

CURING OF NATURAL RUBBER AND EPOXY ADHESIVE

A M Motawie* and E M Sadek

Petrochemical Department, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

(Received 17 June 1999; accepted 19 September 2000)

Low molecular weight epoxy resin based on diglycidyl ether of bisphenol A was synthesized and mixed at constant percentages with natural rubber. The rubber/epoxy system was cured with various types of curing agents such as ethylene diamine, maleic anhydride as well as the prepared resole phenol formaldehyde. A study of the photo-induced crosslinking of the prepared elastic adhesives and film samples was carried out by exposure to ultraviolet lamp (300 W) for 2 weeks at 20°C. Samples containing ethylene diamine were cured at 25±1°C for 24 h while samples containing maleic anhydride or resole phenol formaldehyde resins were thermally cured at 150-170°C for 10 min. Cured adhesive compositions were tested mechanically and physically and evaluated as wood adhesives. While hardness, chemical resistance as well as heat stability of the prepared cured film samples were investigated. The obtained data indicate that the highest epoxy resin content and the presence of resole phenol formaldehyde resin in compositions improve the tensile strength and adhesion properties on wood. While their cured film samples have the best hardness properties, chemical resistance and heat stability.

Key words: Wood adhesives, Natural rubber, Epoxy resin, Ethylene diamine, Maleic anhydride, Resole phenol formaldehyde, Ultraviolet curing, Thermal curing.

Introduction

Natural rubber and synthetic elastomers consist of long-chain structures that are randomly zigzagged in the relaxed state but more or less straight in the stretched state. An elastomer is cured subsequent to the introduction of few crosslinks between polymer chains. A large variety of the types of cure systems has been described (Kirk-Othmer 1985; Jacqueline 1990) of these, the most important are resin cures. Phenolic resin curing systems are used extensively to cure latex tirecord dips and butyl curing bladders (Kirk-Othmer 1985).

Absorption of electromagnetic radiation or light by polymers leads to highly excited states of polymer molecules. If the excitation energy is sufficient to cause breakage of chemical bonds or create other reactive species, then the polymer molecules undergo chemical reactions including crosslinking reactions. The formation of three dimensional network structures can lead to improve the overall physical or chemical properties of the original substrate including strength, heat resistivity and recovery from deformation (Jacqueline 1990). Radiation curing of polymers with ultraviolet light is used widely in photomaging and photore-sist technology (James and Bo 1994). Such materials have potential applications in coatings, adhesives and photolithography (Mohammad and Harun 1993; Matusi *et al* 1994; Thames 1994; Kondyurin and Klyachkin 1996; Obara and Omori 1997; Stark *et al* 1997).

Thermally cured rubber epoxy resins on its surface was studied for casting and for electrical insulating parts (Hanyu and Yoshizumi 1995).

Adhesive composition based on phenol resorcinol formaldehyde/resorcinol-formaldehyde of high bond strength in the wood adherent (Vick *et al* 1996). Epoxy resins can be cured over a wide range of curing temperatures with low shrinkage upon cure. The cured epoxy resins exhibit high mechanical properties, excellent adhesion to variety of substrates; chemical resistance, thermal stability, electrical insulation as well as corrosion resistance (Bauer 1985; Kroschwitz 1991).

The main objective of this work is the preparation of elastic adhesives based on natural rubber/epoxy system with high tensile strength values and good adhesion to wood. The effects of curing process type (e.g. ultraviolet radiation curing or thermal curing) and the curing of agent structure on the properties of the prepared cured samples are also studied.

Experimental

Preparation of low molecular weight epoxy resin (ER) based on diglycidyl ether of bisphenol A. Sodium hydroxide solution (2.2 moles in 100 ml H₂O) was added dropwise to a mixture of bisphenols (1 mole) and epichlorohydrin (2 moles) at 65-70°C. After complete addition, the formed resin was washed with water until it became neutral. The ER was then dried at 120°C. The experiment was carried out according to the procedure described in (Motawie *et al* 1988). The prepared epoxy resins have an average molecular weight of

*Author for correspondence

370; dropfalling temperature of 65°C, viscosity at 25°C of 1100-1500 mPas; epoxy group content 18.8% and hydroxyl group content 22%.

