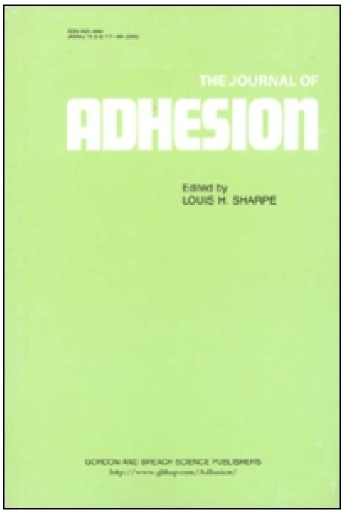

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Reusable Dry Adhesive: Aluminium–Aluminium Bonding by Self-Vulcanisable Blend Based on Carboxylated Nitrile Rubber and Chlorobutyl Rubber

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A self-vulcanisable blend of chlorobutyl rubber and carboxylated nitrile rubber can be used as an adhesive for aluminium–aluminium bonding. The peel strength depends on the state of cure of the adhesive, testing temperature and carboxyl content of the carboxylated nitrile rubber. At moulding times below 15 minutes, the adhesive was found to be reusable after repeated post-peel mouldings.

KEY WORDS Dry adhesive; reusable; aluminium–aluminium bonding; self vulcanisable rubber blend; state of cure.

1 INTRODUCTION

Recently De and coworkers have developed novel self-vulcanisable blends based on rubbers with reactive groups.[1–4] During processing some of these blends were found to be extremely "sticky" on metal surfaces. One such blend is based on carboxylated nitrile rubber and chlorobutyl rubber. In the present communication, we report the results of our studies on the use of this rubber blend as an adhesive for bonding two aluminium foils. Use of flexible aluminium foils enabled us to determine the adhesive strength by a 180° peel test.[5]

The novelty of this adhesive system lies in its reusability, high strength and reproducibility. Earlier it has been reported that an adhesive based on carboxylated rubber and chlorinated rubber can cause metal bonding.[6–14]

2 EXPERIMENTAL

2.1 Materials used

The aluminium foils (thickness 0.05 mm, hardness 52.70 V.P.N.) were obtained from INDAL, Bombay. Chlorobutyl rubber (CIIR) used was chlorobutyl 1168

(Chlorine content, wt.% 1.2) of Exxon Chemical Company, U.S.A. Carboxylated nitrile rubber (XNBR) used was Krynac 231 of Polysar Ltd, Canada. In order to study the effect of carboxyl content of XNBR on metal–metal bonding, we also used two other grades of XNBR, namely Krynac 221 and Krynac 110 carboxyl content of XNBR follows the order, Krynac 231 > Krynac 221 > Krynac 110.

2.2 Preparation of the rubber blend

CIIR was first masticated for one minute in a 14″ × 6″ (35.5 cm × 15.2 cm) two roll mill. Next, XNBR was blended with CIIR and further masticated for 8 minutes. A blend thus prepared is ready for use as a bonding agent between the metal foils. In order to characterise the blend, Mooney viscosity of both blend and neat rubbers was determined according to ASTM D 1646-1963 using a Negretti Automation Mooney Shearing disc viscometer, model MK-III. In order to confirm that such a blend undergoes self-vulcanisation during moulding at high temperature, we took a rheograph of the blend on a Monsanto Rheometer R-100.

2.3 Preparation of the composite

Aluminium foils were cut into 150 × 200 mm sizes and cleaned with acetone. 3 gm of the rubber blend was passed four times through the two-roll mill at the closest

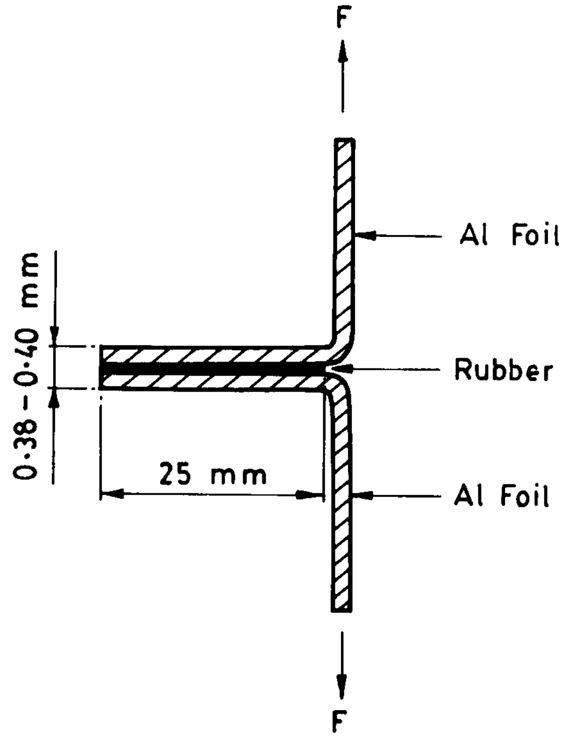


FIGURE 1 Schematic diagram of the test specimen.

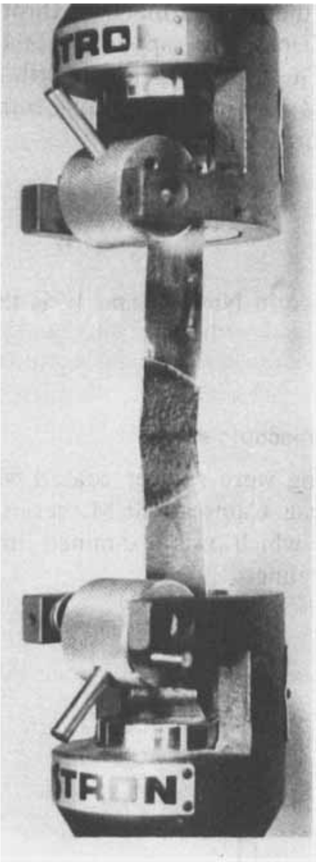


FIGURE 2 Photograph showing the test specimen fixed to the grip of the Instron UTM.

nip gap and a thin rubber layer was obtained. This rubber layer was put in between the two aluminium foils. This assembly was then kept under pressure in a rubber moulding press. A part of the metal foil assembly was not filled with rubber and was kept outside the mould during moulding and this part was fixed with the grip of the Instron machine during testing of the adhesive strength. The dimensions of the test specimen were 100 × 25 mm., while the bonded region was 50 × 25 mm. Figure 1 shows the details of the test specimen. Figure 2 is the photograph showing the whole assembly fixed in the grip of the Instron UTM.

