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The Use of Carboxy Terminated Liquid Natural Rubber (CTNR) as an Adhesive in Bonding Rubber to Rigid and Non-rigid Substrates

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ABSTRACT: Carboxy Terminated Liquid Natural Rubber (CTNR) was prepared by photochemical reaction using maleic anhydride and masticated natural rubber (NR). The use of CTNR as an adhesive in bonding rubber to rubber and rubber to metal was studied. The peel strengths and lap shear strengths of the adherends which were bonded using CTNR were determined. The effect of using a tri isocyanate with CTNR in rubber to metal bonding was also studied. It is found that CTNR can effectively be used in bonding rubber to rubber and rubber to mild steel.

KEY WORDS: CTNR, adhesion, rubber to rubber bonding, rubber to metal bonding.

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INTRODUCTION

THE DEVELOPMENT OF rubber based adhesives used for high strength structural applications like aircraft, automotives and other industries is the subject of active attention. The prospects and possibility of using carboxylated elastomers in bonding rubber to rigid and non-rigid substrates has been summarized in the literature. The superior bonding capability of these adhesives may be due to the ability of the carboxyl group to enter into ionic, covalent and hydrogen bonding which imparts various degrees of adhesion and cross linking with cellulosics, metals, rubbers and plastics [1–4]. Here the use of carboxy terminated liquid natural rubber (CTNR) as an adhesive in bonding NR to NR, NBR to NBR, NR to mild steel and NBR to mild steel is studied. The effect of a tri isocyanate and phenol–formaldehyde resin in combination with CTNR in bonding rubber to mild steel is also investigated [5–7].

EXPERIMENTAL

Materials

Natural rubber (NR;ISNR-5) was supplied by RRII, Kottayam, Kerala, India. The compounding ingredients zinc oxide (ZnO), stearic acid, dioctyl phthalate, aromatic oil, silica, carbon black (HAF N330) were of commercial grade. Styrenated phenol, Vulkanox 4020 (*N*-phenyl *N*′(1,3-dimethyl butyl) *p*-phenylene diamine), mercapto benzothiazole (MBT), tetramethylthiuramdisulphide (TMTD) were of rubber grade. Toluene and diethylene glycol were of analar grade and were used as such. The phenol–formaldehyde resin (HR6410) used was of adhesive grade, supplied by Bakelite – Hylam (India Ltd.).

The 4,4′, 4″ triphenyl methane tri isocyanate (Desmodur-R) was of reagent grade, supplied by Baeyer (I) Ltd.

Mild steel was used as an adherend metal for testing the adhesive bond strength in rubber to metal bonding.

CTNR was prepared in the laboratory by the ultraviolet irradiation of 100 g masticated natural rubber in 1L toluene and 20 g maleic anhydride. The unreacted maleic anhydride was removed by repeated reprecipitation using toluene–methanol (1 : 1 v/v) mixture and the product CTNR was characterized by H^1-NMR, IR, GPC and TGA [8].

NR and NBR compounds, to be used as adherend rubber pieces were prepared as per the formulations given in Table 1. These compounds

Table 1. Formulations for adherend rubber test pieces.

	A	B	C	D
Natural Rubber (NR)	100	100	0	0
Acrylo-nitrile Butadiene Rubber (NBR)	0	0	100	100
Zinc Oxide (ZnO)	4	4	4	4
Stearic Acid	2	2	2	2
Styrenated phenol	0	1	0	1
Sulphur	2.5	2.5	2.5	2.5
Vulkanox-4020	1	0	1	0
Silica	0	40	0	40
HAFN-330	40	0	40	0
Aromatic Oil	5	5	0	0
Mercaptobenzothiazole	0.6	0.6	1	1
Tetramethylthiuramdisulphide	0.1	0.1	0.5	0.5
Dioctylphthalate	0	0	5	5
Diethylene glycol	0	0	1.5	1.5

were moulded in an electrically heated hydraulic press at 150°C up to their optimum cure times.

The optimum cure times of the compounds were determined on a Mon Santo Moving Die Rheometer-2000.

The adhesives used to bond rubber to rubber were prepared as per the formulations in Table 2. The adhesives for rubber to metal bonding were prepared according to the formulations given in Table 3.

The bonding was evaluated by determining the peel strength and lap shear strength of the bonded test pieces, bonded using different adhesives given in Tables 2 and 3. The rubber test specimens for the determination of peel strength and lap shear strength were cut out from the moulded sheets and had the dimensions 6 in. × 1 in. and 5 in. × 1 in. respectively. The mild steel test specimens used for rubber to metal bonding, were also cut to similar dimensions.

Table 2. Adhesive formulations for rubber to rubber bonding.

