Thiol Addition to Epoxidized Natural Rubber: Effect on the Tensile and Thermal Properties

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Epoxidized natural rubber (ENR) samples of various epoxidation degrees were synthesized from natural rubber (NR) latex, and 25 mole% epoxide of ENR was used to prepare ENR room temperature-curable films for coating applications. The films were prepared from rubber solutions. Trimethylolpropane tris(2-mercaptoacetate) (TMP-SH) was used as a curing agent. The effect of the thiol additive on the tensile and thermal properties of epoxidized natural rubber (ENR) was investigated. For the sake of comparison, NR and TMP-SH-containing formulations were also prepared.

It was observed that the addition of TMP-SH improved the tensile, thermal and swelling properties of ENR, indicating the formation of crosslinks. On the other hand, the addition of TMP-SH didn't improve the properties of NR, indicating the absence of reaction with TMP-SH. On the basis of data on the properties of the ENR films of this work it is demonstrated that these are appropriate for coating applications.

Keywords   coatings, crosslinking, epoxidized natural rubber, tensile properties, thermal properties, thiol

INTRODUCTION

The growing interest in the exploitation of renewable raw materials for the development of new materials makes natural rubber (NR) a material of choice among known rubbers. This is due to its low cost and wide availability, not to mention the set of mechanical properties it bears [1].

The increased use of NR results from improvements in physical and mechanical properties through blending (polymers or fillers) or chemical modification. One of the most important ways of chemically modifying NR is the introduction of a few epoxide groups in its structure, obtaining epoxidized natural rubber (ENR) [2–4]. As a consequence, limiting properties of NR like oil resistance, damping, and gas permeation are improved due to the epoxide group which is responsible for the introduction of polarity and reactivity, besides adhesion, which is an important property in coating applications [2,5].

Coatings, varnishes, inks or paints are designed to improve the surface properties of metals, plastics, paper, wood, and textiles. Rubbers are particularly promising for use as coatings in view of their solubility in organic solvents, adhesion to various materials, excellent elasticity and impact resistance, facilitating the application of flexible materials [6].

As in NR, double-bond crosslinking of epoxidized natural rubber results from conventional sulfur vulcanization. ENR can equally be crosslinked by reaction of the epoxide groups [2,7]. ENR vulcanization is significantly faster than that of NR and a much higher degree of crosslinking is achieved in view of the additional activation brought about by the epoxide group [2]. However, the vulcanization reaction proceeds at high temperature only [1] and is usually done with the rubber in solid form. Some coating applications require low temperatures and rubber solutions.

It is well-known that unsaturated polymers can be cured at room temperature with the aid of the thiol-ene curing system, even in the absence of initiator, when subjected to radical initiation or high energy [8,9]. Ene-containing rubbers are also susceptible to reaction with this curing system [10]. Therefore the thiol-ene system is adequate for reaction with the ENR double bond [8]. Besides, the epoxide group reacts readily with thiols [11], which makes possible the ENR ambient temperature cure with a thiol.

Until now, there have only been limited attempts to carry out the cure of ENR in solution. Thus, this paper reports the effect of a thiol tri-functional additive on the mechanical and thermal properties of ENR as films designed for coating applications, the films being obtained from dissolved ENR rubber.

In order to enhance its reactivity, natural rubber was epoxidized [2]. Various degrees of epoxidation were obtained and the reaction was carried out in the latex phase. The ENR was characterized by FTIR while the epoxide content was determined by ^{1}HNMR.

The thiol used as crosslinking agent was trimethylolpropane tris(2-mercaptoacetate) (TMP-SH). Room temperature curable ENR films were prepared using dissolved rubber. For the sake of comparison, a nonepoxidized, TMP-SH–containing natural rubber formulation was also prepared. Crosslinking formation was evaluated by equilibrium swelling, tensile properties, thermal stability by thermogravimetric (TGA) and FTIR analyses. The obtained data were compared to the values of the same parameters for pure NR and ENR.

EXPERIMENTAL

Materials

The 60% dry rubber content (DRC) (ABNT NBR 11598) high ammonia natural rubber latex (HANR) [12] used in this study was supplied by Teadit Indústria e Comércio Ltda from the State of Acre, Brazil. Ultranex NP 95, nonylphenylpoly(ethylene glycol) of 9.5 EO (number of ethylene oxide molecules) was supplied by Oxiteno. 98% formic acid, 30% hydrogen peroxide aqueous solution and toluene were obtained commercially. Trimethylolpropane tris(2-mercaptoacetate) (TMP-SH) was synthesized in our laboratory.

