

Reactive Bonding of Natural Rubber to Metal by a Nitrile–Phenolic Adhesive

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ABSTRACT: The mechanism of adhesive bonding of rubber to metal using an interlayer of bonding agent (adhesive) is discussed with respect to various physical and chemical events such as adsorption at the metal surface, chemical crosslinking within the adhesive, interdiffusion, and formation of interpenetrating networks at the rubber–adhesive interface. An investigation on the peel strength of a natural rubber (NR)–adhesive–metal joint, made by vulcanization bonding using nitrile–phenolic adhesive containing various concentrations of toluene diisocyanate–nitrosophenol (TDI–NOP) adduct, is presented. A single-coat adhesive, consisting of a *p*-cresol phenol formaldehyde resin, nitrile rubber (NBR), and vulcanizing agents in methyl ethyl ketone solvent, was selected for the study. Considerable improvement in the peel strength was obtained by the incorporation of TDI–NOP adduct into the nitrile–phenolic adhesive. The peel strength increases as the concentration of TDI–NOP adduct in the adhesive composition increases, then levels off with a transition from interfacial failure to cohesive tearing of rubber. The peel strength improvement is believed to be attributed to the interfacial reactions between the bonding agent and natural rubber, when TDI–NOP adduct is incorporated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2597–2608, 2001

Key words: rubber-to-metal bonding; nitrile–phenolic adhesive; reactive bonding of rubber; toluene diisocyanate–nitrosophenol adduct

INTRODUCTION

In recent years, adhesive bonding of rubber to metal has been widely used in the manufacture of rubber/metal composites for many applications in aerospace and other industries.¹ Adhesive bonding of rubber to metal enables one to combine the reinforcement quality of metal with the flexibility, vibration isolation, and other qualities of rubber. Technology of adhesive bonding of rubber to metal is by either joining the rubber during vulcanization or bonding the vulcanized rubber products to the metal.² The function of the adhesive is to join rubber and metal by the establishment of interfacial contact at the molecular level through wetting and by physical and/or chemical links.

Single-coat or two-coat (primer, overcoat) adhesive systems are used in rubber–metal bonding to achieve a reliable joint.

There have been attempts to resolve the complexity of the mechanism of adhesive bonding of rubber to metal. It was proposed that strong metal–adhesive–rubber joint formation results from a combination of various physical and chemical processes, including adsorption and establishment of strong interfacial forces at the metal–adhesive interface, chemical crosslinking within the adhesive, interdiffusion, and cross-bridging at the rubber–adhesive interface.^{3,4} A rubber–metal adhesive tends to be highly complex and usually contains some rubber, resins, and active ingredients that wet, spread, establish strong interfacial forces on the metal surface, and then migrate into the rubber and crosslink into a mechanically strong film, producing a modulus gradient in the sequence metal > adhesive > cured rubber with-

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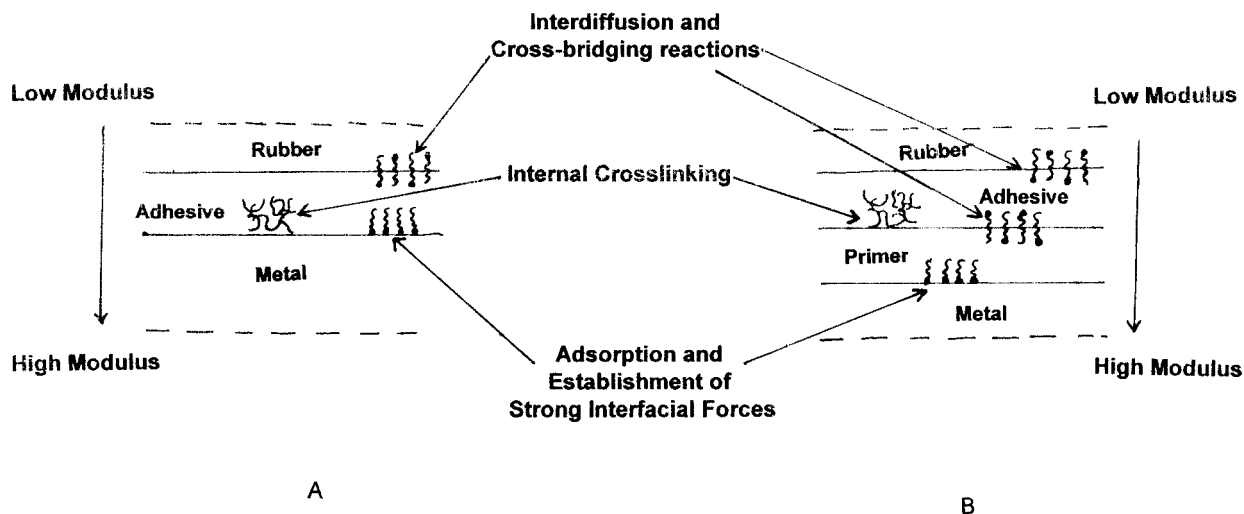


Figure 1 The proposed mechanism of rubber–adhesive–metal joint formation: (A) single-coat adhesive; (B) two-coat (primer, overcoat) adhesive.

out discontinuities in the bond region⁵ (Fig. 1). Failure in the rubber, rather than at an adhesive–rubber or adhesive–metal interface, when the rubber–adhesive–metal joint is pulled apart, is adopted as the criterion for a good joint.⁶