Adhesive	Carboxy Terminated Liquid Natural Rubber (CTNR)	Natural (NR)	Phenol–formaldehyde Resin
1	100	0	0
2	0	100	0
3	100	0	25
4	0	100	25

Table 3. Adhesive formulations for rubber to metal bonding.

Adhesive	Natural Rubber (NR)	Carboxy Terminated Liquid Natural Rubber (CTNR)	Phenol-formaldehyde Resin	Desmodur-R
1	0	100	0	0
2	0	100	25	0
3	0	100	0	25
4	100	0	0	0

The peel strength and the lap shear strength were evaluated using a Prolific Universal Testing Machine, model 1.3 D using a cross head speed of 50mm/min, in accordance to ASTM D-419.

For the determination of peel strength, 5 in. length of the surfaces to be bonded were abraded using fine emery paper to a dull finish. The prepared adhesives were thoroughly agitated before use, then applied to the surfaces to be bonded using a brush. After sufficient drying time was given, the surfaces were then bonded firmly, pressed with hand and rolled using a cylindrical rod of 25 mm.

Similarly, for lap shear strength determination, 1 in. length of the surfaces to be bonded were applied with the adhesives and were bonded firmly. The specimens were kept at least 24 h before they were tested.

RESULTS AND DISCUSSION

Table 4 shows the variation in peel strengths of the adherends given in Table 1; bonded using the adhesives given in Table 2. CTNR based adhesives showed greater adhesive strength than that of masticated NR based adhesives. The effect of CTNR is more pronounced when silica is used as the filler. This may be due to the ionic cross linking involving –COOH groups in CTNR and OH groups in silica. The addition of

Table 4. Variation in peel strengths of the adherends given in Table 1, using the adhesives given in Table 2 (N/in.).

Adhesive	A to A	B to B	C to C	D to D
1	10.5	11.5	14	15.6
2	6	7.5	12.3	13.9
3	7.5	10.5	14.3	16.1
4	5.5	8	12.1	13.6

Table 5. Variation in lap shear strengths of the adherends given in Table 1, using the adhesives given in Table 2 (N/in.^{2}).

Adhesive	A to A	B to B	C to C	D to D
1	145	120	190	170
2	100	110	150	136
3	83	58	89	64
4	37	39	47	43

Table 6. Variation in peel strengths of the adherends given in Table 1, bonded to mild steel, using the adhesives given in Table 3 (N/ in.).

Adhesives	A to Mild Steel	B to Mild Steel	C to Mild Steel	D to Mild Steel
1	47.5	36	59	53
2	61	59.4	73	79
3	86	82	108	106
4	35.6	36	59.1	58.8

phenol–formaldehyde resin (PF resin) in adhesives is found to increase the peel strength of NBR adherends. But the effect is not much pronounced in the case of NR. This may be due to the incompatibility of PF resin and NR.

Table 5 shows the variation in lap shear strengths of the adherends given in Table 1, bonded using the adhesives given in Table 2. The superior bonding properties shown by the adherends confirms that CTNR based adhesives can be used for bonding NR as well as NBR.

Table 6 shows the variation in peel strengths of the vulcanizates A, B, C and D used as adherends in bonding rubber to mild steel using the adhesives given in Table 3. The peel strength values of adherends bonded by CTNR based adhesives is superior to that of masticated NR. The bonding properties were enhanced by the addition of PF resin and Desmodur-R. The greater enhancement in peel strength values of NBR adherends, in presence of Desmodur-R may be attributed to

Table 7. Variation in lap shear strengths of the adherends given in Table 1, bonded to mild steel, using the adhesives given in Table 3 (N/in.^{2}).

Adhesives	A to Mild Steel	B to Mild Steel	C to Mild Steel	D to Mild Steel
1	42.5	41	60	45
2	57.5	56	77.5	70.9
3	78	74.2	86.7	82.1
4	41.1	40.2	58.6	41.1

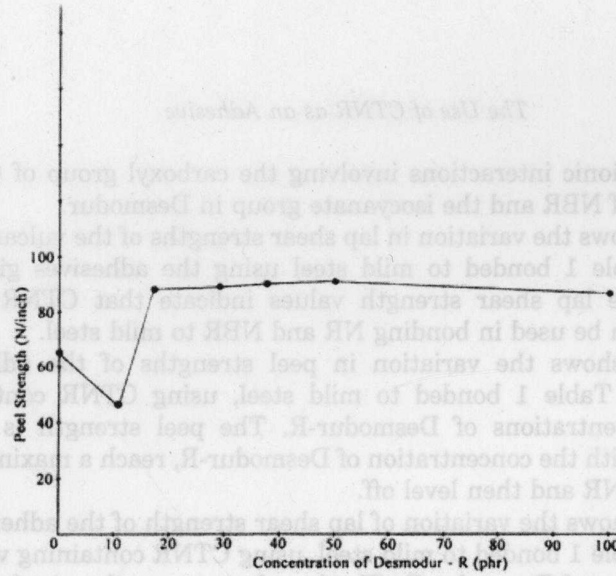

FIGURE 1. Variation in peel strengths of the adherend A shown in Table 1 bonded to mild steel, using CTNR containing varying concentrations of Desmodur-R.

