We are IntechOpen, the world's leading publisher of Open Access books
Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Evaluation of Addition of Reactive Resin for an Adhesive Formulation of Pressure-Sensitive Adhesive

Tzeitel Hernández-Martínez,

Beatriz Adriana Salazar Cruz,

José Luis Rivera-Armenta,

María Yolanda Chávez-Cinco,

María Leonor Méndez-Hernández and

Ulises Paramo-García

Abstract

Nowadays, adhesive industry is growing, and its development will be important in a short future because it offers good returns, and in some cases it is a better option for packaging and sealing with advantages in prices, productivity and weight reduction. In terms of joining and/or sealing, adhesives are well positioned among joining systems; however, knowledge about adhesives is need for their efficient use and only through proper design of the union can be achieved satisfactory results. In this chapter, a development of a formulation of pressure-sensitive adhesive based on styrene-butadiene copolymers using a reactive resin is reported. Non-aromatic solvents were used in adhesive formulation with the aim of avoiding the emission of harmful solvents into the Atmosphere, and the adequate combination and amount of solvents were found. The effect of addition of a phenolic resin in the adhesive formulation as a crosslinking agent was evaluated. By means Fourier Transform Infrared spectroscopy (FTIR), the crosslinking reaction was also studied. The performance of adhesive formulation was evaluated by means of dynamic mechanical analysis (DMA).

Keywords: reactive resin, crosslinking, adhesive properties, radial SBS

1. Introduction

Adhesives have been used since ancient times, since the discovery of materials with adhesive properties from natural and animal resources. Then, through the study of the properties and appearance of new materials, several kinds of adhesives with synthetic components have been developed with the aim of improving their performance properties in specific application areas.

An adhesive is a material capable of joining two substrates through mechanisms of adhesion and cohesion through surface contact; it is applied over surfaces to keep them joined permanently. Also, the adhesives can be used as sealants.

Adhesion referred as the state between two bodies in intimal interfacial contact that transferred as interfacial forces in substrate area to carry out the joining or adhesion.

The adhesion phenomena can be understood by some theories: the adhesion chemical theory refers to intermolecular and Van Der Waals forces and chemical bonds that are generated between the adhesive and substrate. The diffusion theory explains the adhesion based on polymeric chain movements through the interphase, determining higher mobility according to molecular weight resulting in partial penetrations between materials. The weak limit layer theory proposes the existence of zones in the adhesion surface with cohesive breakages or weak joint forces originated by impurities in adhesive or adherent. The mechanical theory explains that adhesion can be achieved according to porosity and rugosity of the substrate surface when the adhesive penetrates forming anchor zones. The electrostatic theory proposes the formation of electrostatic forces at the adhesive-substrate interphase and is commonly applied in polymer-metal adhesion. The adsorption theory refers to the forces generated in the adhesive-substrate interface considering the superficial tension of adhesive to wetting the substrate and forming a contact angle [1].

The adhesive joint can be considered of two types: structural and non-structural. The structural adhesive joint is applied on substrates that experiment high deformations, over its yield point. This type of joints can be capable of transferring strain without loss in the integrity of the system in the design limits. The non-structural adhesive joints are those that do not require support substantial charges; its function is to keep materials of light weight in established place in the system of joint design. The sensitive adhesives to pressure and package adhesives are examples of non-structural adhesives.

1.1. Adhesive formulations

There are several types of adhesives that are developed in function of its final application, among contact adhesive base solvent with Polychloroprene for applications in wood, canvas and felt, etc. A disadvantage of these adhesives is when it comes to the environmental field, due to the kind of polymer, so it is necessary to find alternatives to replace Polychloroprene, styrene-butadiene-styrene copolymers (SBS) an option, using a reactive resin to obtain contact adhesive base solvent from equal or better performance. However, in attempts to establish a formulation with these components, there are some problems in stability and precipitation

during storage; therefore, a formulation is required based on a proposal of resin and polymer that makes adhesives capable to cover all the performance parameters during storage and application.