Preparation of resole phenol formaldehyde (PF) resins. Phenol (17.5 g) was mixed with a 40% formaline solution (17.75 g), then 25% liquid ammonia (1.50 g) was added as a catalyst, heated in a water bath at 90°C. The experiment was carried out according to the method described in (Motawie *et al* 1988). The prepared (PF) resins have specific gravity at 20°C of 1.05, they also have specific viscosity at 20°C of 1700-1800 mPas.

Preparation and evaluation of adhesive. Natural Malizian rubber (NR 100 g) was completely dissolved in acetone (500 ml) at 20-25°C followed by dropwise addition and stirring of different weight ratio percentages of the prepared ER. Ethylene diamine (EDA) (30% of the resin content, with boiling point at 1 atm = 117.0°C and viscosity at 20°C = 16 mPas) or maleic anhydride (MA) (30% of the resin content) or alcoholic solution of the prepared resole phenol formaldehyde resin (50 % of the resin content) were added as hardeners with continuous stirring until a homogenous solution was obtained. Unmodified NR samples were also prepared for the purpose of comparison (Table 1). The more viscous resin blends were applied on wooden samples (12 cm length, 2 cm width and 0.5 cm thickness) on an area of 4 cm² at the end of the two wooden pieces. Then the two pieces were made to overlap through the adhesive area and were pressed together under pressure of 2 kg cm⁻², so that the thickness of adhesive was about 1 mm (BS 3544 1962; BS 1204 1979). The samples were then cured at suitable temperature for different periods. Samples containing (EDA) hardener were cured at 25±1°C for 24 h while others containing (MA) and (PF) resin hardners were cured at 150-170°C for 10 min. Samples were also cured by exposure to UV lamp (3000 Watt). The UV lamp was configured perpendicular and mounted at a distance of 10 cm from the samples for a period of 2 weeks at 20°C. Tensile strength and elongation percentage were determined by the standard method (ASTMD 638-77a 1989), using Instron testing machine (Model 1026) at 23±2°C with cross-head speed 100 mm min⁻¹, chart speed 200 mm min⁻¹ and load cell range 0-500 Newton. While adhesion test was carried out according to (ASTM D 3359-1995). On the other hand, hardness properties, chemical resistance and heat stability of the prepared cured film samples (with thickness approximately 1-1.3 mm) were also determined (Table 1).

Evaluation techniques of film samples. (a) *Hardness properties:* Hardness shore A test of the cured film samples was carried out according to (ASTM D 2240 1986). (b) *Chemical resistance tests, chemical sport tests:* The tests

were carried out according to the method described by Mohammad and Harun (1993) using different chemicals with different concentrations such as 5% acetic acid, 50% ethanol, 1% sodium carbonate, 10% sulphuric acid and 10% sodium hydroxide. A drop of each chemical was placed on different spots of a cured film, covered with a watch glass with its edge sealed with cellophane tape. They were left for more than 6 h. To check whether the spots have been affected or not, the drops were wiped off with tissue paper before performing visual inspection. (c) *Head resistance:* The aging of the studied cured samples was estimated by placing the samples in an air circulated oven. The loss percentage in weight was calculated for each sample at 150°C until 4 h (ASTM D 2584 1994).

Results and Discussion

Some of the more important applications of epoxy resins are adhesives and coatings. The high performance of epoxy adhesives is due to the high polarity of the macromolecules and to the fact that the presence of aliphatic hydroxyl and ether groups create electromagnetic bond attraction (e.g. interfacial bond) between the macromolecules and the surfaces being bonded. Also, the oxirane ring forms chemical bonds with most surfaces, particularly those having active hydrogens, such as metals (Feldman and Barbalata 1996).

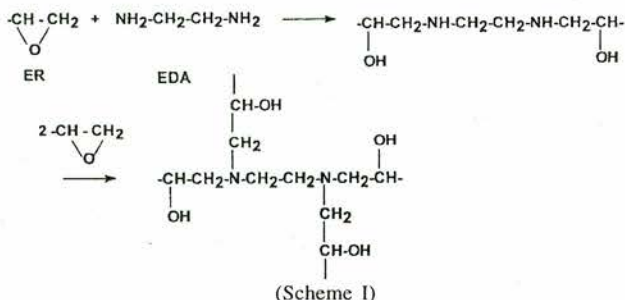
Upon direct absorption of UV, polymer substrates undergo chain scission and crosslinking. Crosslinking or curing of polymer materials can be markedly enhanced through used of special photosensitive molecules that are mixed into the polymer matrix or that chemically attach to the backbone of the polymer chains (Kirf-Othmer 1985).