Methods

Synthesis of ENR

The epoxidation of NR was performed according to the literature [13,14] with minor modifications. HANR latex (140.0 g) was diluted to 30% DRC and stabilized with 5 phr (parts per hundred parts of rubber) Ultranex NP 95 before epoxidation. The mixture was neutralized and acidified by slowly adding the desired amount of formic acid ([HCOOH]/[polyisoprene unit] = 0.4 mole/mole). After raising the temperature to 40°C, an aqueous hydrogen peroxide solution ([H_2O_2]/[polyisoprene unit] = 1.46 mole/mole) was added by dripping during 40 min. The reaction medium was then kept at 50°C. The reaction time was counted from the first hydrogen peroxide drop. Aliquots were taken at various time intervals, neutralized with 10% aqueous sodium carbonate solution, and immediately precipitated in absolute ethanol, washed with distilled water and dried under vacuum at room temperature to constant weight.

The epoxide content of the ENR samples was calculated from proton nuclear magnetic resonance spectroscopy (^{1}HNMR) spectra using the following Eq. (1) [15]:

$$Mol \% \; epoxide = 100\left(\frac{A_{2,7}}{A_{5,1} + A_{2,7}}\right)$$

where $A_{2,7}$ and $A_{5,1}$ are the peak integrated areas at chemical shifts 2.7 and 5.1 ppm, respectively. The ^{1}HNMR was recorded on a Varian Mercury VX 300 spectrometer operating at 300 MHz, using 2%(wt/v) solutions in chloroform-D. All chemical shifts reported are internally referenced to TMS.

Preparation of ENR Curable Films

In order to prepare the curable films, epoxidized natural rubber (ENR) was first dissolved in toluene (5% wt/v) until total solubilization. To the rubber solution was then added the TMP-SH curing agent under ambient conditions and magnetic stirring, to be reacted with the ENR. In order to effect incorporation of thiol groups into the ENR polymeric chains the ENR-thiol reaction was kept for 24 h. Compositions containing 5, 10 and 20 phr TMP-SH were obtained. The resulting mixture was then cast over a plane glass plate for gelation resulting from evaporation under controlled saturated atmosphere, and finally the films were dried under vacuum at room temperature up to constant weight according to the procedure described in the literature [16]. The thickness of the obtained films was about 0.7 mm. Attempts to produce nonepoxidized NR curable films at room temperature failed. Only by working at drying temperatures of 80°C or higher and long drying times was it possible to succeed in curing the NR films. Then the NR film was tested to be compared to other formulations. Two formulation controls were also selected following the same procedure, one control of pure NR and another one of pure ENR, the formulations being prepared from their respective latexes after being coagulated and dried. All formulations are given in Table 1.

Equilibrium Swelling

Equilibrium swelling of the dried films was determined in toluene, under ambient conditions [17]. 12.7 mm diameter circular specimens of known weight were cut from films, immersed in solvent at 0.5% (wt/v) and kept in the dark until the equilibrium swelling point. The specimens reached the equilibrium swelling in up to 24 h [16], except for controls and the NR formulation that dissolved in a few hours.

Table 1: Formulations for the preparation of natural rubber and epoxidized natural rubber films.

	Amount (phr)[a]					
Components	**NR**	**NR 10**	**ENR**	**ENR 5**	**ENR 10**	**ENR 20**
NR	100	100				
ENR			100	100	100	100
TMP-SH		10		5	10	20

[a]Parts per hundred parts of rubber.

The result for each sample was obtained from the average of three determinations. The equilibrium swelling ratio (%) was calculated using the following Eq. (2):

$$\alpha = \frac{(W_f - W_i)}{W_i} \times 100$$

where W_f is the final swollen weight and W_i is the initial weight, in g.

Tensile Properties

The tensile specimens were punched out from the dry cast films using DIN Die S 2, and the tensile tests were recorded in a universal testing machine EMIC DL 3000 with a TRD 22 cell, according to the DIN 53504 method [18]. The crosshead speed was modified to 200 mm/min and the tests were carried out at $25 \pm 2°C$. The median value of five tests was reported for each sample.