On the other hand, development of adhesive formulations that are environmental friendly is a requirement according to several organizations, with the aim of covering regulations, because it is necessary for incorporation of substitution of harmful materials. Adhesives can be formulated by several paths, according to applications and compliance, which depends on cohesive and adhesive properties that can be tailored with a good polymer selection or amount of reactive resin or with the presence of another additive. Polychloroprene is one of the most used polymers in pressure-sensitive adhesive (PSA) formulations, because there are regulations that the material needs to be replaced. Among the materials that have been used in PSA formulations, styrene-butadiene copolymers represent a good option [2, 3]. In adhesive formulations, crosslinking reaction is the main step that controls the adhesive properties, and it can be carried out by means of addition of different agents; the most common crosslinking agent is sulphur [4], but organic peroxides and ester, ether and phenolic resins can also promote the crosslinking agent with appropriate conditions, for instance radiation, heat, change in pH, etc.

SP-154 is a heat-reactive phenolic resin that was developed for adhesive formulation; it is soluble in aromatic hydrocarbons and ketones and partially soluble in alcohols. Adhesive formulations with SP-154 resin have excellent heat resistance and high cohesive strength [5].

Styrene-butadiene copolymers (SBC) have a wide field of applications as shoe soles, impact modifiers, asphalt modifiers, adhesives and sealants. Several kinds of SBC have been used in adhesive formulations and as films in adhesives [2, 6, 7]; however, study of radial structure is not reported before.

There is a report that studied the adhesion properties of SBS copolymer and an epoxy resin after crosslinking with ultraviolet light, and that crosslinking grade of polybutadienic block was high and the adherence strength depends on the crosslinking level [6].

The amount and resin type in an adhesive formulation affect its performance, so it is necessary to evaluate the corresponding amounts to obtain the desired properties. Previous report [8] carried out the shear test for single overlap in cured probes using as substrate aluminium with adhesive formulations prepared with phenolic resin in different concentrations. According to the results, a higher resin concentration increases the shear strength; it was also found that the failure kind depends on resin concentration in formulation, so phenolic resin was shown to be an effective additive to improve adhesive properties.

An important characteristic to be considered in adhesive formulations is the polymer structure. Researchers prepared two copolymers, one of radial structure and the second one random from poly (methyl methacrylate) and poly (2-ethylhexylacrylate-co-methylacrylate), reporting high differences between block copolymer and random, due to the ability of the last one to form physical networks by phase separation [9].

1.2. Resin effect on adhesive

According to international standards ISO 472, ISO 4618/3, the resins are defined as "organic solids, semisolids or pseudo solids that have an indefinite and relative high molecular weight, and often melt over a wide temperature range".

The resins have the following characteristics: average molecular weight lower than 10,000 g/mol, amorphous and complex structures, and do not exhibit a well-defined melt point, but have a glass transition temperature and softening temperature.

The resins can be divided into natural and synthetic. The first are from animal and vegetal sources; the second result from controlled chemical reactions and are divided into:

- Hydrocarbon resins that are produced by means of polymerization, and they are added to polymer to provide adhesion, flow and toughness.

- Synthetic resins obtained by addition polymerization and polycondensation; they are intermediates in plastic synthesis of high molecular weight [10].

The selection of resin for use in thermoplastic rubbers was based on its tendency to associate with intermediate or final block, depending on the desired effect on adhesive properties. The resin with softening point over 85°C tends to associate with the final copolymer blocks. This category of resins tends to provide rigidity to formulation and hold the cohesive strength in high temperature, and is used to improve the specific adhesion of the final block phase and adjust the flow viscosity [11].

1.3. Phenolic resins

The phenolic resins are used widely in industrial level due to its high thermal stability, toughness and stress resistance, and provide wide application areas especially in coatings, adhesives, insulation and laminates. The classic phenolic resins are resol and novalac; its structure can be modified to obtain desired properties in several applications [12].

The resol and novalac resins are intermediate reactive that under some transformations variety (for instance, novalac in production of poly (aril ether amides) and resol by means of reaction with acetals to produce wire varnish) among some improvements and in some cases improved resin systems that produce reactive resins for value-add products [13].

The phenolic resins are used also in combination with reinforcers such as carbon or fiberglass. In these systems, the mechanical properties are lower than when epoxy resin is used, but with better fire behaviour. One of the most important applications is in aircraft interiors.