In the work reported here natural rubber (NR) was mixed with different weight percentages of the prepared epoxy resin ER. The NR/ER samples were thermally cured as well as ultraviolet radiation cured in the presence of various types of crosslinkers. Among these crosslinkers, ethylene diamine (EDA), maleic anhydride (MA) and the prepared resole phenol formaldehyde (PF) resins have been mixed with NR/ER compositions (samples represented by GI, GII and GIII, respectively). Each group was classified into three samples according to the ER percentage (20, 40, 60%). Preliminary experiments showed that (EDA) and (MA) have been mixed at 30% with respect to ER percentage, while (PF) resins were used at 50%. The curing process in the case of (EDA) required prolonged cure time at a lower temperature (25±1° for 24h) than that in the case of (MA) or (PF) resin (150-170°C for 10 min). Unmodified rubber samples were also prepared for the purpose of comparison (samples represented by No.1). Finally the

prepared cured samples were tested and evaluated as wood adhesives (Table 1).

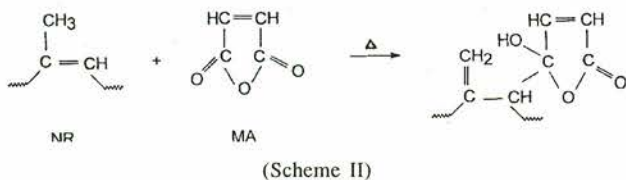
The data (Table 1) show that cured NR/ER/EDA (samples represented by GI) have good mechanical properties when cured by UV radiation as compared to those composition cured at $25 \pm 1^\circ\text{C}$ for 24 h.

Throughout curing reaction an epoxy group of ER reacts with EDA, as a co-reactive curing agent, to produce a secondary alcohol and a secondary amine. The secondary amine, in turn, reacts with an epoxy group to give a tertiary amine and two secondary hydroxyl groups, (Kroschwitz 1991), scheme I.



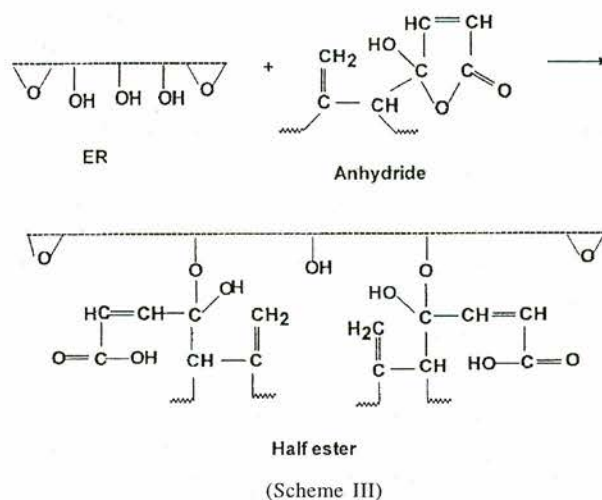
Then the produced cured ER acts as a reinforcer at rubber matrix in composite.

The results (Table 1) show that cured NR/ER/MA (samples represented by GII) have good mechanical properties when cured thermally at $150\text{--}170^\circ\text{C}$ as compared to those compositions cured by UV radiation. On the other hand, sample of GII have better mechanical properties than those obtained in the case of GI. It was found that MA reacts with NR at $150\text{--}170^\circ\text{C}$, the reaction imparts polarity to the nonpolar natural rubber (Jacqueline 1990), scheme II.

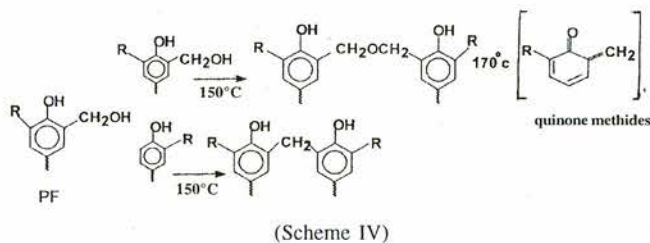


Then the epoxy resin reacts with the formed anhydride to give network structure, as in (scheme III).