Thermogravimetric Analysis (TGA)

A Q500 TA Instrument was used for the thermogravimetric analysis (TGA) measurements. Samples were scanned from 30 to 700°C at a heating rate of 30°C/min under N_2 atmosphere.
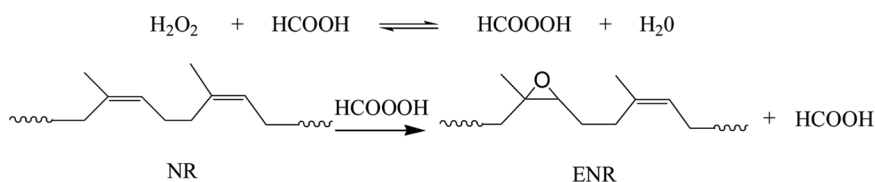
Infrared Spectroscopy

The ENR and ENR/TMP-SH films were characterized by FTIR on a Varian Excalibur 3100 in the attenuated total reflectance (ATR) mode, using the ZnSe/diamond crystal. All spectra were acquired with 100 scans at a $4 \, cm^{-1}$ resolution. The TMP-SH FTIR spectrum was acquired with 20 scans using direct film casting on a KBr cell. The ENR/TMP-SH FTIR films spectra were run on samples dried after the swelling test in toluene.

RESULTS AND DISCUSSION

The NR latex was epoxidized by in situ generation of peroxyformic acid [2], with formic acid and hydrogen peroxide. The reaction is illustrated in Scheme 1.

Characterization of ENR

The epoxide content of the ENR samples was determined using ^{1}HNMR spectroscopy. To this end, the integration area of the peaks of the methine

$$H_2O_2 \quad + \quad HCOOH \quad \rightleftharpoons \quad HCOOOH \quad + \quad H_2O$$

NR $\xrightarrow{\text{HCOOOH}}$ ENR $\quad + \quad HCOOH$

Scheme 1: Epoxidation of NR with in situ generation of peroxyformic acid.

proton adjacent to the oxirane ring (2.7 ppm) and that of the proton adjacent to the carbon-carbon double bond of the polyisoprenic structure at 5.1 ppm were compared [15].

Figure 1 illustrates the synthesis of ENR of various epoxide contents by varying the reaction time at constant temperature. It could be observed that the extension of epoxidation was directly proportional to the reaction time, which is in agreement with the literature [14,19]. Hydrogen peroxide and formic acid require extended periods in order to react with the NR latex before high epoxide contents are formed within the rubber [2,19]. 25 mole% epoxide of ENR films were prepared for the present study.

Figure 2 depicts the FTIR spectrum of ENR with the main features of the NR epoxidation where the absorption at $1250 \, cm^{-1}$ is assigned to the symmetric stretching of the epoxy ring while the $870 \, cm^{-1}$ band corresponds to the asymmetric stretching of the epoxy ring [5,13,15]. Absorptions corresponding to the NR: C=C stretching at $1650 \, cm^{-1}$, CH olefin wagging at $835 \, cm^{-1}$, and CH_3 deformation at $1376 \, cm^{-1}$. The absence of the carbonyl
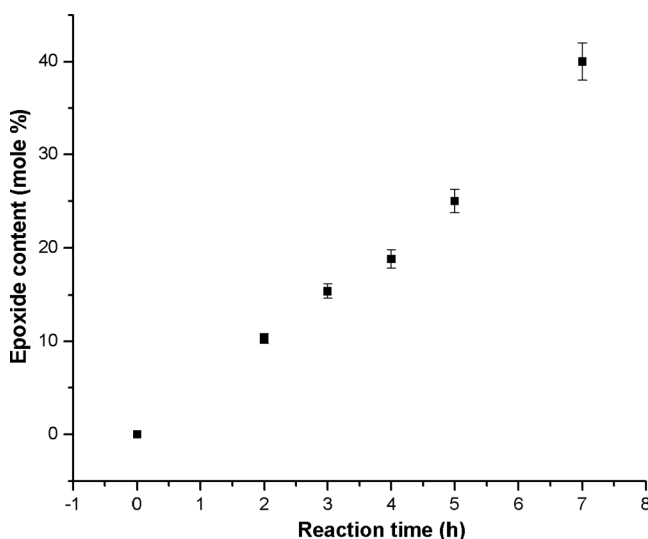