The novalac resins are stable, thermoplastic, solid, soluble and meltable. They are prepared under acidic conditions with less than equimolar proportion of formaldehyde with phenol, and these kinds of resins are preferred to moulding materials [14]. **Figure 1** shows the obtaining of a contact adhesive using a resol resin.
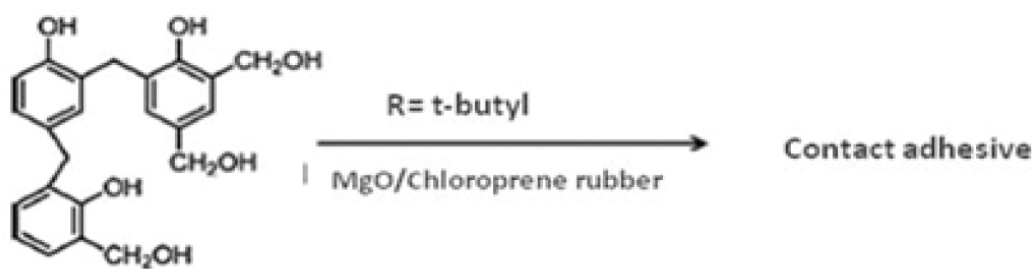
Figure 1. Obtaining of contact adhesive from a resol resin [14].

In this kind of contact adhesives based on chloroprene (**Figure 1**) are added magnesium oxide and zinc, with the aim of acting as HCl acceptors and crosslinkers. The magnesium oxide plays an important role to form and no meltable but soluble metallic complex with phenolic resins. This complex improves the adhesive cohesive strength at high and room temperatures. The resins family of Terc-butylphenolics is the most widely used in neoprene adhesives because it provides high thermal resistance when reacting with magnesium oxide present in these formulations [14]. The rubber properties change when crosslinked. These changes are reflected in thermoplasticity reduction, improving the abrasion and increasing tension strength.

1.4. Curing kinetic study

The chemical reactions involve formation and rupture of chemical bonding. The associate energy to a chemical bonding is a potential energy form, so that the chemical reactions involve potential energy changes. Often, for a reaction to occur, certain covalent bonds must be broken for others to emerge, which only occurs if the molecule orientation is appropriate to collide with enough kinetic energy to overcome the stabilization of potential energy of the bonds. The average kinetic energy of a molecule group is proportional to absolute temperature.

The kinetic contemplates the chemical reaction study and laws that govern that rate. The experimental fact that is based on the reaction rate of a system, at specific pressure and temperature, is only a state function. According to that, the basic equation of rate is:

$$\frac{da}{dt} = kf(a) \tag{1}$$

Eq. (1) relates reaction rate da/dt, at pressure P and constant temperature T, with a function that shows the reactive species concentration $f(a)$, through the rate constant k. The k units depend on global reaction order; the calculated value corresponds to the reaction at a particular temperature and varies if temperature changes. Experimentally, it has been probed that for most of the homogeneous and heterogeneous reactions, the reaction constant depends on temperature. This dependence follows the Arrhenius equation [3]:

$$K = A^{(-E_a/\mathrm{RT})} \tag{2}$$

where K is the reaction constant, E_a is the activation energy, A is the preexponential factor or frequency factor, R is the gas constant (8.314 J/mol K), T is the absolute temperature and often E_a and A are considered temperature independents.

The activation energy E_a represents the energy limit to be overcome to carry out a reaction. The frequency factor is understood as the constant of rate to an infinite temperature. For a first-order reaction, the logarithmic form of Arrhenius equation is reordered for a unique temperature and is compared with straight line equation [3]:

$$\ln k = -\left(\frac{Ea}{R}\right)\left(\frac{1}{T}\right) + \ln A \tag{3}$$

The frequency factor value of the collisions of A is almost constant in moderated temperature changes; thus, $\ln A$ can be determined with the constant term of the equation (the interception). The line slope is obtained when a graph of $\ln k$ in function of $1/T$ is $-Ea/R$ is plotted; in this way, it is possible to determine the E_a value from the slope.