In an earlier study⁷ we reported that nitrile–phenolic adhesive, prepared by blending a *p*-cresol phenol formaldehyde resin, nitrile rubber (NBR), and vulcanizing agents in a suitable solvent, can form an effective bonding agent for vulcanization bonding of NBR to metal. It was previously reported that phenolic resins can establish strong chemical interactions on a metal surface by virtue of dipole, ionic, covalent, and chelate bond formation of *O*-methyl hydroxyl phenol with the hydrated metal oxide surface.^{8,9} During the curing process interdiffusion and cross-bridging reactions occur at the adhesive–rubber interface. The adhesive is converted into a network by the crosslinking reactions of nitrile rubber with phenolic resin,¹⁰ self-hardening reactions of phenolic resin,¹¹ and vulcanization reactions of nitrile rubber.¹² Previously, we found that incorporation of *p*-cresol into the phenolic resin improves the adhesive and mechanical properties of a phenolic resin/nitrile rubber blend and the optimum *p*-cresol/phenol mole ratio is in the vicinity of 2 : 1.⁷ The present study is devoted to an investigation of the peel strength of a natural rubber (NR)-to-metal joint made by vulcanization bonding using a single-coat nitrile–phenolic adhesive. The adhesive formulation consists of a *p*-cresol phenol formaldehyde resin (*p*-cresol/phenol mole ratio of 2 : 1), nitrile rubber, and vulcanizing

agents. Nitrile–phenolics form strong chemical bonds with the metal surface, but the NR side is not bonded by the adhesive as a result of the lack of strong interfacial interactions between the nitrile–phenolic adhesive and NR, which are incompatible because of the dissimilarity in polarity. To enhance adhesive strength, very strong interpolymer bonds in the interfacial region of the nitrile–phenolic adhesive and NR are necessary.

Many investigators^{13–17} have been able to strengthen the interfacial region of incompatible dissimilar polymers either by introducing a reactive interfacial agent that could be capable of reacting with both the components at the interfacial region or by adding *graft*- or *block*-copolymer that contains segments of both components. Reactive compatibilization methods have been shown to be effective in a variety of blended systems. Such methods are dependent on the amount of interfacial agent introduced into the system and its reactivity with the blend components.¹⁷ It was previously reported¹⁸ that nitrosophenol-blocked isocyanate dissociates into nitrosophenol and diisocyanate at the vulcanization temperature of rubber. The nitrosophenol then reacts with natural rubber molecules, through the nitroso group leaving the phenolic side, which are then linked by diisocyanate. In this study, we explore the effect of incorporating varying concentrations of toluene diisocyanate nitrosophenol (TDI–NOP) adduct into the nitrile–phenolic adhesive on the peel strength of the NR–adhesive–metal joint. The results of this investigation show that significant improvement in peel strength is

Table I Formulation of the Nitrile-Phenolic Adhesive (20 wt % Solution in Methyl Ethyl Ketone)

Ingredients	Parts by Weight (phr)
NBR	100
PCPF resin	100
Zinc oxide	5
Sulfur	1.5
2-Mercapto benzothiazole	1.5
TDI-NOP adduct	Variable

obtained, in vulcanization bonding of NR to metal, by the incorporation of TDI-NOP adduct into the nitrile-phenolic adhesive.

EXPERIMENTAL

Materials

The adhesive formulation used in this investigation consists of a nitrile rubber (NBR), vulcanizing agents, *p*-cresol phenol formaldehyde (PCPF) resin, and varying amounts of TDI-NOP adduct dispersed in methyl ethyl ketone solvent. NBR used in this study was Perbunan NS 3307, which contains 33% acrylonitrile units. NBR, 2-mercapto benzothiazole and tetramethyl thiurum disulphide used in this work were obtained from Bayer, Germany. Dibutyl tin dilaurate (DBTDL) was procured from E. Merck, Germany. Carbon black (oriented black N-550) was obtained from Philips Carbon Black, Cochin, India. Toluene diisocyanate (TDI) was supplied by SMPE, Gironde, France. Other chemicals used were analytical reagents obtained from S.d fine Chem Pvt. Ltd., Mumbai, India. PCPF resin and TDI-NOP were prepared by the procedures described below.

Preparation of *p*-Cresol Phenol Formaldehyde (PCPF)

The preparation and characterization of PCPF resin were described previously.⁷ Phenol (1 mol), *p*-cresol (2 mol), formaldehyde solution (1.5 mol), and NaOH (0.02 mol) catalyst were added and heated at 60°C in a three-neck flask equipped with a water bath, reflux condenser, thermometer, and stirrer. After stirring for 30 min at 60°C, the temperature was raised to 80–85°C and held at that temperature with stirring for 7 h. The PCPF resin that formed was neutralized and iso-

lated by removing water at 60°C under reduced pressure until the volatile matter was less than 2%. The percentage volatile matter was determined by drying a known weight of the sample at 105°C for 5 h in a hot-air oven and was calculated by the expression $[(W_1 - W_2)/W_1] \times 100$, where W_1 is the initial weight of the resin and W_2 is the weight of the resin after drying.

Preparation of Toluene Diisocyanate-Nitrosophenol (TDI-NOP) Adduct

TDI-NOP adduct was prepared by a two-step process. Phenol was converted into nitrosophenol by nitrosylation reaction with $\text{NaNO}_2/\text{H}_2\text{SO}_4$ using a previously reported procedure.¹⁹ The product formed was confirmed by melting point (133°C).

Nitrosophenol and toluene diisocyanate were reacted in a 2 : 1 molar ratio using dibutyl tin dilaurate (DBTDL) as catalyst and tetrahydrofuran (THF) as reaction solvent. Dried nitrosophenol and catalyst along with 80 wt % of freshly distilled THF were charged into a dry round-bottom flask equipped with stirrer, reflux condenser, and N_2 gas inlet. The flask was heated to reflux in an oil bath and TDI was added slowly using a dropping funnel while stirring. The reaction was allowed to proceed at reflux temperature for about 20 h in nitrogen atmosphere. Completion of the reaction was checked by IR spectrum. The reaction mixture was cooled and the precipitate that formed was filtered, dried, and characterized.