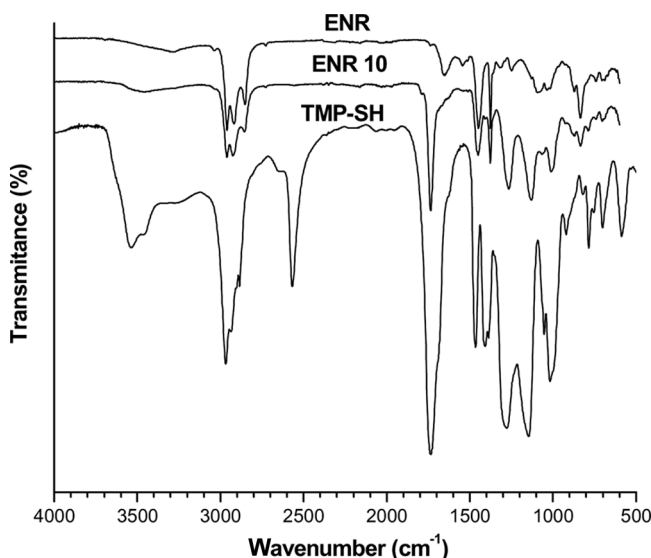**Figure 1:** Epoxide content of ENR synthesized from various reaction times at 50°C reaction temperature.

Figure 2: FTIR spectra of ENR, ENR 10 and TMP-SH.

absorption ($1740\,\mathrm{cm}^{-1}$) in the spectrum demonstrates that no side reaction entailing opening of the epoxide ring [19] during the epoxidation reaction has occurred.

Characterization of the ENR Curable Films

The main feature of the formation of the ENR curable films was insolubilization, with the consequent improvement in tensile properties and thermal stability. The equilibrium swelling profile of ENR/TMP-SH films in toluene under ambient conditions is presented in Figure 3. In a few hours all specimens reached the equilibrium swelling, keeping the same value for up to 24 h. The increase in TMP-SH content in the compositions decreased the swelling ratio, the value obtained in 24 h being 640% for ENR 5, 367% and 372% for ENR 10 and ENR 20, respectively. The decrease in swelling is related to rubber crosslinking and 10 phr TMP-SH seems to be a limit value for addition to ENR. The ENR 10 swelling ratio value is considered to be that of a fully crosslinked rubber [20]. The low swelling ratio value for ENR 10 makes it suitable for coating applications.

As mentioned earlier, ENR is more reactive than NR [2], which is evidenced by the failure of NR to form a curable film at ambient temperature. The NR 10 film obtained at 80°C became a gel in the swelling test in toluene prior to one hour of swelling, rendering it impossible to weigh, which means no or poor crosslinking formation.
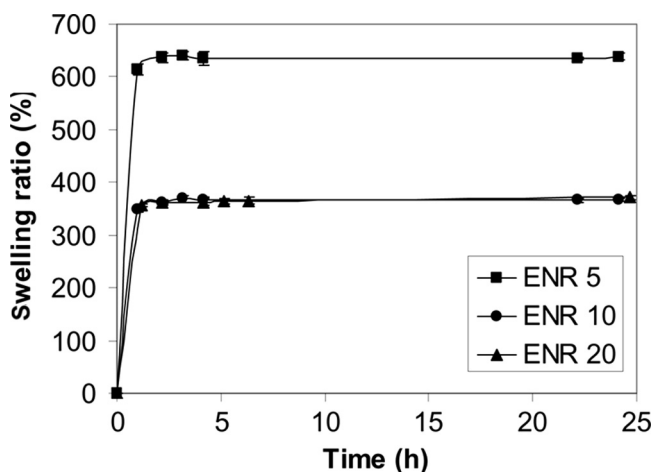
Figure 3: Equilibrium swelling profile of ENR/TMP-SH films in toluene up to 24 h.

Additionally, drying of the NR film under prolonged heating could have originated oxidative products in the rubber, such as esters, hydroperoxides and other carbonyl compounds [21].