The reaction conversion is defined as a function $f(\alpha)$ that depends on the reaction mechanism. The model can be iso-conversional or named of n order and autocatalytic model [15, 16].

In the present work is reported the adhesive formulation based on a styrene-butadiene copolymer using a phenolic reactive resin. The effect of resin amount and combination of non-aromatic solvents was also studied. By means of infrared spectroscopy, the crosslinking reaction was monitored, and adhesive properties were evaluated by means of dynamic mechanical analysis and tensile test.

2. Methodology

2.1. Materials

A thermoplastic copolymer styrene-butadiene-styrene (SBS) of radial block structure with polystyrene content of 30% and density of 0.94 g/cm³ provided by Dynasol Elastomers was used. As reactive resin, a commercial phenolic type resin named SP-154 from Ameripol Chemical S.A. de C.V. was used, with phenolic content >95%, formaldehyde content 200–400 ppm, melt point 79.4°C, flammability point 176.7°C and specific gravity 1.1 g/cm³; it was non-water soluble. As solvents were used ethyl acetate ≥99.5%, cyclohexane HPLC grade, Aldrich, and acetone ACS grade, Analytyka. The solvent selection was according to solubility parameter.

After proper solvent selection, solubility parameter of mix (δ_{mix}) was determined, according to Eq. (4), and it is possible to determine the amount of each solvent.

$$\delta_{mix} = \Sigma_{i=1}^{n} \delta_i f_i \tag{4}$$

where δ_i is the solubility parameter of each component and (f) is the volumetric fraction. **Table 1** shows the individual solubility parameter, mix solubility parameter and volume fraction.

Solvent	Solubility parameter		Phr	Volume fraction
Ethyl acetate	9.1		140	0.367
Cyclohexane	8.2		203	0.533
Acetone	10.0		38	0.1
Σ			381	1.0
δ_{mix}				8.71

Table 1. δ_{mix} for SBS polymer and solubility parameter of used solvents.

Adhesive formulation-based solvent consists of SBS elastomer, phenolic resin with commercial name SP-154, zinc oxide powder as filler and a mix of solvents (**Table 2**).

Component	Phr
Polymer	100
Phenolic resin (SP-154)	0, 30, 50, 70
Zinc oxide	0, 1.0
Cyclohexane	203
Acetone	38
Ethyl acetate	140

Table 2. Experimental matrix for adhesive formulation.

2.2. Adhesive preparation

Adhesive preparation consists of mixing all components in a Kettler glass reactor using a mechanical stirrer (IKA Euro-STPCV 600051 model) at 3500 rpm as maximum speed, at room temperature and 50% relative humidity. The material addition sequence was established according to several experimentations, based on solubility, dispersion, among others; first, SBS was added to solvent mix, after the zinc oxide and finally the phenolic resin and was continuously stirred for 2 h.

The thermogravimetric analysis (TGA) was carried out on materials in SDT2960 TA instrument equipment under a N_2 atmosphere with 20 ml/min flow, in a temperature range from 40 to 600°C with 10°C/min rate, using 15 mg sample amount. DMA analysis was carried out in a DMA 2980 TA Instruments equipment, with a film tension clamp with multifrequency mode

in a temperature range from −100 to 400°C with heat ramp of 5°C/min, 1 Hz of frequency and sample dimensions of 17 × 6 × 1 mm. Infrared (IR) analysis was carried out to evaluate crosslinking reaction and possible secondary reactions. IR spectra were recorded in Spectrum One Perkin Elmer equipment using the ATR technique with 12 scans and resolution of 4 cm^{-1} in wavenumber range of 4000–500 cm^{-1}. Adhesive films were cured at 193°C, and different times since 0 until 60 min, with the aim of evaluating crosslinking process.

3. Results and discussion

3.1. Thermogravimetric analysis

From thermogravimetric analysis, with initial decomposition temperature, can be predicted the thermal stability of materials, and from the derivative curve of loss weight can be determined the maximum decomposition temperature.