The expected product structure is confirmed by infrared spectra (Fig. 1). This figure shows absorption bands at the wave numbers (Bellamy 1980) per cm for the following functional groups: 823, 887, 1233 (epoxy groups), 1028 (aliphatic ether linkage), 1713 (carbonyl groups), 3376 (hydroxyl groups), 1597 (benzene rings), 1111 (aromatic substituent), 3023 (C-H stretch in aromatic rings of bisphenol A), 1370 (methyl group in natural rubber), 2352 (traces of nitrogenous compounds in natural rubber).

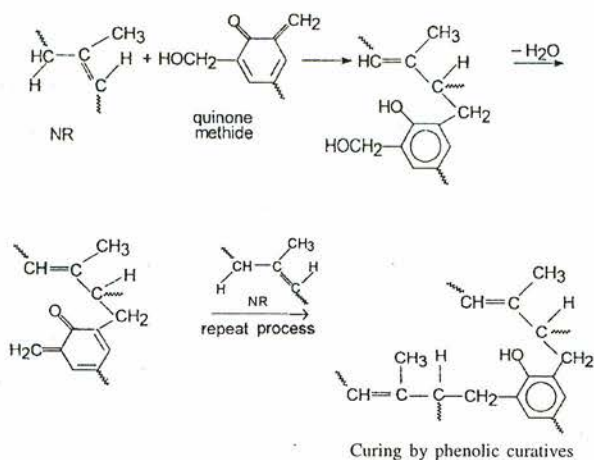


The results (Table 1) show that thermally cured NR/ER/PF compositions (samples represented by GIII) have good mechanical properties as compared to those cured by UV light. The data also reveal that (1) adhesive composition based on PF resins provide the greatest tensile strength values and the least flexibility. This may be attributed to: (a) The aromatic structures of these resins provide bubble free products with high levels of crosslinking (Masse 1997). (b) The very strong physical chemical bonds, which can be formed through the crosslinking formation of PF resins at 150°C . Also self crosslinking reactions take place involving the formation of quinone methides at 170°C via condensation of ether linkage with the phenolic groups (Brydson 1975) as indicated in scheme IV.

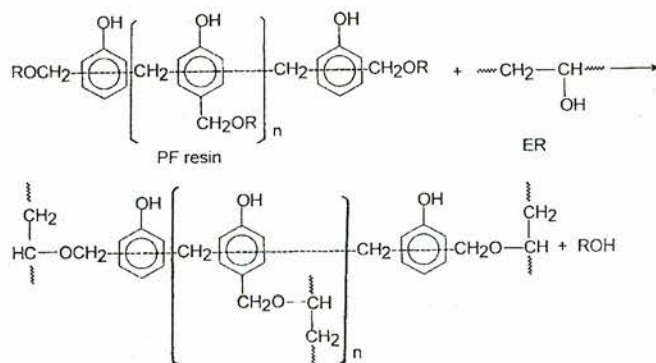


(c) The chains sliding over each other is restricted by the presence of polar groups under an applied stress leading to the least elongation as compared with samples represented by No.1, GI and GII.

(2) Increasing weight ratio percentage of ER increases the tensile strength of adhesive composition. Maxima values can be attained at 60% ER, with a sharp decrease in flexibility. Natural rubber can be cured by the action of phenolic compounds which contain sites for proton acceptance and electron acceptance in proper steric relationship (Mark 1994). This will then permit the reactions as shown in scheme V.



(Scheme V)



(Scheme VI)

PF resins may also react with secondary hydroxyl groups on epoxy resin backbone to afford crosslinked networks as illustrated in scheme VI.

Thus the presence of PF resins as well as MA in the NR/E system leads to formation of interpenetrating network structure and consequently an improvement in mechanical properties is observed.

The adhesion properties of the above tested samples were studied. The obtained data (Table 1) indicate that:

1) Adhesive compositions based on PF resins (samples represented by GIII) show excellent adhesion to wood materials as compared with samples represented by No.1, GI and GII. This can be attributed to their polar nature, furthermore, the phenol methylol present in PF resins structure may form physical chemical bonds through absorption and adsorption in the wood adherent.

2) Increasing weight ratio percentage of ER improves the adhesion properties of adhesive compositions. Excellent adhesion properties can be attained at 60% ER.

Results of the chemical tests, of film samples, carried out using chemicals such as 5% acetic acid, 50% ethanol, 1% sodium carbonate, 10% sulphuric acid and 10% sodium hydroxide are all positive (unaffected).