The composites were moulded for different times, temperatures and pressures. The thickness of the adhesive layer was measured by scanning electron microscopy studies of a peeled sample, where failure took place from rubber to metal. The thickness of the adhesive layer could be varied by changing moulding pressure as shown in Table III.

2.4 Determination of 180° peel strength of the composite

The 180° peel strength was determined in accordance with ASTM D 413 using an Instron Universal Testing Machine model 1195. The test specimen was fitted horizontally to the grip of the Instron machine through the non-bonded part of the metal foils. A steady load was applied at the rate of 50 mm/min until separation was complete. The average peel strength in terms of force/width was calculated from the plot of force *versus* displacement obtained in the Instron machine according to the formula,

$$\text{Peel strength} = \frac{2F}{W}$$

where F is the average force in Newton and W is the width of the specimen in meters.

2.5 Scanning electron microscopic study

Test specimens after peeling were sputter coated with gold within 24 hours of peeling and studied under a Camscan SEM, series 2DV. Figure 3 shows the section of the composite which was examined under the scanning electron microscope (SEM) after peeling.

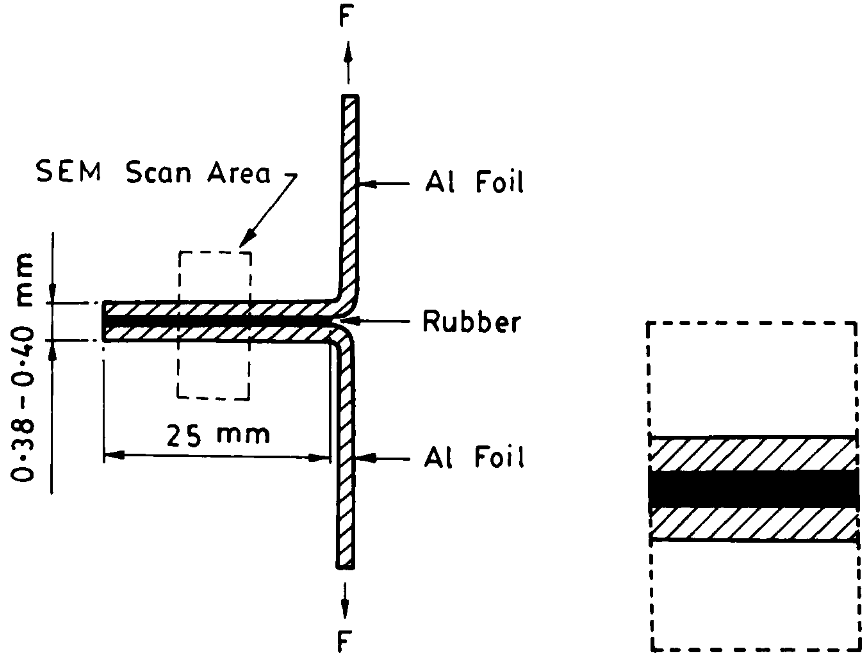


FIGURE 3 Section of the composite for SEM scan.

3. RESULTS AND DISCUSSION

Mooney viscosity values of CIIR, XNBR and the 1:1 blend were 50, 30 and 10 respectively. Low viscosity of the blend ensures its free flow while placed in between the two aluminium foils prior to being self-crosslinked during moulding.

Figure 4 is the Monsanto rheograph of the 1:1 blend of CIIR and XNBR at 180°C. Increase in rheometer torque with vulcanisation time indicates progressive crosslinking. Continuous increase in rheometric torque with curing time implies that cure reversion is absent at 180°C even up to 120 minutes and that the vulcanised network is thermally stable at this temperature.

Further evidence of self-crosslinking of the two rubbers in the blend was obtained from swelling studies. Single rubbers were soluble in chloroform, but the solubility of blend in the same solvent decreases progressively with moulding time. Beyond 15 minutes moulding the blend becomes insoluble in chloroform and it only swells. The extent of swelling decreases with increase in moulding time due to progressive crosslinking.

Figure 5 shows the force-displacement plots of the aluminium–aluminium composite moulded for different times. For comparison we have also included results of two composites bonded by the single neat rubbers, CIIR and XNBR, moulded for 30 minutes. It is evident that the single rubbers do not cause aluminium–aluminium bonding and in both cases we noted rubber–metal failure during peeling. The blend of CIIR and XNBR, however, is very effective in causing this bonding and the degree of bonding or peel strength depends upon moulding time. The strength increases with increase in moulding time, reaches a maximum at 30 minutes and then decreases at longer moulding time. The results are shown in Figure 6 and summarised in Table I. The mode of failure also depends on moulding time. Rubber-to-rubber failure occurs when moulding time is below 30 minutes. During peeling, the rubber layer is uniformly distributed between the two metal foils as seen in Figure 7. At 45 minutes of moulding time, we observed a mixed type of failure in the sense that the initial mode of rubber-to-rubber failure changes to rubber-to-metal failure (Figure 8). At higher moulding times (60 min and 90 min) we observed dominance of metal-rubber failure (Figure 9) and the peel strength was also found to be low (Table I). Since at low moulding time the level of crosslinking is low, and the adhesive itself has poor strength, this causes cohesive failure in the rubber. With increase of moulding time the peel strength increases, because the strength of the adhesive layer also increases with the increase in extent of crosslinking. But there exists an optimum moulding time, where we observed the maximum peel strength. Above this optimum moulding time peel strength decreases, because the extent of crosslinking in the adhesive layer becomes high and the rubber undergoes a gradual transition from a viscoelastic state to an elastomeric solid and loses its ability to adhere to the metal surface. Thus, metal–rubber failure occurs.