Figure 2 shows the TGA thermogram where derivative indicates that region decomposition begins at 193°C, while at 217, 356 and 457°C other resin composites are degraded. Previous reports [17, 18] found a decomposition temperature at 199°C when a phenolic resin was used in adhesive formulation, mainly due to metylol and hydroxyl groups from phenolic structure. With higher phenolic group content, the temperature decomposition is lower. Around 350°C, this resin type can present active sites that condensed with metylol groups showing a constant degradation and at 400°C can be produced the breaking of phenolic groups with methyl groups from phenol structure.
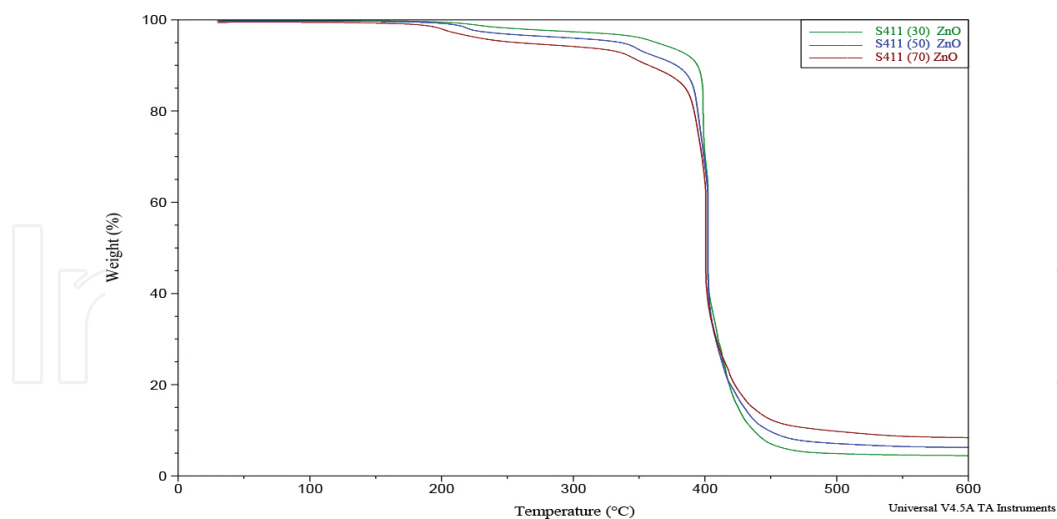

Figure 2. TGA thermogram of adhesive formulations 30, 50 and 70 phr of resin SP-154 and zinc oxide.

3.2. Dynamic mechanical analysis (DMA)

DMA results were compared to evaluate the effect of resin in adhesive mixtures and the effect of addition of ZnO, monitoring the storage modulus and Tan δ. **Figure 3** left shows the DMA

thermogram for SBS, SBS with 30 and 70 phr of reactive resin. At lower temperatures, the storage modulus (E') increases with resin content from 0 to 70 phr at low temperatures, and when temperature increases E' decreases. It can be observed that over 193°C, the E' values increase, which is more evident for adhesive with 30 phr of reactive resin which presents higher E' value, attributed to recovering behaviour from crosslinking reaction of elastomer with resin, indicating that higher resin content is not favourable for crosslinking. When zinc oxide was added in adhesive formulation (**Figure 3** right), the behaviour was similar to adhesive formulations without zinc oxide but with higher E' values due to addition of fillers, such as zinc oxide. Improvement of the elastic properties of a polymeric matrix at higher temperatures in rubber region is attributed to interactions between particles and polymer matrix due the presence of a high surface area. This behaviour can be corroborated with Tg displacement to higher temperatures [19].
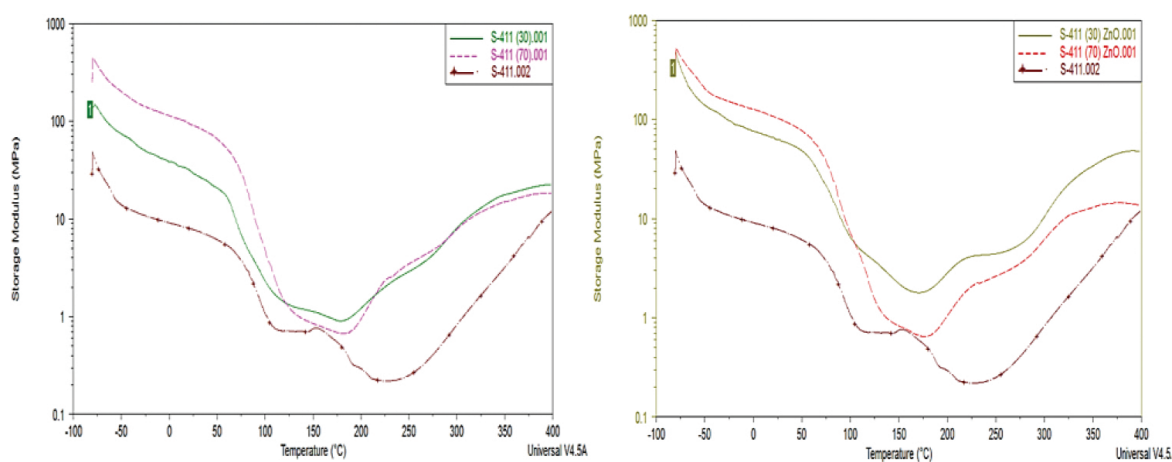