It is interesting to study the effect of heat on the crosslinked NR/ER system. Heat resistance, as weight loss percentages,

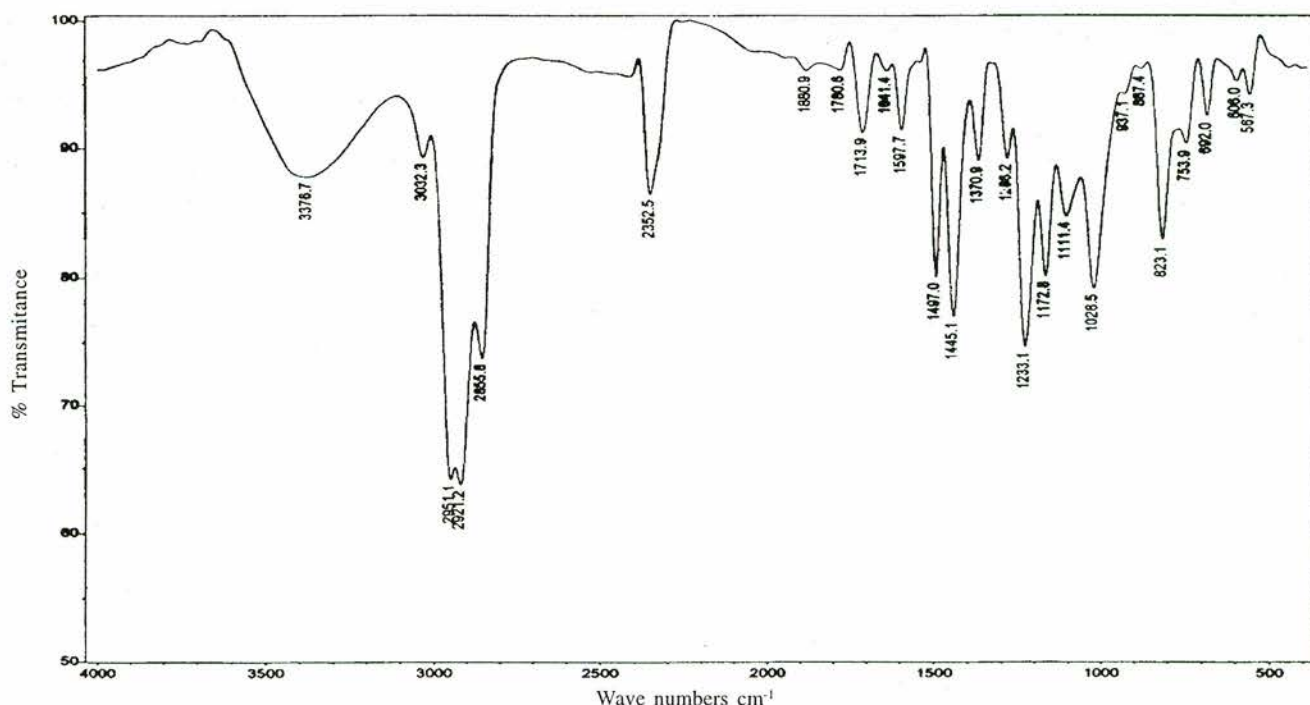


Fig 1. Infra-red spectra of the formed crosslinked NR/ER/MA composition.

Table 1
Formulation and properties of cured natural rubber/epoxy composition

Samples Group No.	Formulation for each 100g NR				Mechanical properties								Heat resistance	
	ER	EDR	MA	PF resin	After thermal curing*				After UV curing for 2 weeks, at 20°C				After thermal curing	After UV curing for 2 weeks, at 20°C
					For wood adhesives		For film Samples**		For wood adhesives		For film Samples**		For film samples** Weight loss % at 150°C for 4 h	
					Tensile strength N cm ⁻²	Elongation %	Adhesion	Hardness shore A	Tensile strength N cm ⁻²	Elongation %	Adhesion	Hardness shore A		
	1	-	-	-	2.88	300	P	41.18	4.91	310	P	43.25	1.49	1.46
GL	2	20	6		29.56	252	G	45.42	31.13	241	G	48.12	1.39	1.365
	3	40	12		31.71	220	G	48.60	36.19	205	G	56.11	1.24	1.21
	4	60	18		38.18	163	E	54.40	41.12	180	E	59.12	1.19	1.14
	5	20		6	46.14	121	G	62.23	38.14	173	G	50.18	1.07	1.09
GII	6	40		12	51.33	103	E	72.18	44.88	152	G	58.44	0.93	0.94
	7	60		18	66.25	84	E	85.57	52.55	132	E	64.12	0.85	0.86
GIII	8	20		10	68.72	82	E	71.14	48.18	148	G	62.15	0.73	0.74
	9	40		20	74.75	77	E	85.33	58.12	123	G	71.24	0.61	0.62
	10	60		30	81.63	65	E	98.20	68.14	101	E	82.18	0.585	0.59