Adhesive Formulation

The compounding ingredients of the adhesive formulation are given in Table I. NBR, vulcanizing

Table II Recipe and Mechanical Properties of the Natural Rubber Compound

Ingredients	Parts by Weight (phr)
NR	100
Carbon black	40
Zinc oxide	5
Sulfur	2
2-Mercapto benzothiazole	1.5
Tetramethyl thirumdisulphide	0.25
Stearic acid	1
Tensile strength (kg/cm ²)	165
Elongation (%)	633
Hardness (Shore A)	65

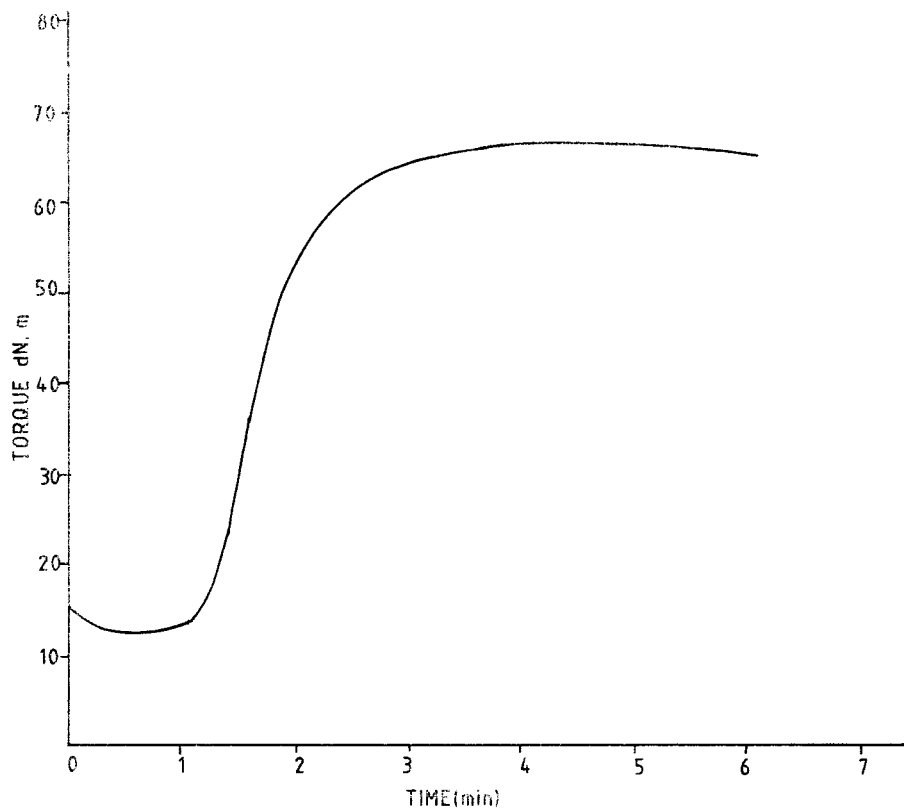


Figure 2 Rheograph of the natural rubber compound.

agents, PCPF resin, and TDI-NOP adduct were homogenized in a laboratory-size two-roll mill and then dissolved in methyl ethyl ketone solvent

in a jar mill for about 8 h to obtain 20 wt % total-solids solution with various levels of TDI-NOP adduct.

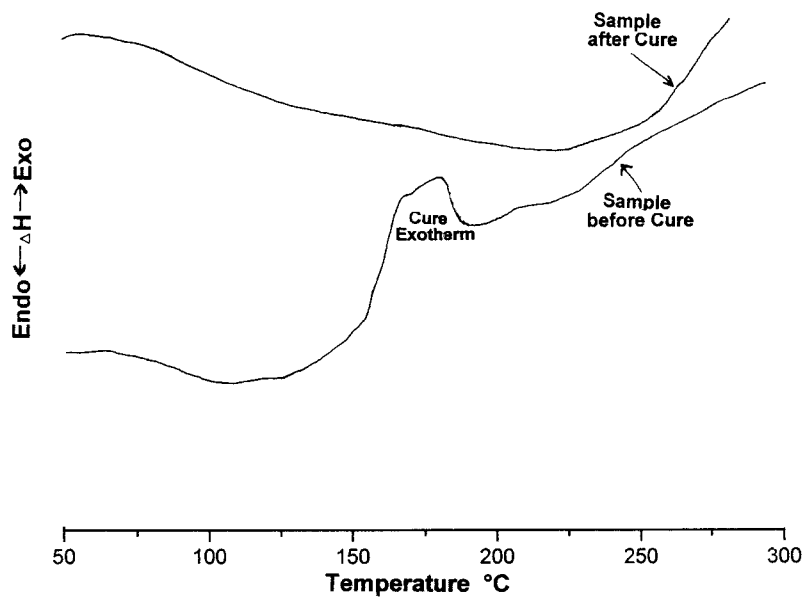


Figure 3 DSC traces of nitrile-phenolic adhesive with 10 phr toluene diisocyanate nitrosophenol (TDI-NOP) adduct.

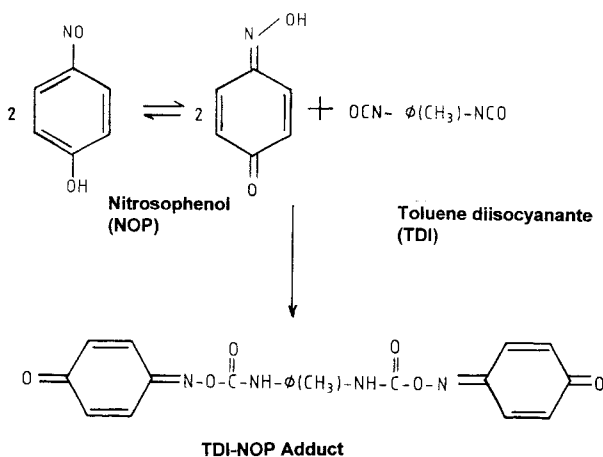


Figure 4 Reaction of nitrosophenol with toluene diisocyanate.

Preparation of Natural Rubber Compound Strips for Peel Strength Measurement

Natural rubber compound was prepared according to the recipe given in Table II. Natural rubber ISNR-5 (supplied by Rubber Research Institute of India, Kottayam) was used. The mixing of rubber and the ingredients was done on a laboratory two-roll mill. The compound was then sheeted out to a thickness of about 6 mm. The cure characteristic of the rubber compound was determined with a Monsanto rheometer (Monsanto, St. Louis, MO) at 170°C (Fig. 2). The mechanical properties of the rubber compound after vulcanization at 170°C for 90 min at 5 MPa pressure are given in

Table III Elemental Analysis of TDI-NOP Adduct

	C (%)	H (%)	N (%)
Calculated	60	3.8	13.3
Experimental	59.6	4	13.1

Table II. These curing conditions were selected to match those of the nitrile-phenolic adhesive. The adhesive film cured under the preceding conditions showed no residual cure exotherm in the DSC thermogram, which indicated a complete cure (Fig. 3).