Figure 3. DMA thermogram of adhesive formulations with 30, 50 and 70 phr of resin SP-154 without (left) and with zinc oxide (right).

A non-uniform crosslinking has no considerable effect over the macroscopic properties of a material, such as E', but in fracture properties the affectation must be bigger due to the presence of weak localizable zones that act as failure initiation points [20].

The transitions of adhesive formulations were determined by means of Tan δ curves from DMA (**Figure 4**). It was possible to observe that adhesive formulation with 70 phr resin has higher Tan δ quotient compared with others, in the polystyrene Tg region. The deformations from this are attributed to non-homogeneous crosslinking between elastomer and resin. The increasing in Tg value is due to the crosslinking reaction that generates more rigidity [2]. In the crosslinking process, a three-dimensional network is generated, and the chain flexibility controls the physical and thermo-mechanical properties [20]. These changes are more notable when zinc oxide is added to adhesive formulation, because the particles cause an increase of interfacial areas in the system diminishing the crosslinking grade. The peak over 80°C is attributed to crosslinking process of elastomer, and it can be seen that it is affected by resin addition. **Figure 4** shows the Tan δ curve from DMA for adhesive formulations with zinc oxide.

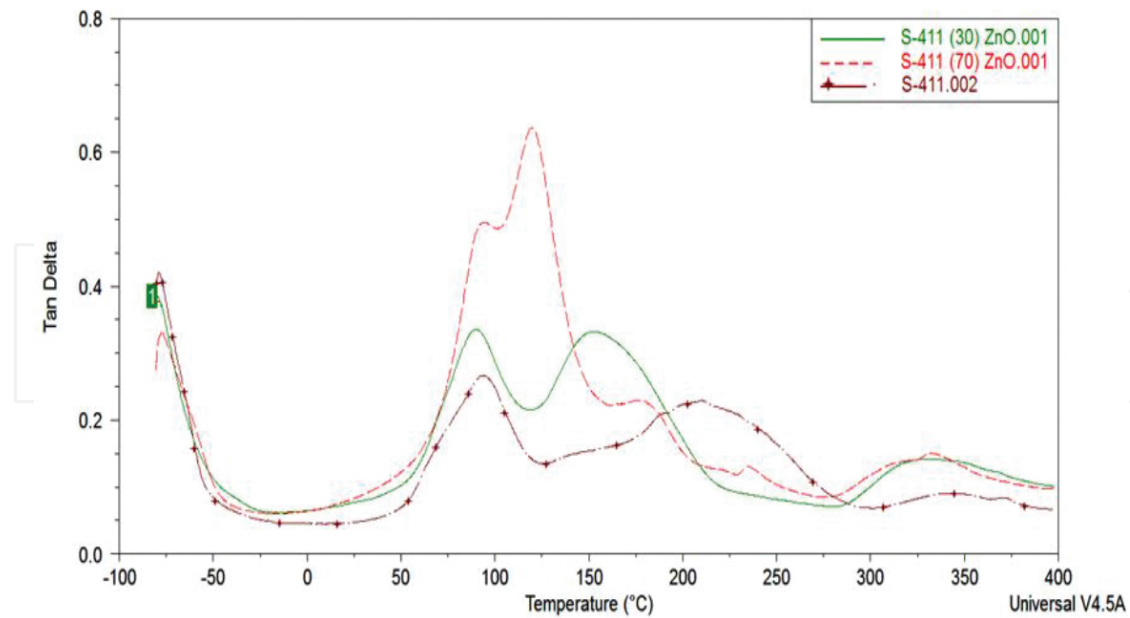**Figure 4.** Tan δ curve from DMA for adhesive formulations with elastomer and 30 and 70 phr of resin SP-154 and zinc oxide.

