling.

(f) IR Spectroscopic Studies

The infrared spectra of the blend of PVC and NBR (50/50 by wt) prepared at 150°C were analyzed to study the possibility of chemical interaction. Figure 4 shows the IR spectra of this blend molded at 150°C for 2 and 60 minutes. The changes in the absorbance in the regions 3500–2900 cm^{-1} and 1750–1500 cm^{-1}, correspond to the chemical interaction between the functional groups in the system. The broadening of the peak at 3500–2900 cm^{-1} is assigned to N—H and O—H bonds, formed by the hydrolysis of the ACN (C$\equiv$N) group in the presence of HCl liberated during thermal degradation of the PVC.[6] The peaks at 2946 and 2222 cm^{-1} correspond to the C—H and C$\equiv$N stretching vibrations, respectively.[18] The increase in absorbance at 1730 cm^{-1} may be attributed to the formation of amide, acid and/or ester groups in the system. The amide and ester crosslinks are thus formed via the reaction between the allylic chlorines in PVC and amide/acid groups in NBR.[6] The reduction in the peak at 1532 cm^{-1} may be due to the ring opening of the triazine derivatives in NBR, formed by the cyclization of the nitrile groups.[19] The different amide bands could not be distinguished from the C=C stretching vibrations.

This suggests the possible chemical interaction between the reactive groups in the interdiffused chains across the interface in the joints, at high contact temperatures and time. The fact that stabilized PVC-NBR joints which failed cohesively at high test temperatures were separated at the interface after swelling, shows that the stabilizer prevents the chemical interaction as also seen in the case of PVC/NBR blends.[6] Such a type of chemical interaction across the interface, where each

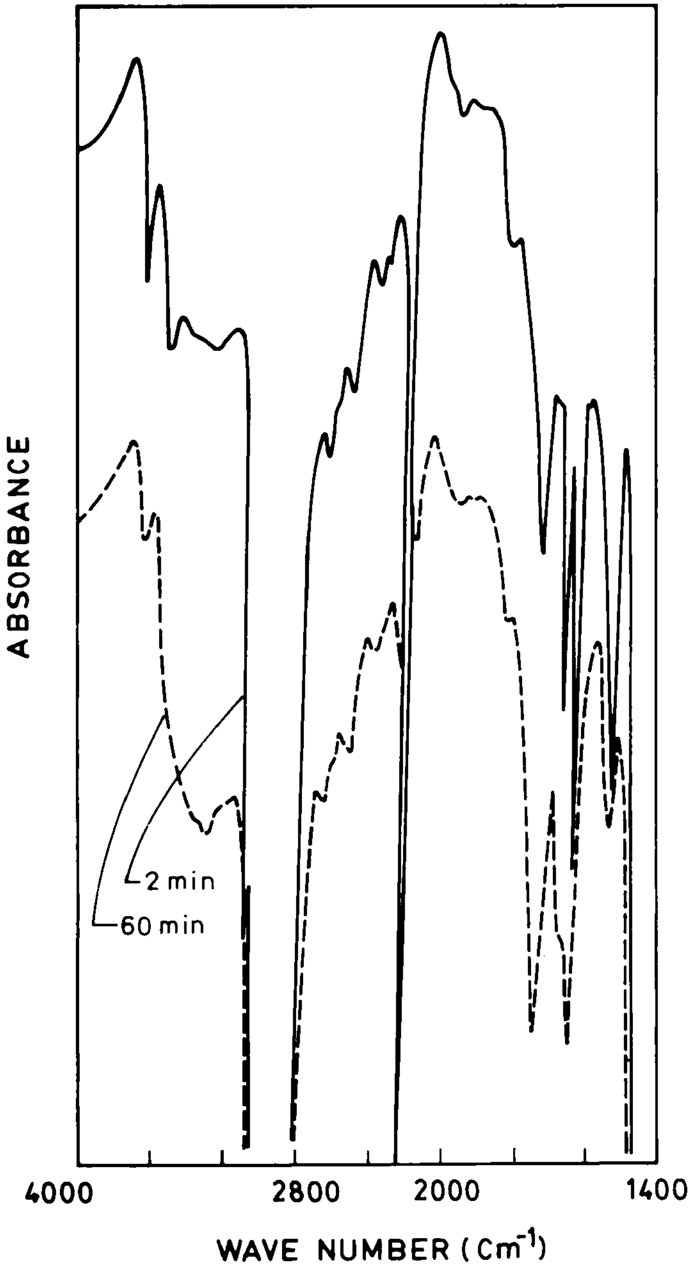

FIGURE 4 Infrared spectra of PVC-NBR blends (50/50 by wt.) molded at 150°C for 2 and 60 min.

substrate contains a component which can diffuse to the interface and chemically interact, thereby coupling the two adherends, has been reported.[20-22] Such an interface becomes a new physical entity rather than just a physical blend.[7] As a result, the interface becomes stronger than the rubber matrix which fails under stress, with the interface remaining intact.

CONCLUSION

The adhesion between PVC and nitrile rubber depends on the acrylonitrile content and presence of the carboxyl group in the rubber phase. The plasticization of PVC also improves the adhesion. In addition to molecular diffusion and entanglements, at high contact temperatures and long contact times chemical interaction between the reactive groups in the two phases takes place, especially at the interface, as established by swelling and IR spectroscopic studies. A PVC stabilizer (TBLS) prevents this type of interaction.

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