Bonding of Rubber to Metal

A rubber-to-metal-bonded specimen was made by vulcanizing a strip of the above-described rubber compound over the adhesive-coated metal strip [75 × 25 × 2 mm (length × width × thickness)]. The metal used was B51 SWP aluminum alloy containing 0.4% Fe, 0.6% Si, and 0.8% Mg. The aluminum surface was abraded with emery paper, cleaned with trichloroethylene, etched²⁰ with Na₂Cr₂O₇/H₂SO₄ solution at 65°C for 15 min, washed in water, and dried at 70°C for 2 h. The nitrile-phenolic adhesive solution was applied uniformly with a brush onto the metal surface over an approximate area of 6.25 cm² and the solvent was allowed to evaporate to give an adhesive film thickness of 100–150 μm. The rubber

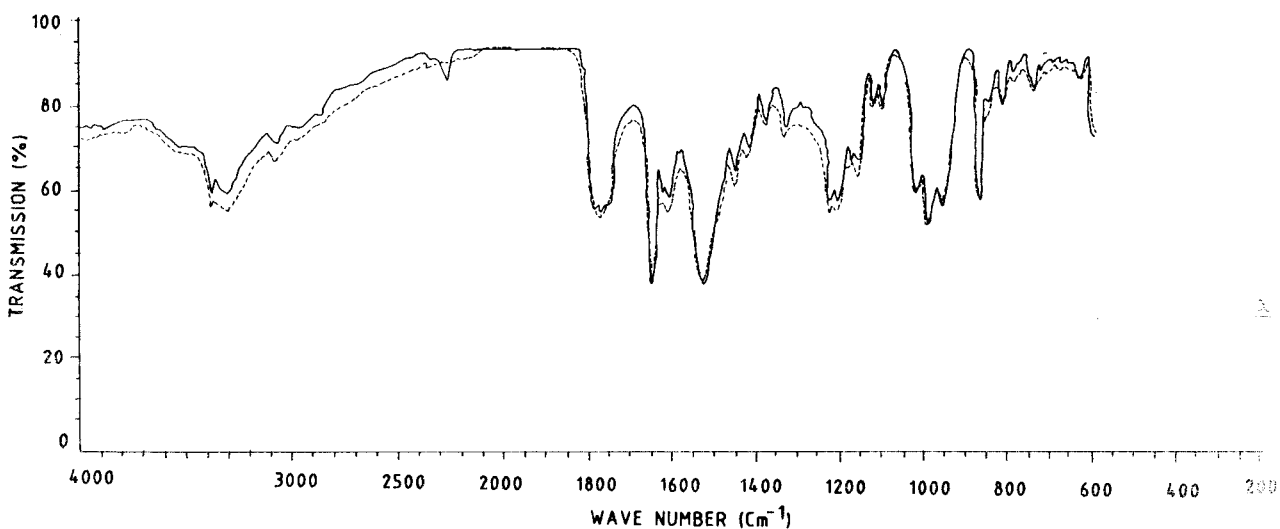


Figure 5 Infrared spectra during the reaction of nitrosophenol and toluene diisocyanate: (—) after 10 h and (---) after 20 h (final stage of reaction).

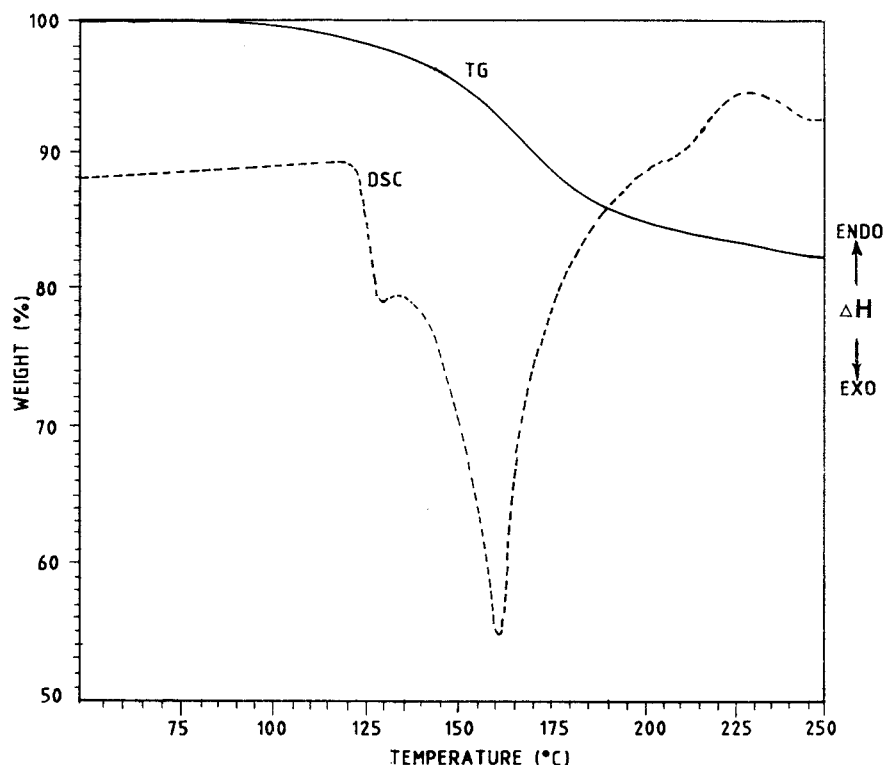


Figure 6 TG and DSC curves of TDI-NOP adduct.

strip was placed over the adhesive-coated metal and the assembly was vulcanized in a hydraulic press at $170 \pm 2^\circ\text{C}$ for 90 min at 5 MPa pressure in a 6-mm-thick cavity mold, according to ASTM-D-429B.