3.3. Kinetic study of crosslinking process

By means of DSC analysis, the curing parameters of adhesive formulations were determined, and the measurements were carried out in isothermal conditions at 180, 190, 200 and 210°C. From general reaction rate equation is possible to realize kinetic studies by following the reactions that were carried out in solid state in function of time at constant temperature according to the next equation [3]:

$$\gamma = \frac{d\alpha}{dt} \tag{5}$$

where γ is the reaction rate, α is the conversion grade or reaction extension and dt is the differential time.

By means of DSC, it was assumed that in material crosslinking during an exothermic process, the conversion rate is directly proportional to heat flow with the next equation [3]:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{H_T} = kf(\alpha) \tag{6}$$

where dH/dt represents heat flow, H_T is the total enthalpy when crosslinking reaction has been completed, k is the rate constant and $f(\alpha)$ is a function that depends on the reaction model. α can be expressed as with equation [21]:

$$\alpha = \frac{H_t}{H_T} \tag{7}$$

where H_t is enthalpy at time t. The total enthalpy can be estimated by means of integration of the main exothermic peak of DSC non-isothermic curves [21].

For the crosslinking process to adjust to a model of order, the reaction kinetic is described as a function of conversion grade $f(\alpha)$, which provides a dependence of the reaction rate by means of the next equation [21]:

$$f(\alpha) = k(1-\alpha)^n \tag{8}$$

where n is the reaction order. In the kinetic order n, the maximum conversion rate $d\alpha/dt$ corresponds to $t = 0$ and is proportional to material concentration that has been reacted [15]:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{9}$$

It is assumed that reaction rate depends on the temperature; thus, the constant rate can be determined by means of the Arrhenius equation [15]:

$$k = Ae^{-E_a/RT} \tag{10}$$

where A is the pre-exponential factor, E_a is the activation energy, T is the absolute temperature and R is the gas constant. Reordering Eq. (9) [15]:

$$\ln\frac{d\alpha}{dt} = \ln k + n\ln(1-\alpha) \tag{11}$$

By means of lineal regression, the $\ln(d\alpha/dt)$ vs $\ln(1-\alpha)$ is possible to determine the kinetic parameters k and n. Studies have been conducted for crosslinking reactions from dynamic and isothermal methods in which the very similar results are obtained in the values of the kinetic parameters [15].

The kinetic parameters n and H_T from model of order reaction n were calculated with Pyris software of Perkin Elmer using isothermal curves. The H_T values can be introduced in the software if reaction heat or melting heat of sample is known, however. All adhesive formulations were carried out by duplicate at corresponding temperatures 180, 190, 200 and 210°C for comparing the kinetic values and obtaining an average.

Using a multilinear regression, parameters A, E_a and n were obtained from the next equation [22]:

$$\ln\left(\beta\frac{d\alpha}{dt}\right) = ln(A) - \frac{E_a}{RT} + n \cdot \ln(1-\alpha) \qquad (12)$$

where β is the heating rate.