Figure 10 is the SEM picture showing the failure surface of the composite and Figure 11 is the aluminium X-ray mapping of the same failure surface. In Figure 10, no sharp boundary could be seen between rubber and metal. Figure 11

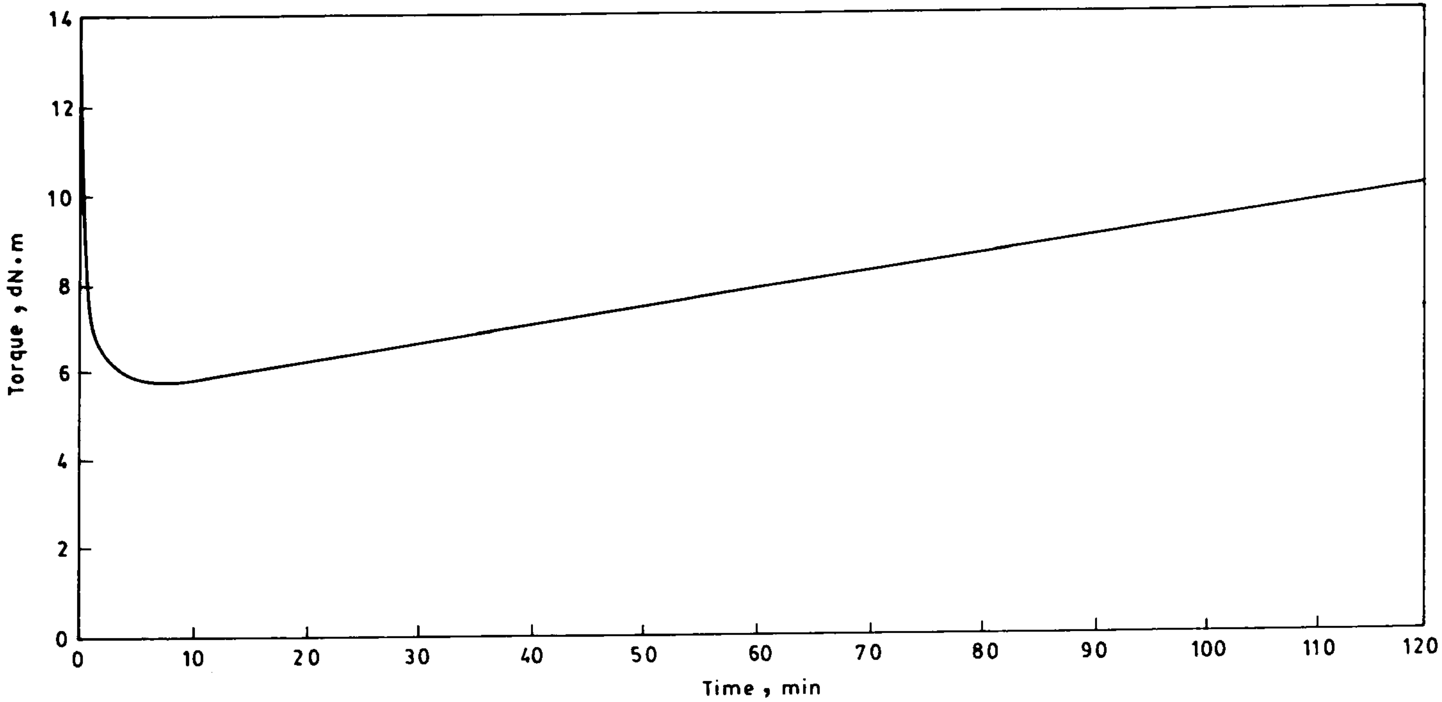


FIGURE 4 Monsanto rheograph of 1:1 blend of chlorobutyl rubber and carboxylated nitrile rubber at 180°C.

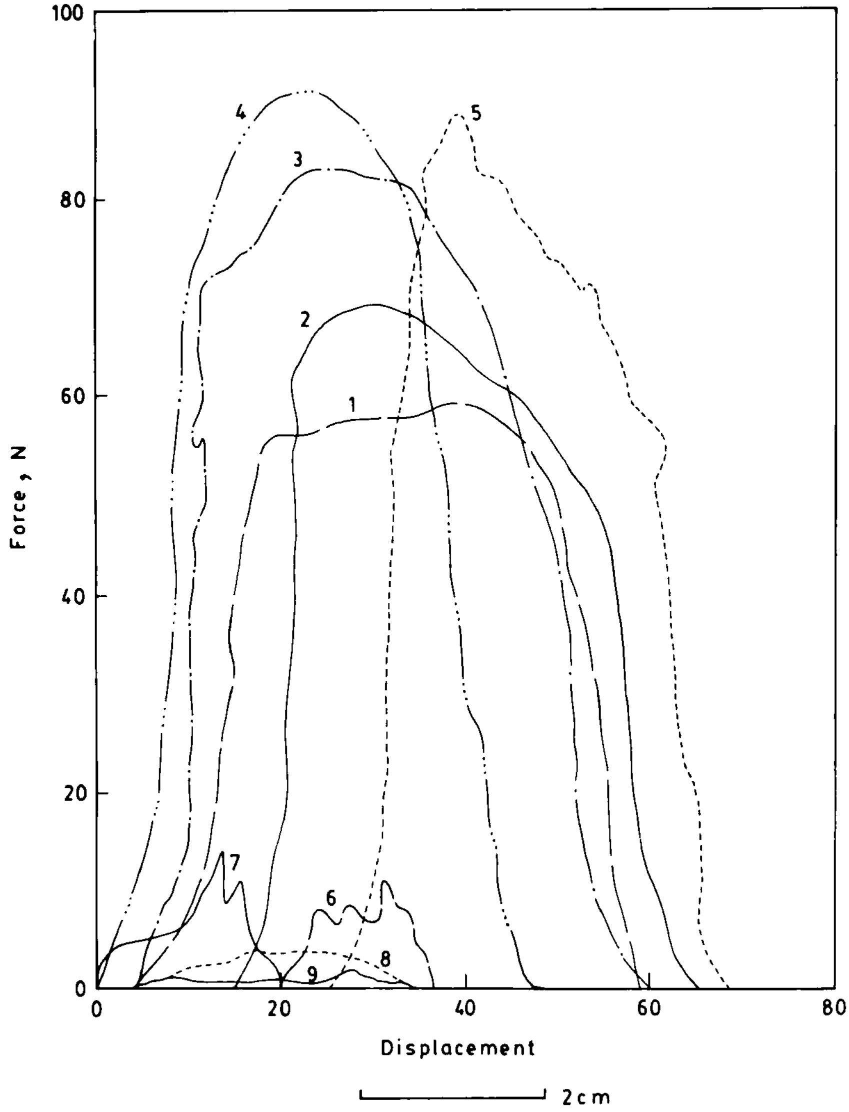


FIGURE 5 Force-displacement plots for composites prepared at varying moulding times. 1, 5 min; 2, 10 min; 3, 15 min; 4, 30 min; 5, 45 min; 6, 60 min; 7, 90 min; 8, XNBR alone, 30 min; 9, CIIR alone, 30 min.

indicates that the soft rubber blend might have diffused into the aluminium surface during the early stages of moulding.