Testing Methods

Elemental analysis of the TDI-NOP adduct was carried out on a Perkin-Elmer CHN elemental analyzer model 2400 (Perkin-Elmer Cetus Instruments, Norwalk, CT). A Perkin-Elmer IR spectrophotometer was used to record the IR spectrum. Differential scanning calorimeter (DSC) thermograms were obtained by using a Dupont thermal analyzer (Dupont, Wilmington, DE) with a 902 DSC cell at a heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was carried out on a Dupont 951 thermogravimetric analyzer in N_2 atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. Stress-strain tests were performed on an Instron model 4202 at a crosshead speed of 10 mm/min.

The unblocking temperature of the TDI-NOP adduct was determined by the procedure of Griffin and Willwreth.²¹ TDI-NOP adduct, silicone oil, and 4-Å molecular sieves saturated with wa-

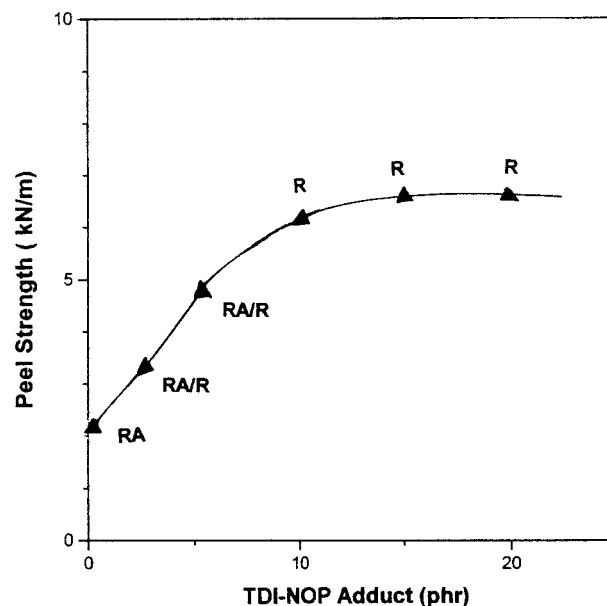


Figure 7 Peel strength of natural rubber (NR)-adhesive-metal joint made by vulcanization bonding using a nitrile-phenolic adhesive containing various concentrations of TDI-NOP adduct. R, failure within rubber; R/A, rubber/adhesive failure; RA/R, mixed failure.

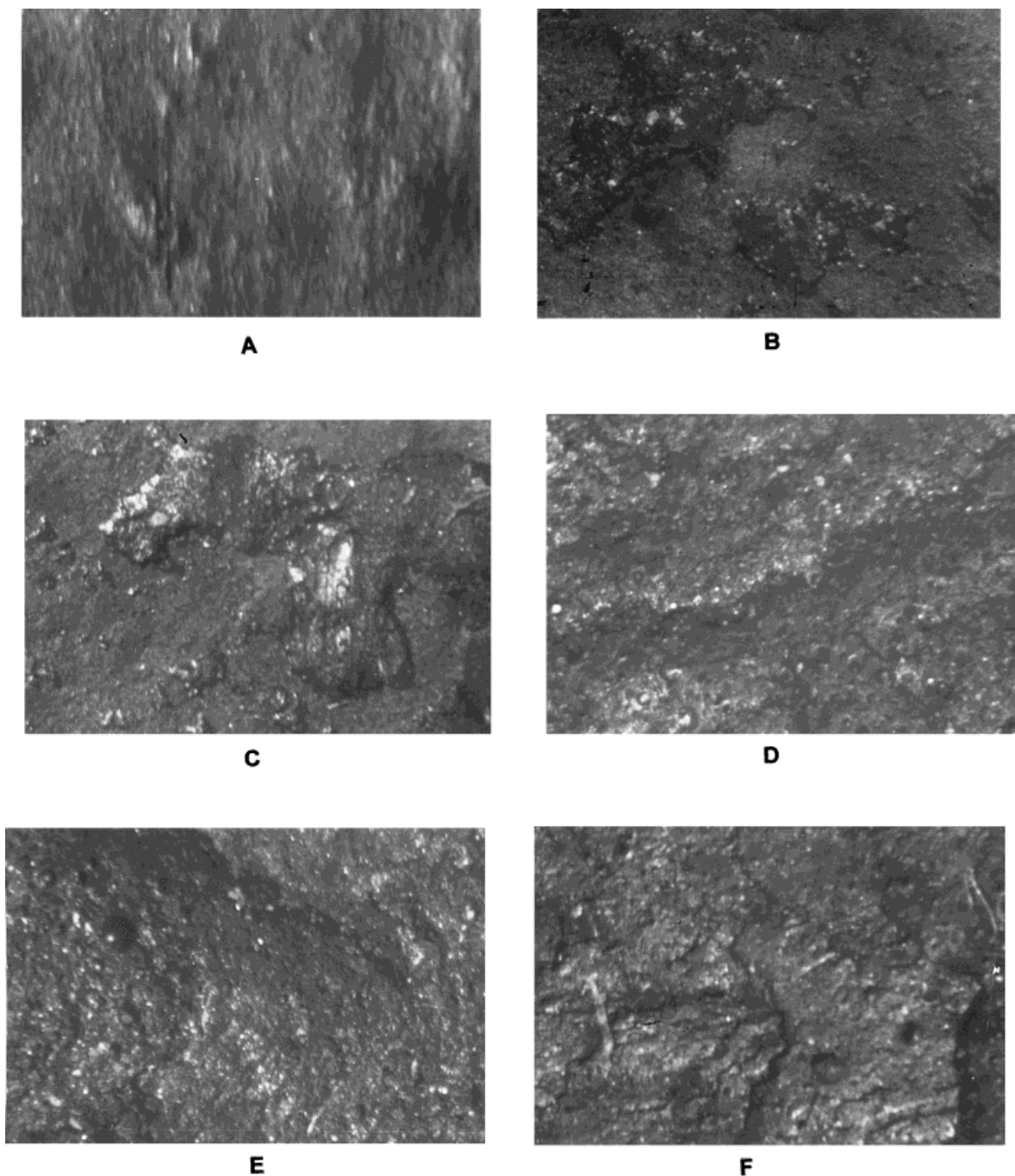


Figure 8 Optical micrographs of the metal adherend peeled from the NR-adhesive-metal joint bonded using nitrile-phenolic adhesive containing various amounts of TDI-NOP adduct: (A) without TDI-NOP adduct; (B)-(F) with 2.5, 5, 10, 15, and 20 phr TDI-NOP adduct, respectively.

ter were placed in a three-neck flask fitted with a condenser, N_2 gas inlet, and a thermometer. The condenser was connected to a trap containing saturated $Ba(OH)_2$ solution. The flask was slowly heated and a slow stream of N_2 gas was main-

tained. The temperature at which the solution in the trap became turbid was noted as the unblocking temperature.