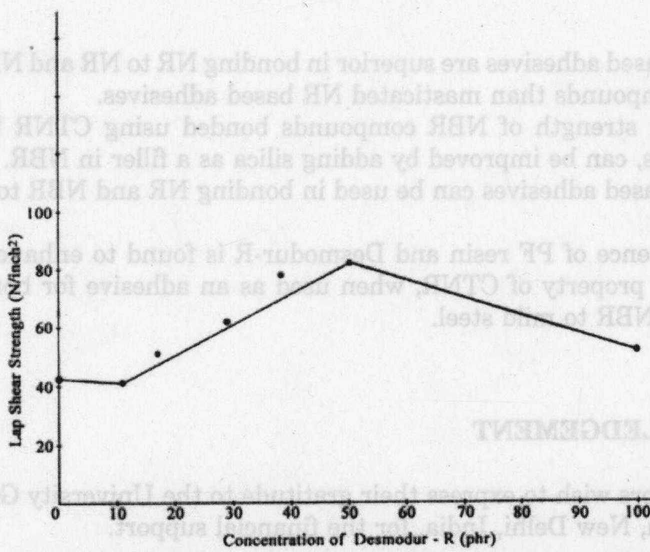

FIGURE 2. Variation of lap shear strength of the adherend A shown in Table 1 bonded to mild steel, using CTNR containing varying concentrations of Desmodur-R.

the possible ionic interactions involving the carboxyl group of CTNR, nitrile part of NBR and the isocyanate group in Desmodur.

Table 7 shows the variation in lap shear strengths of the vulcanizates given in Table 1 bonded to mild steel using the adhesives given in Table 3. The lap shear strength values indicate that CTNR based adhesives can be used in bonding NR and NBR to mild steel.

Figure 1 shows the variation in peel strengths of the adherend A shown in Table 1 bonded to mild steel, using CTNR containing varying concentrations of Desmodur-R. The peel strength is found to increase with the concentration of Desmodur-R, reach a maximum at 50 phr of CTNR and then level off.

Figure 2 shows the variation of lap shear strength of the adherend A shown in Table 1 bonded to mild steel, using CTNR containing varying concentrations of Desmodur-R. The lap shear strengths are found to increase up to 50 phr of CTNR and then to decrease.

CONCLUSIONS

1. CTNR based adhesives are superior in bonding NR to NR and NBR to NBR compounds than masticated NR based adhesives.
2. The peel strength of NBR compounds bonded using CTNR based adhesives, can be improved by adding silica as a filler in NBR.
3. CTNR based adhesives can be used in bonding NR and NBR to mild steel.
4. The presence of PF resin and Desmodur-R is found to enhance the adhesive property of CTNR, when used as an adhesive for bonding NR and NBR to mild steel.

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REFERENCES

1. Gross, M.E. and Weber, C.D. In: Skeist, I. (ed.), (1977). *Carboxylic Polymers in Adhesives-Handbook of Adhesives*, **2nd Edn**., p. 331, Van Nostrand Publishers.

2. Sexsmith, F.H. In: Bhowmick, A.K. (ed.), *Rubber to Metal Bonding-Manufacture and Design*, p. 449, Marcel Dekker, NY.
3. Job, L. PhD Thesis - Cochin University of Science and Technology, p. 56.
4. Wake, W.C. In: Skeist, I. (ed.), *Natural Rubber and Reclaimed Rubber Adhesives-Handbook of Adhesives*, **2nd Edn**., p. 242, Van Nostrand Reinhold Publishers.
5. John S. Autenrieth. In: Skeist, I. (ed.), *Resins for Rubber Based Adhesives-Handbook of Adhesives*, p. 222, Van Nostrand Reinhold Publishers.
6. Hepburn, C. *Polyurethane Elastomers*, p. 232, Applied Science Publishers.
7. Zapp, R.L., Serniuk, G.E. and Minckler, L.S. (1970). Isocyanate Reactions with Difunctional Polyisobutylenes, *Rubber Chemistry and Technology*, **43**: 1154.
8. Dileep. U. and Shanti, A. (2002). Avirah-Studies of Carboxy Terminated Liquid Natural Rubber in NBR, *J. Appl. Polym. Sci.*, **84**: 261–267.