Reusability of the rubber blend as a dry adhesive was tested by moulding the peeled samples for consecutive times. For example, in Figure 12(a) curve 1 shows the force-displacement plot of the composite moulded for a second time (5 min., 180°C) after the first peeling was over. Curves 3 and 4 are similar plots after third

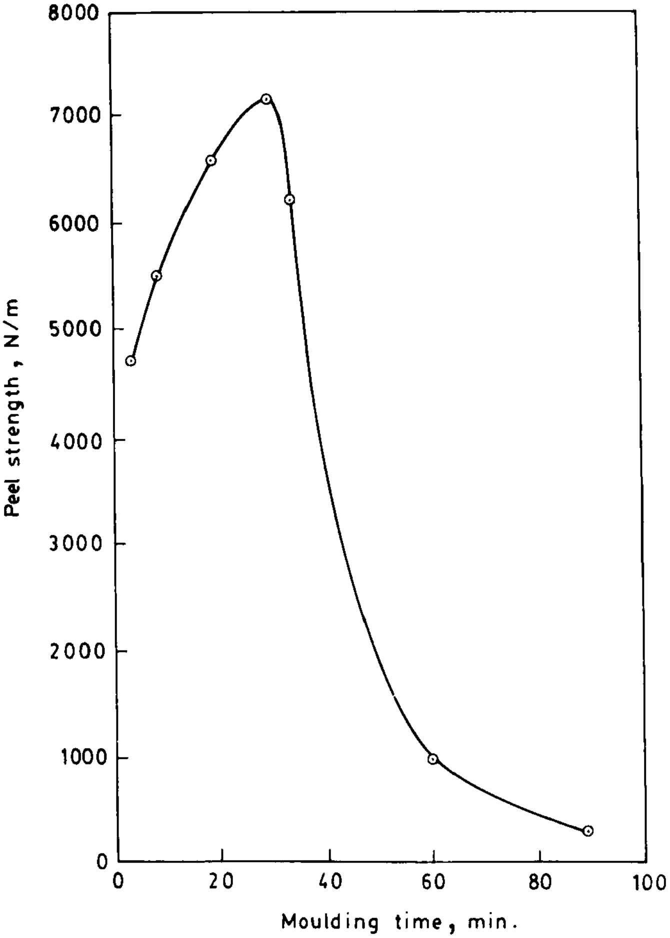


FIGURE 6 Dependence of peel strength on moulding time.

TABLE I
Dependence of peel strength on moulding time[a]

Moulding time (min)	Peel strength (N/m)	Mode of failure
5	4800	Rubber to rubber
10	5600	Rubber to rubber
15	6640	Rubber to rubber
30	7200	Rubber to rubber
45	6240	Combination of rubber–rubber and rubber–metal
60	960	Rubber to metal
90	400	Rubber to metal

[a] Composites moulded at 180°C under a pressure of 50 psi (344 kPa).

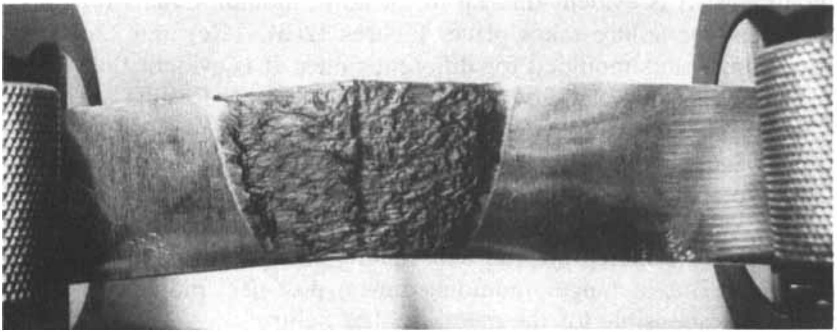


FIGURE 7 Rubber-rubber cohesive failure.

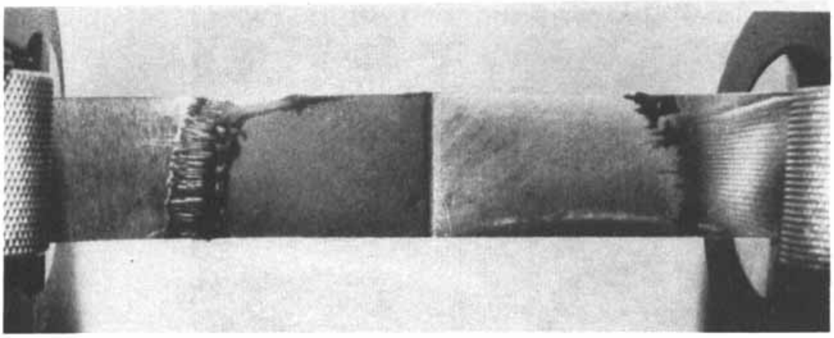


FIGURE 8 Rubber-metal adhesive failure.

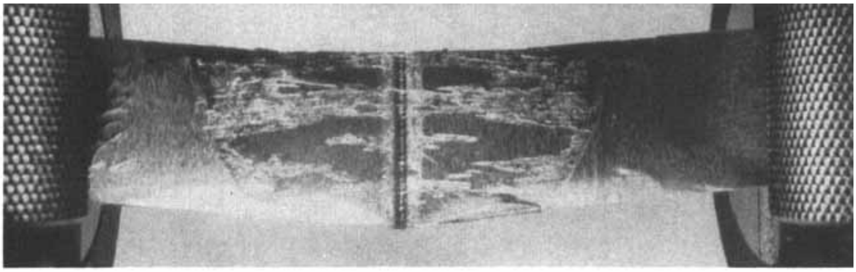


FIGURE 9 Combination of rubber-rubber and rubber-metal failure.