The peel strength of the bonded rubber-to-metal specimens was determined by pulling at an angle of

180° on an Instron model 4202 at a rate 50 mm/min. The peel strength was calculated as F/W , where F is the peel load and W is the width of the specimen. After peel testing, the nature of failure was examined by optical observations of the metal surface at $\times 50$ magnification.

RESULTS AND DISCUSSION

The blocking of toluene diisocyanate by nitrosophenol is described in Figure 4. The course of the reaction was followed spectroscopically by observing the $-NCO$ peak in the IR spectrum (Fig. 5). After about 20 h of reaction, the absorption at 2270 cm^{-1} characteristic of $-NCO$ group disappeared in the IR spectrum, indicating completion of the reaction. The elemental analysis of TDI-NOP adduct is shown in Table III. TDI-NOP adduct is a stable powder at room temperature and the unblocking temperature, determined by the procedure of Griffin and Willwreth,²¹ was 106°C. The unblocking temperature is the temperature at which the TDI-NOP adduct becomes active by the regeneration of isocyanate and nitrosophenol. The unblocking of TDI-NOP adduct was also indicated by thermal analysis. On heating to about 120°C an exothermic process occurred, with weight loss reaching a maximum at 170°C (Fig. 6).

The blocked isocyanates are stable at room temperature, but dissociate to generate isocyanate functionality under the influence of heat. The resulting isocyanate can react with other active hydrogen compounds to form more thermally stable linkages.²² Blocked isocyanates are used to formulate one-component adhesives and coatings with good stability at ambient storage temperature and cure by heat.²³ Figure 7 shows the effect of the addition of TDI-NOP adduct to the nitrile-phenolic adhesive on the peel strength of the NR-adhesive-metal joint. Substantial enhancement of peel strength resulted from the introduction of even a small percentage of TDI-NOP adduct into the nitrile-phenolic adhesive. Figure 7 reveals that the nitrile-phenolic adhesive without TDI-NOP adduct gives only very low peel strength in vulcanization bonding of NR to metal. The phenolic resin present in the nitrile-phenolic adhesive produces strong adhesion to metal and the heat supplied during the vulcanization process of rubber converts the adhesive into a mechanically strong film.⁷ Thus it appears that the low peel strength obtained in the vulcanization bonding of NR to metal using nitrile-phenolic adhesive can

be attributed to the weak NR/adhesive interfacial strength. On the other hand, when even a low concentration (10 phr) of TDI-NOP adduct is mixed with the nitrile-phenolic adhesive, strong bonding developed at the NR/adhesive interface.

We believe the enhancement of peel strength that occurs on addition of the blocked isocyanate to the adhesive composition is the result of interfacial reactions at the NR/adhesive interface. Figure 7 shows that the peel strength is enhanced significantly as the amount of TDI-NOP adduct in the adhesive is increased. When the amount of TDI-NOP adduct in the nitrile-phenolic adhesive was 10 phr, the peel strength reached a maximum value and then leveled off. The optical micrographs (Fig. 8) of the metal adherend peeled from the NR-adhesive-metal joint shows a relatively smooth adhesive film surface for the sample without TDI-NOP adduct, which indicates that chains at the NR/adhesive interface are not sufficiently anchored. NR is incompatible with the nitrile-phenolic adhesive and the chain ends of NR and the adhesive are located in opposite sides of the interface, with no interpolymer bond formation at the interface. The chains that are not sufficiently bonded or entangled provide less stress transfer across the interface, resulting in low peel strength with NR/adhesive interfacial failure. As the TDI-NOP adduct concentration in the adhesive increases, the fractured surfaces were observed to be quite rough. After 10 phr TDI-NOP content, the NR-adhesive-metal joint failed by cohesive tearing of rubber, significantly away from the interfacial region, and had peel strength of approximately threefold higher magnitude compared to that of its counterpart without TDI-NOP adduct.

It is reasonably expected that the increase in peel strength is primarily the result of the additional chemical bonds formed at the NR/bonding agent interface, when TDI-NOP is present. A schematic representation of bonding at the NR/

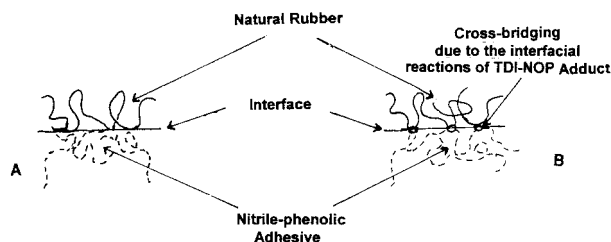


Figure 9 A schematic representation of bonding at the NR/adhesive interface: (A) without TDI-NOP adduct; (B) with TDI-NOP adduct.