Figure 4 shows curves of stress and elongation at break representative of tensile tests of various ENR formulations and NR 10, besides those of pure NR and ENR as controls. The improvement in tensile properties exhibited by ENR compared to those of the controls suggests the occurrence of reaction of ENR with the trifunctional curing agent (TMP-SH) [22]. The modulus depends
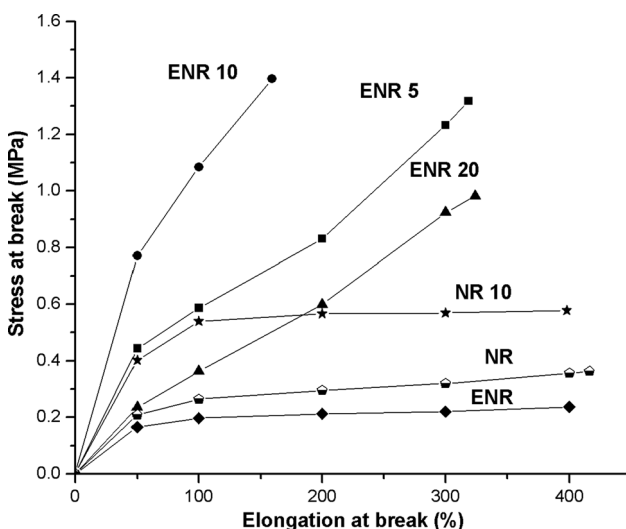

Figure 4: Curves of stress and elongation at break obtained from tensile tests for pure NR, pure ENR, and ENR/TMP-SH and NR/TMP-SH films.

directly on the crosslinking density [23]. The tensile modulus values increased with the increased TMP-SH addition to the formulations until 10 phr (Figure 5), indicating this as the upper TMP-SH concentration limit to reach the number of crosslinks that do not alter the rubber properties [24]. The 10 phr TMP-SH addition limit to ENR as relates to tensile properties is in agreement with swelling test results.

The values for tensile properties found in this work for ENR films are in agreement with the literature [22,16] and the formulations are suitable for coating applications.

For NR films the TMP-SH addition leads to a slight increase in modulus at 100% elongation as well as in the values of stress at break, indicating the restricted influence of the thiol curing agent on NR.

The thermal stabilities of pure ENR and NR, as well as that of films were studied by TGA. Figure 6 presents the TGA curves for all components while Table 2 lists the thermal degradation temperatures. The thermal degradation of pure NR and ENR involves one-step reactions, with the degradation onset temperatures at 352°C and 359°C for NR and 25 mole% epoxide of ENR, respectively. The increase in degradation temperature for epoxidation-modified natural rubber has been described [25], it being due to the epoxide ring opening during the test and consequent slowing of rubber degradation.

The ENR/TMP-SH films showed two degradation steps, the first one at 100°C degradation onset temperature with ending at around 155°C. The first degradation step can be related to the residual solvent (toluene) inside the thick films, or to the epoxide ring opening reaction occurring during the analysis. This reaction was detected at about 155°C by Poh [21]. The degradation onset temperature (T_{onset}) of the second step is around 352°C, being attributed
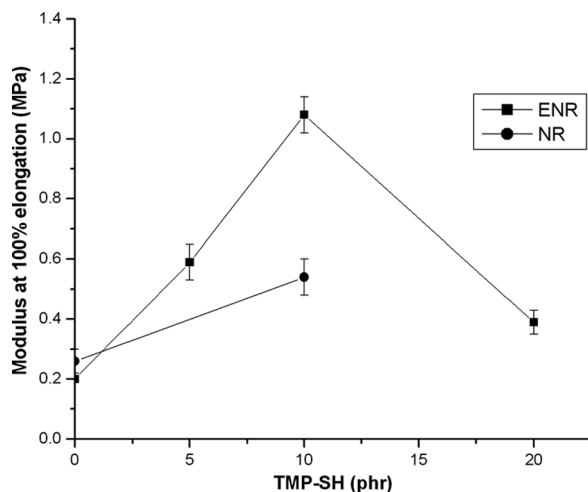