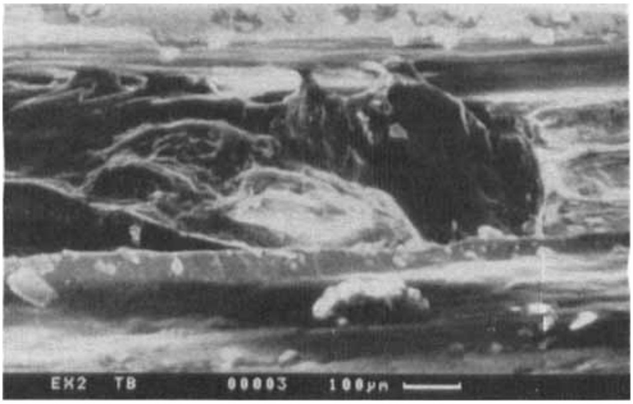


FIGURE 10 SEM photograph showing the failure surface.

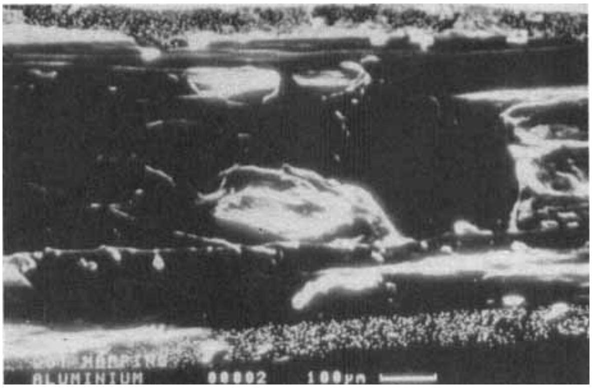
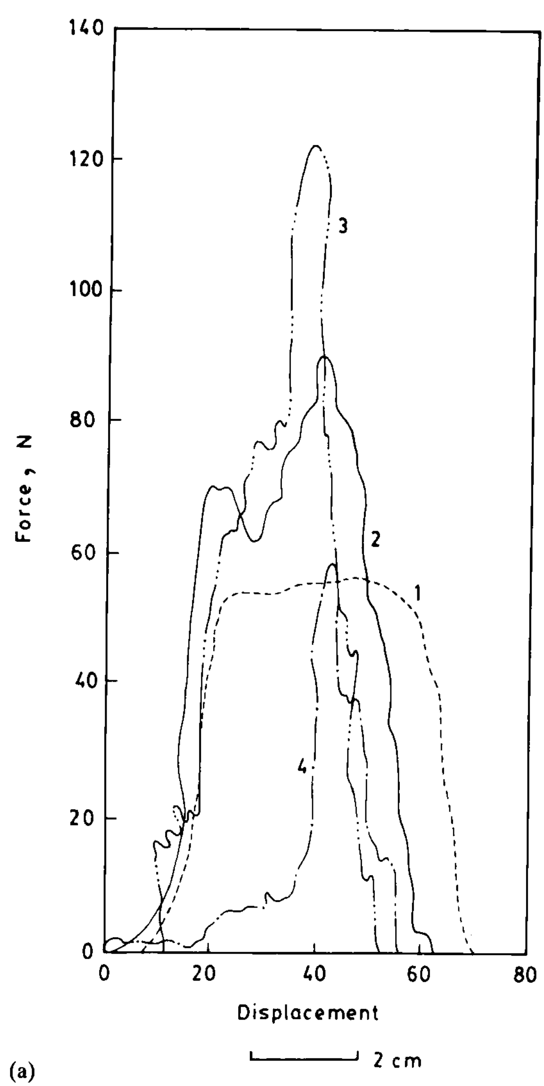


FIGURE 11 Aluminium X-ray mapping of the failure surface.

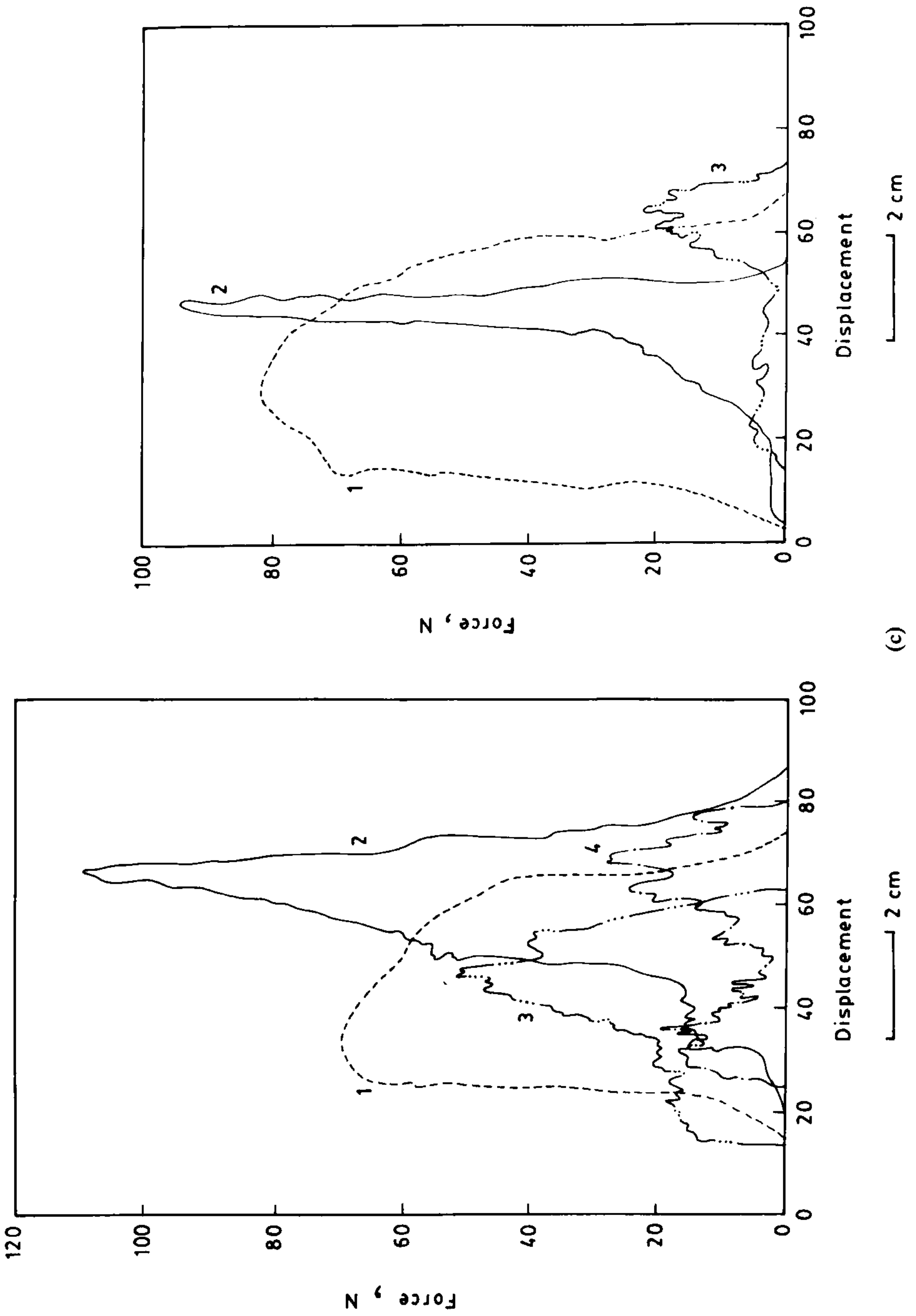
and fourth mouldings. It is evident that up to the third moulding the strength is high and rubber–rubber failure takes place. Figures 12(b), 12(c) and 12(d) are similar plots for composites moulded for different times. It is evident that when moulding time increases, recyclability progressively decreases. Results are summarised in Table II. Since the extent of crosslinking in the adhesive layer increases with the increase of moulding time, peel strength increases when the layer is subjected to a second moulding after the first peel testing. This is true in the case of 5 mins or 10 mins moulding time because at such short moulding time the rubber was grossly undercured and subsequent post-peel mouldings cause increase in strength. But at longer moulding times, post-peel moulding causes overcuring which is responsible for the metal–rubber failure.