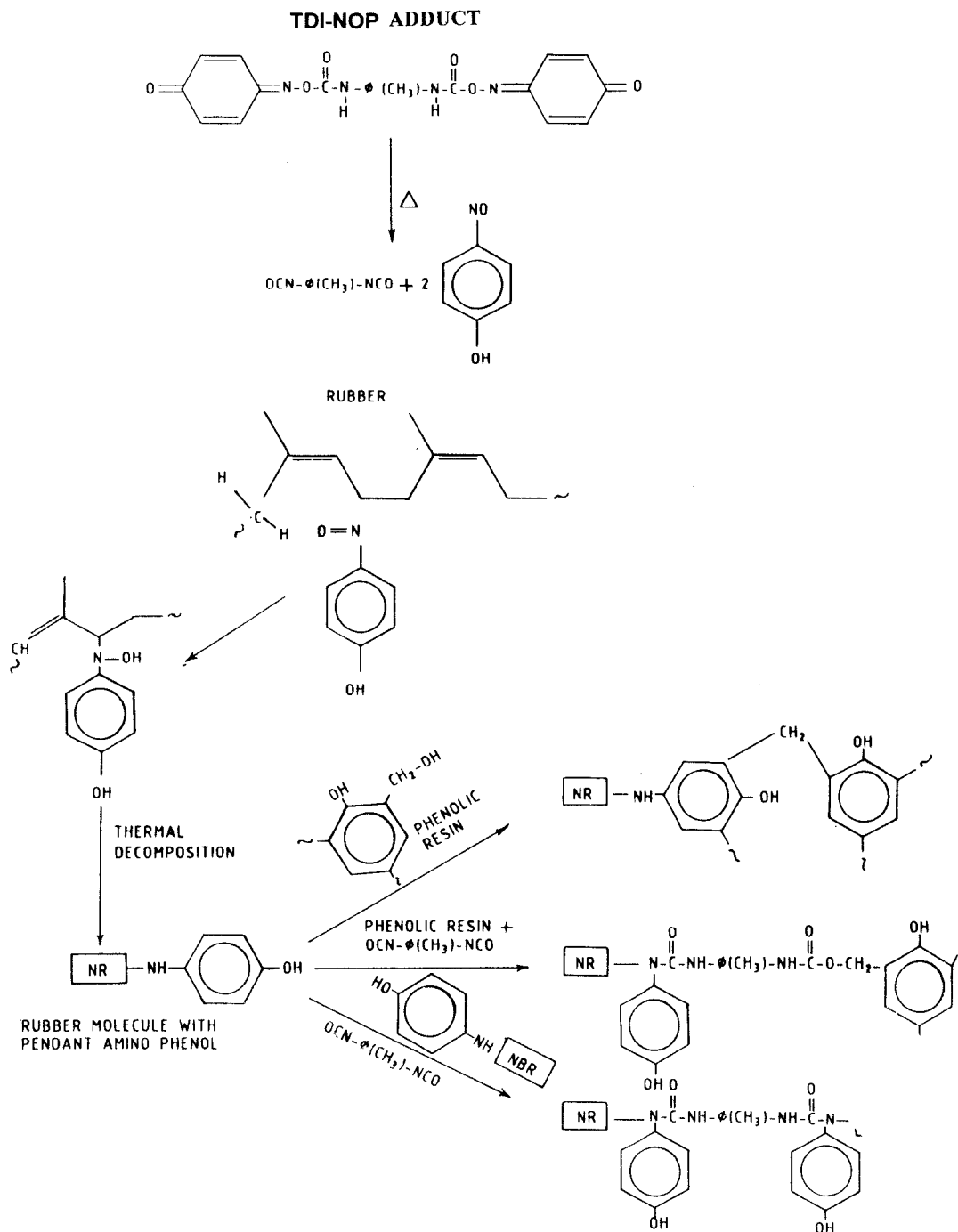


Figure 10 Possible reactions of TDI-NOP adduct at the interfacial region of NR/nitrile-phenolic adhesive.

adhesive interface, both without and with TDI-NOP adduct, is proposed in Figure 9. TDI-NOP acts as a reactive interfacial agent and improves the adhesion between NR and the nitrile-phenolic adhesive by creating attachment sites through the formation of chemical links at the

interface. The reactive interfacial agent possesses specific functional groups and generates *block-* or *graft-*copolymer at the interface *in situ* through the reaction of the functional groups.^{24,25} Sexmith and Polaski²⁶ reported that nitrosophenol, formed by the thermal decomposition of the TDI-NOP

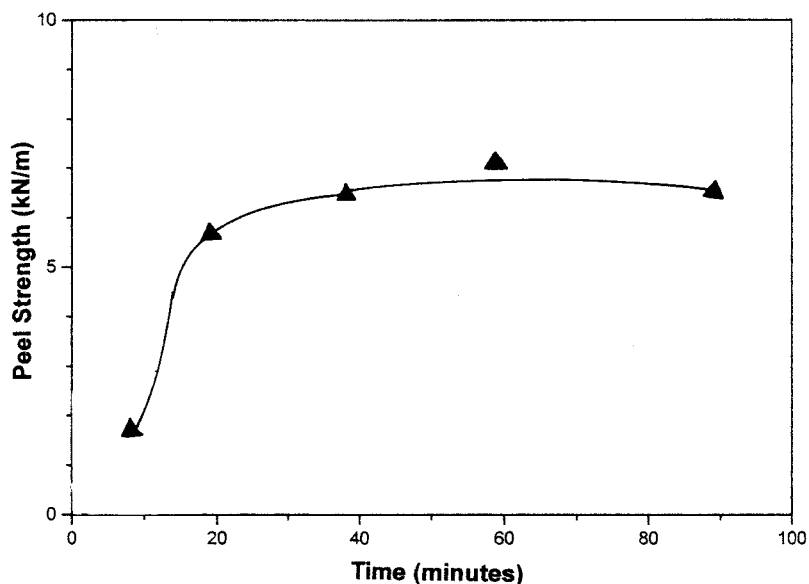


Figure 11 Peel strength of NR–adhesive–metal joint as a function of bonding time at 170°C. (NR–adhesive–metal joint made by vulcanization bonding using nitrile–phenolic adhesive containing 15 phr TDI–NOP adduct.)

adduct, reacts with the natural rubber molecule via an *-ene* addition reaction and provides aminophenol in the rubber chain. The pendant aminophenol is then linked either by the released TDI or by the phenolic resin present in the nitrile–phenolic adhesive, creating chemical bonds at the interfacial region. Possible reactions of TDI–NOP adduct at the NR/nitrile–phenolic interface during the bonding process are shown in Figure 10. At room temperature, the chain ends of NR and the adhesive molecules are located on opposite sides of the interface. When the temperature is increased to the vulcanization temperature with an applied pressure, interpenetration starts with *in situ* formation of copolymer networks at the NR/adhesive interface through the reactions of TDI–NOP adduct, which leads to an increase in peel strength. At about 10 phr of TDI–NOP adduct, the chains at the NR/adhesive interface are sufficiently anchored and the strength of the interfacial region becomes as great as the cohesive strength of the rubber and exhibits a transition from interfacial failure to cohesive tearing of rubber. Increasing the amount of TDI–NOP beyond this point does not further increase the peel strength because the joint has reached a cohesive plateau.