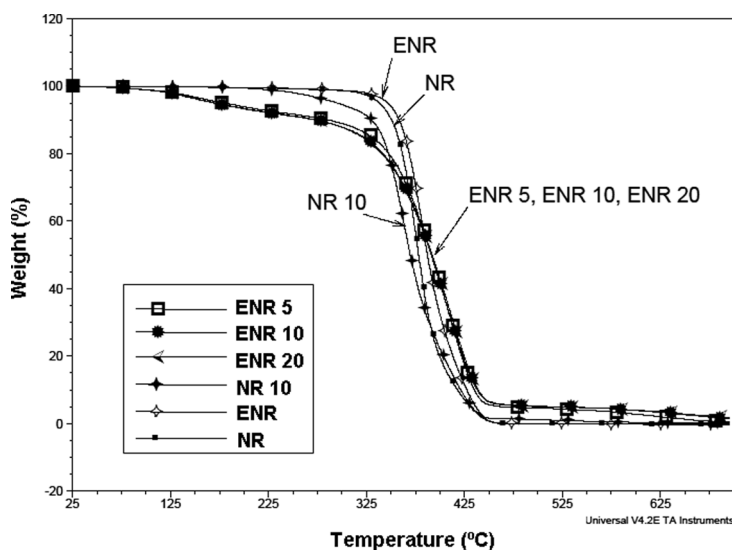**Figure 5:** Effect of TMP-SH addition on modulus at 100% elongation.

Figure 6: TGA of pure NR, pure ENR, and ENR/TMP-SH and NR/TMP-SH films.

to the decomposition of the polymer main chain. As compared to pure NR and ENR, TMP-SH addition to ENR induces higher maximum degradation temperatures (T_{max})(the temperature corresponding to the maximum value in the derivative thermogram), around 400°C, the increase in temperature being proportional to the amount of added TMP-SH. This increase results from a rise in the amount of oxygen-containing compounds in the thermal degradation products of the films, the polarities and volatilities of these compounds being responsible for the augmented T_{max}. TMP-SH addition increases the thermal stability of epoxidized natural rubber [25].

The degradation curve of NR/TMP-SH film has the same decomposition curve pattern than that of the NR, except that the onset and maximum degradation temperatures are shifted towards lower temperatures. This is

Table 2: Temperatures of thermal degradation of pure NR and ENR, and NR and ENR films.

Sample	TMP-SH (phr)	First step		Second step	
		T_{onset} (°C)	T_{dMax} (°C)	T_{onset} (°C)	T_{dMax} (°C)
NR	0	–	–	352.65	377.84
NR 10	10	–	–	336.71	362.83
ENR	0	–	–	359.2	380.92
ENR 5	5	102.20	155.75	352.17	405.00
ENR 10	10	101.06	148.93	352.72	407.89
ENR 20	20	102.76	148.37	353.48	410.18

attributed to the degradation of the NR at 80°C during thermal drying for film formation, producing oxidative products [21]. Then, it is probable that NR didn't react with TMP-SH to reach a detectable degree of crosslinking.

In Figure 2 the ENR 10 curable film, which provided the best properties, is compared to TMP-SH and pure ENR using FTIR analysis. It is possible to observe the disappearance of the SH peak of TMP-SH at $2567\,cm^{-1}$ after ENR and TMP-SH react [26]. The disappearance of the epoxy ring peak at $870\,cm^{-1}$, formation of the aliphatic ether group at $1113\,cm^{-1}$ resulting from the epoxide ring opening [27,28], and decrease in intensity of the $835\,cm^{-1}$ peak related to unsaturation is also observed. The restricted presence of OH absorption due to the reaction of ENR and TMP-SH by epoxide ring opening is also evidenced in Figure 2.

From these observations it is suggested that crosslinks are formed in ENR films resulting from low temperature reactions of up to 30°C, the reactions involving the epoxide ring as well as the residual unsaturation [10,28].

CONCLUSIONS

Epoxidized natural rubber (ENR) specimens were successfully synthesized via in situ epoxidation from NR latex. Several epoxide contents were obtained by varying the reaction time; extension of epoxidation was directly proportional to the reaction time. 25 mole% epoxide of ENR was used in this work.

For coating applications it was possible to prepare from dissolved rubber solutions room temperature-curable ENR films using a tri-functional thiol (TMP-SH) as a curing agent.

The addition of TMP-SH improved the ENR tensile, thermal and swelling properties. 10 phr is considered a limit value of addition as relates to the influence of this additive on tensile and swelling properties. These results indicate reaction between ENR and TMP-SH with crosslink formation, as confirmed by FTIR analysis.

On the other hand, TMP-SH addition didn't improve the NR properties and the film was only formed under higher drying temperatures, indicating that it didn't react with TMP-SH.

The properties of the ENR films prepared and discussed in this work imply that these films are appropriate for coating applications.

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