Peel strength depends on moulding temperature. Figure 13 is the plot of peel strength *versus* moulding temperature at constant moulding time (30 minutes). At low moulding temperature, a 30 min moulding time is not enough for the



(a)

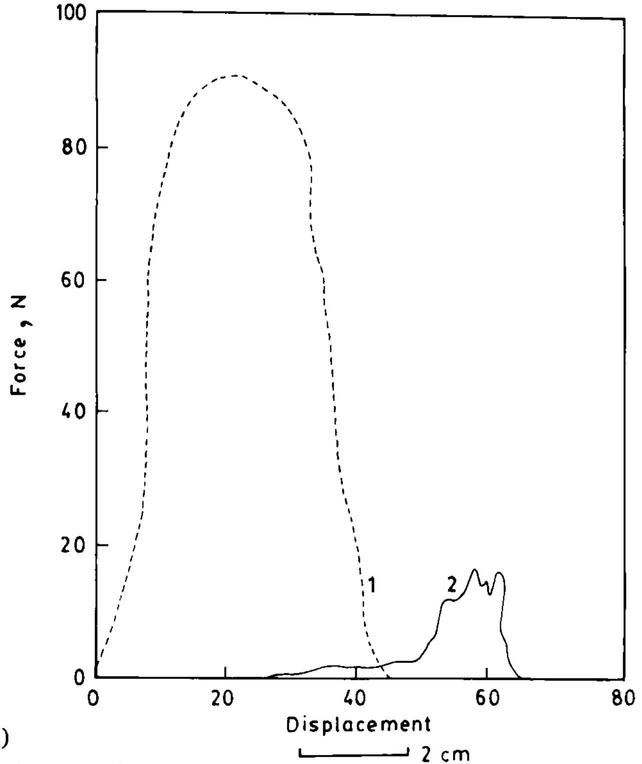
FIGURE 12 (a) Dependence of peel strength on post-peel mouldings for composite moulded for 5 mins. 1, original composite; 2, second moulding after first-time peel; 3, third moulding after second time peel; 4, fourth moulding after third time peel. (b) Dependence of peel strength on post-peel mouldings for composite moulded for 10 mins. 1, original composite; 2, second moulding after first time peel; 3, third moulding after second time peel; 4, fourth moulding after third time peel. (c) Dependence of peel strength on post-peel mouldings for composite moulded for 15 mins. 1, original composite; 2, second moulding after first time peel; 3, third moulding after second time peel. (d) Dependence of peel strength on post-peel mouldings for composite moulded for 30 mins. 1, original composite; 2, second moulding after first time peel.



(c)

(b)

FIGURE 12 (Continued)



(d)

FIGURE 12 (Continued)

TABLE II
Dependence of peel strength on post-peel mouldings

Moulding time (min)	No. of Peels[a]	Peel strength (N/m)	Mode of failure
5	Original composite	4800	Rubber to rubber
	1	6304	Rubber to rubber
	2	4860	Combination of rubber to rubber and rubber to metal
	3	2400	Rubber to rubber followed by rubber to metal
10	Original composite	5600	Rubber to rubber
	1	6400	Mainly rubber to rubber but at the later stage rubber to metal
	2	2560	Initially rubber to rubber, shifting to rubber to metal at the end
	3	1280	Rubber to metal
15	Original composite	6640	Rubber to rubber
	1	3520	Initially rubber to rubber, followed by rubber to metal
	2	1080	Rubber to metal
30	Original composite	7200	Rubber to rubber
	1	984	Rubber to metal

[a] 1 means second moulding after first time peel; 2 means third moulding after second time peel; 3 means fourth moulding after third time peel.