*Thermal curing means: samples represented by GI are cured at 25±1°C for 24 h, while those represented by GII & GIII are cured at 150-170°C for 10 min. ** Film samples are of thickness, 1-1.3 mm; E, Excellent; G, Good; P, Poor.

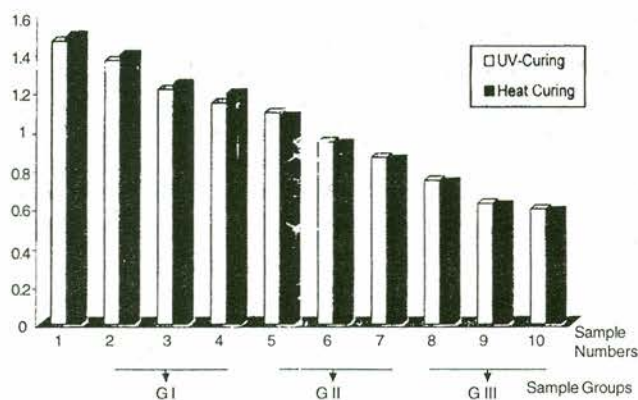


Fig 2. Weight loss percentage of cured NR/E samples at 150°C for 4 h.

of the tested film samples after heating at 150°C till 4 h is studied by bar graph. The drawn graphs (Fig.2) illustrate that:

1. NR chains show the highest weight loss percentages at 150°C for 4 h (samples represented by No.1) as compared with those of other formulated compositions (samples represented by GI-GIII).
2. UV radiation-crosslinkable NR/E/EDA (samples represented by GI) have good heat resistance (e.g. less weight loss percentages) as compared to those compositions cured at 25±1°C for 24 h.
3. Thermally cured NR/E/MA and NR/E/PF compositions (samples represented by GII and GIII, respectively) have less decrease in the weight loss percentages at 150°C for 4 h as compared to those compositions cured using UV radiation.

4. Incorporation of PF resins to NR/ER system leads to the least weight loss percentages as compared with NR/ER system without these resins. In other words, NR/E/PF compositions (samples represented by GIII) are the most thermally stable.

This can be attributed to the fact that, thermal stability is affected by the structure of the hardner (Kroschwitz 1991). The heat resistance of aliphatic amines is low. They are oxidized by atmospheric oxygen to amine oxides, which attack the polymer backbone. Anhydride systems tend to split off the anhydride at temperature over 150°C. This means that anhydride cured formulations exhibit better thermal stabilities than similar amine cured systems. While the presence of methylol groups or etherfied methylol group in phenol formaldehyde leads to the formation of network structure with high temperature resistance and poor UV radiation stability. Therefore phenol formaldehyde cured formulations exhibit the best thermal stabilities as compared to those compositions cured using UV radiation (Kroschwitz 1991).

5. The weight loss percentages of the cured samples decrease with increasing ER content. Thermal stability can be attained at 60% ER.

Conclusion

1. NR/ER/EDA samples have good mechanical properties when cured using UV radiation as compared to those compositions cured at 25±1°C for 24 h.
2. NR/ER/MA as well as NR/ER/PF samples have good mechanical properties when cured thermally at 150-170°C

as compared to those compositions cured by using UV radiation.

3. The presence of PF resins as well as MA in the NR/E system leads to formation of interpenetrating network structure, while cured ER with EDA acts as a reinforcer at rubber matrix in composite.
4. The highest epoxy resin content and the presence of resole phenol formaldehyde resin in NR/ER adhesive compositions improve the tensile strength and adhesion properties on wood.
5. Cured film samples containing resole phenol formaldehyde resin have the best hardness properties, chemical resistance as well as heat stability.

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