Figure 11 presents the peel strength of NR–adhesive–metal joint as a function of bonding time at 170°C for the specimens with TDI–NOP

adduct (15 phr) in the adhesive. The peel strength increases with bonding time and reaches a plateau value after 40 min. This effect might be the

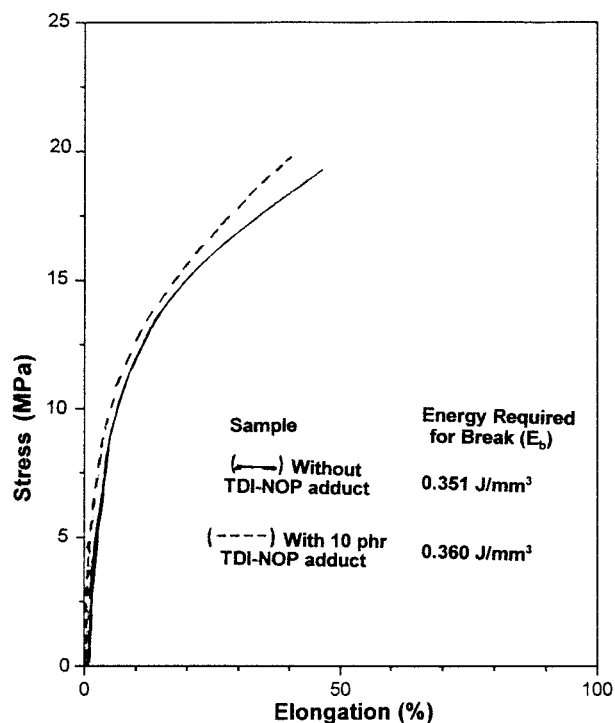


Figure 12 Stress–strain curves of cured nitrile–phenolic films.

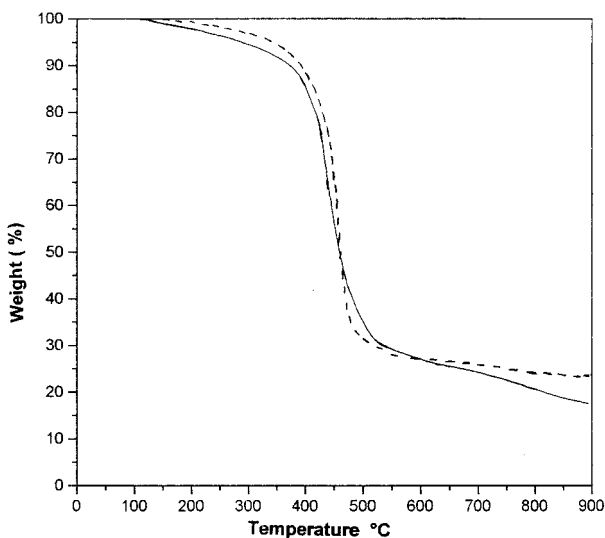


Figure 13 TG plots of cured samples of nitrile-phenolic adhesive: (—) without TDI-NOP adduct; (---) with 10 phr TDI-NOP adduct.

result of the development of strength influenced by the establishment of interfacial contact at the molecular level and the kinetics of network formation through chemical links.

To understand the role of a reactive interfacial agent in enhancing interfacial adhesion, material properties should also be considered. To investigate the effect of introducing the TDI-NOP adduct on the bulk properties of the cured nitrile-phenolic adhesive, the stress-strain behavior and thermal decomposition characteristics were studied for the cured adhesive film, both without and with TDI-NOP. The stress-strain curves (Fig. 12) and TG curves (Fig. 13) show that addition of 10 phr TDI-NOP adduct did not significantly alter the mechanical properties and thermal stability of the cured adhesive film. This implies that enhancement of peel strength of the NR-adhesive-metal joint, with a transition from NR/adhesive interfacial failure to the failure in the bulk rubber, results from the introduction of 10 phr TDI-NOP into the adhesive because of the NR/adhesive interfacial reactions caused by TDI-NOP adduct.

CONCLUSIONS

A nitrile-phenolic adhesive, consisting of a *p*-cresol phenol formaldehyde resin, nitrile rubber, and vulcanizing agents in methyl ethyl ketone solvent, was prepared. The effect of the addition of a toluene diisocyanate-nitrosophenol

(TDI-NOP) adduct into the nitrile-phenolic adhesive on the peel strength of a natural rubber-adhesive-metal joint made by vulcanization bonding was studied by using nitrile-phenolic adhesive compositions containing various concentrations of the TDI-NOP adduct. At a concentration of 10 phr or more of the TDI-NOP adduct in the nitrile-phenolic adhesive, a transition from NR-adhesive interfacial failure to cohesive tearing of rubber occurred in the peel test of the joint and the peel strength value reached a plateau level of approximately threefold higher magnitude compared to that of its counterpart without TDI-NOP adduct. The dependence of bonding time on the peel strength was also investigated. Peel strength was found to reach a plateau value after a certain bonding time. The stress-strain properties and thermal stability of the cured nitrile-phenolic adhesive were not significantly altered by the incorporation of 10 phr TDI-NOP adduct. We propose that TDI-NOP adduct acts as an interfacial agent, increases the chemical interactions at the adhesive-natural rubber interface, and enhances the peel strength.

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