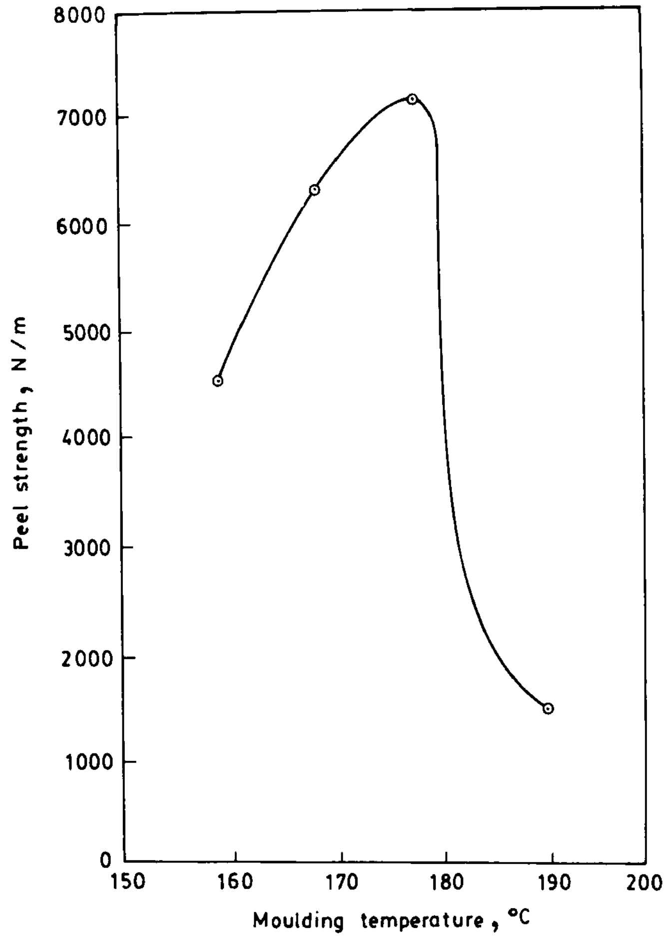


FIGURE 13 Dependence of peel strength on moulding temperature. Moulding time, 30 min, moulding pressure 25 psi (172 kPa).

optimum level of curing, so the strength is low, whereas at high temperature (*e.g.*, 190°C) a 30 min moulding time is beyond the optimum level and the strength is again poor. Adhesive layer thickness was found to have an important influence on the peel strength (Figure 14). With the increase of adhesive layer thickness peel strength increases, (Table III) which shows that more energy is dissipated in a larger volume of adhesive. Maximum adhesive strength of 8064 N/m was obtained when moulding was done at 180°C under 25 psi for 30 mins and when the adhesive layer thickness was 0.75 mm.

Carboxyl content of XNBR was found to have a profound influence on peel strength. Force-displacement plots for composites prepared with different grades of XNBR are shown in Figure 15. Krynac 231 with high carboxyl content shows rubber–rubber failure whereas Krynac 110 with low carboxyl content shows

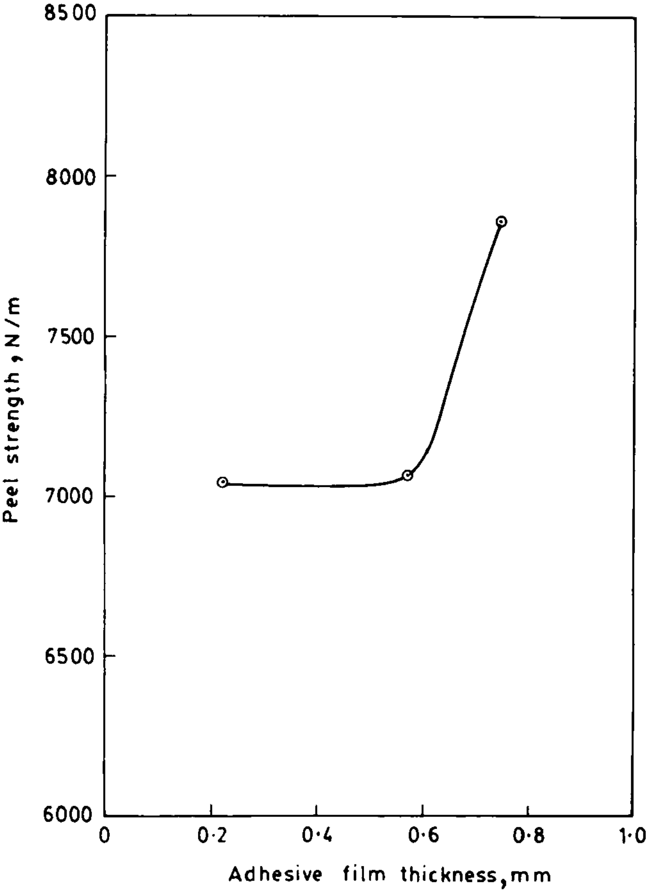


FIGURE 14 Effect of adhesive film thickness on the peel strength. Moulding time, 30 min; Moulding temperature, 180°C.

TABLE III
Dependence of peel strength on the adhesive film thickness[a]

Moulding press (psi)	Adhesive film thickness (mm)	Peel strength (N/m)	Nature of failure
25	0.75	8064	Rubber to rubber
50	0.57	7200	Rubber to rubber
100	0.22	7040	Rubber to rubber

[a] Moulding temperature 180°C; Moulding time 30 min.

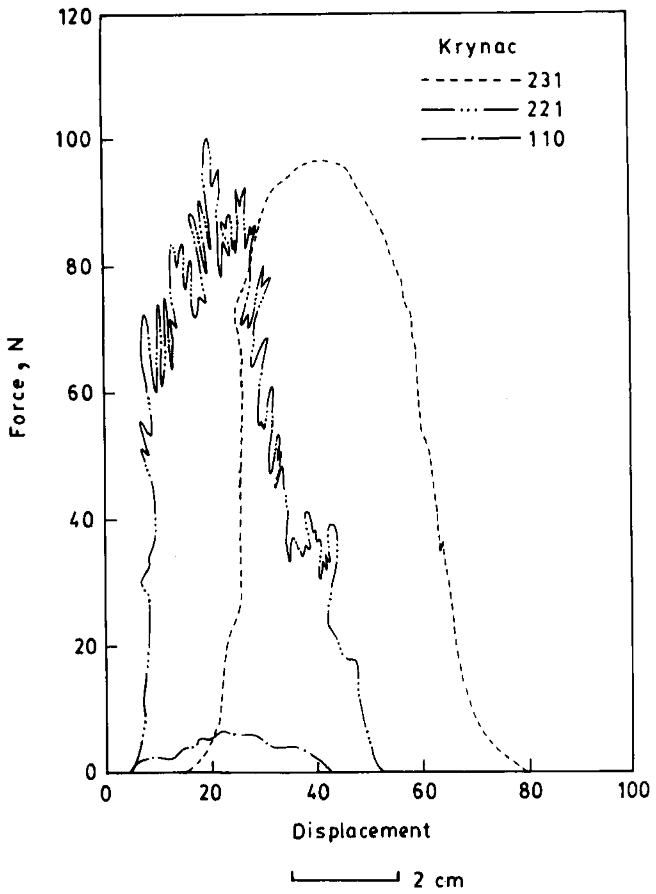


FIGURE 15 Force-displacement plots for composites prepared with XNBR of varying carboxyl content.

TABLE IV
Dependence of peel strength on carboxyl content of carboxylated nitrile rubber[a]

Grade of XNBR	Carboxyl content	Peel strength[a] (N/m)	Mode of failure
231	high	7200	Rubber to rubber
221	medium	5600	Combination of rubber to rubber and rubber to metal
110	low	240	Rubber to metal

[a] Composites moulded at 180°C for 30 min under 50 psi pressure.

TABLE V
Dependence of peel strength on the testing temperature

	Testing temperature					
	Room temperature[a]		50°C		70°C	
Moulding time (min)	Peel strength (N/m)	Nature of failure	Peel strength (N/m)	Nature of failure	Peel strength (N/m)	Nature of failure
5	4800	Rubber to rubber	880	Rubber to rubber	480	Rubber to rubber
10	5600	Rubber to rubber	1200	Rubber to rubber	560	Rubber to rubber
15	6640	Rubber to rubber	1520	Rubber to rubber	640	Rubber to rubber
30	1200	Rubber to rubber	1480	Rubber to rubber	800	Rubber to rubber
45	6240	Combination of rubber to rubber and rubber to metal	1424	Rubber to rubber	840	Rubber to rubber
60	960	Rubber to metal	1440	Combination of rubber–rubber and rubber–metal	800	Initially rubber to rubber, followed by rubber to metal, with preponderance of rubber to rubber
90	400	Rubber to metal	1440	Combination of rubber–rubber and rubber–metal	800	Combination of rubber–rubber and rubber–metal

[a] Values taken from Table II.

metal–rubber failure. But Krynac 221 with medium high carboxyl content shows mixed type of failure, with both rubber–rubber and rubber–metal types. Results are summarised in Table IV. With increase of the carboxyl group the polarity of the adhesive layer increases, which results in better adhesion with aluminium.[6–17]

Table V shows that when test temperature increases peel strength decreases and adhesive failure turns towards cohesive failure. At high testing temperatures of 50°C and 70°C peel strength becomes almost independent of moulding time (Figure 16). The decrease in peel energy with the increase in testing temperature implies that the dissipation of energy by the viscoelastic nature of rubber is reduced. Further work on dependence of peel strength under threshold conditions is in progress and the results will be reported in a future communication.

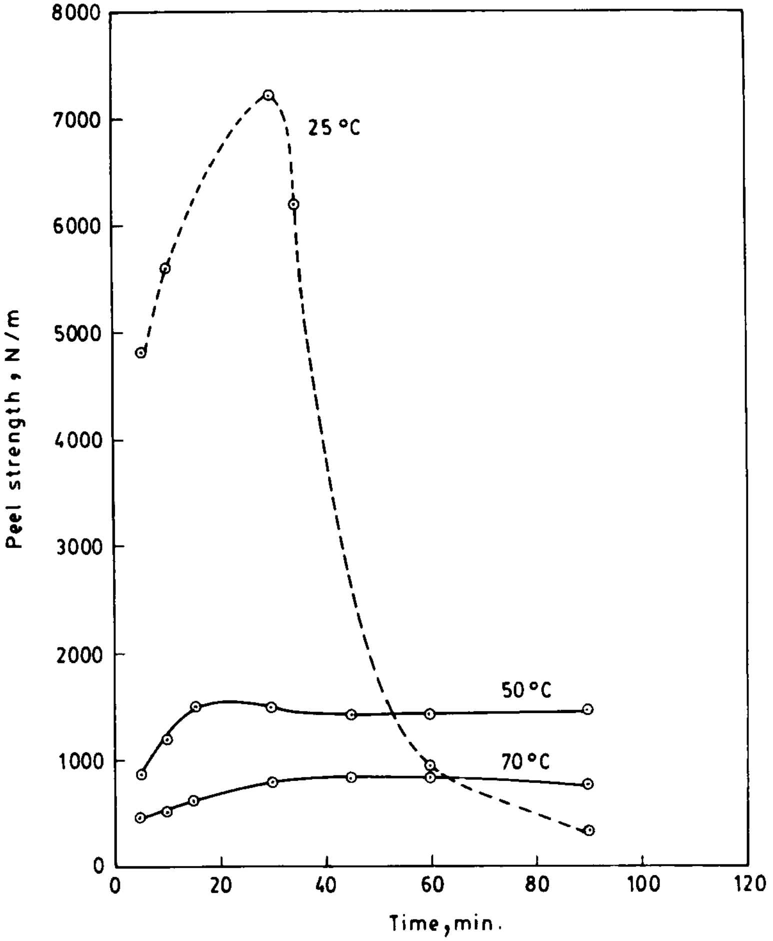


FIGURE 16 Dependence of peel strength on testing temperature.

4 CONCLUSIONS

A self-vulcanisable blend of chlorobutyl rubber and carboxylated nitrile rubber can be used for aluminium–aluminium bonding. At moulding times below 15 minutes, the adhesive was found to be reusable after repeated post-peel mouldings.

The peel strength and failure mode (cohesive, adhesive or combination of both) depend on state of cure, testing temperature and carboxyl content of the carboxylated nitrile rubber. A maximum peel strength of 8064 N/m for a 180° peel test measured at room temperature was obtained when moulding was carried out at 180°C for 30 minutes under 25 psi (172 KPa) pressure. The peel strength at higher testing temperatures (50° and 70°C) is independent of moulding time and the failure mode is of the adhesive type.

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