The adjust quality of dates from kinetic model can be noticed in graph ln k vs $1/T$. In the ideal case, the lines passing through the points (the slope for calculation of activation energy) form parallel straight lines, as is required by the theory of kinetic model applied [22].
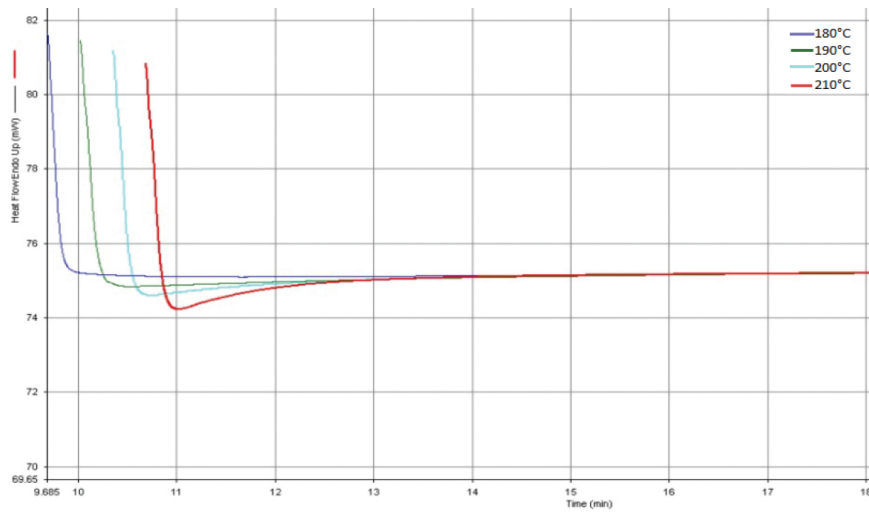

Figure 5. DSC analysis in isothermal mode for adhesive formulation with 70 phr of resin and zinc oxide at different temperatures.
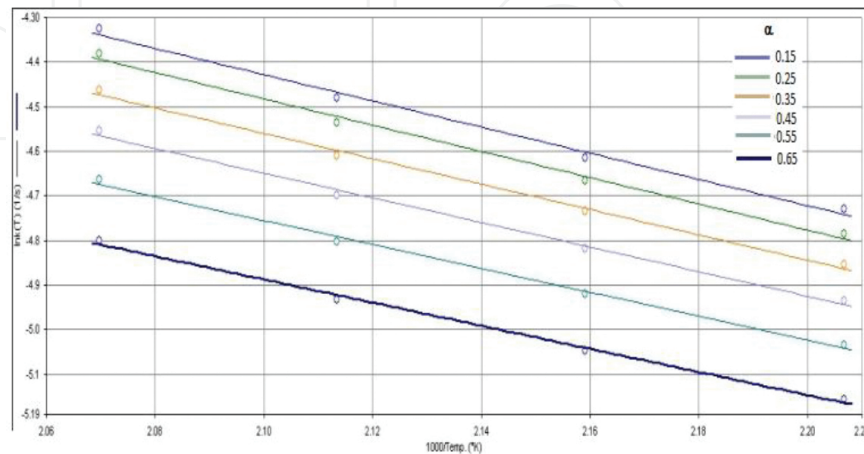

Figure 6. ln k vs 1000/Ta at different values for adhesive formulation with 70 phr of resin and zinc oxide.

In **Figure 5** are presented the isothermal curves obtained for adhesive formulation with 70 phr and zinc oxide at different temperatures, showing the influence of temperature in exothermic region, and **Figure 6** shows the corresponding graph of calculating activation energy (ln k vs $1/T$), obtaining a lineal range in the extension of reaction ensuring that the data are convincing [21].

The selected temperature to obtain the kinetic parameters was 190°C, because it was closer to crosslinking reaction temperature. **Table 3** shows the obtained kinetic values.

Adhesive formulation	T, °C	N	ln A	ln k (s^{-1})	E_a, KJ/mol
Adhesive 0 phr	190	1.72	19.4	−3.8	98.07
Adhesive 30 phr resin	190	1.3	0.52	−4.77	24.91
Adhesive 50 phr resin	190	1.2	−1.44	−5.07	17.86
Adhesive 70 phr resin	190	1.28	−1.87	−5.27	15.38
Adhesive 0 resin phr ZnO	190	1.32	0.98	−4.14	61.98
Adhesive 30 phr resin ZnO	190	1.34	2.27	−4.61	33.46
Adhesive 50 phr resin ZnO	190	1.35	0.92	−4.77	26.85
Adhesive 70 phr resin ZnO	190	1.27	−1.24	−5.08	21.46

Table 3. Kinetic parameters obtained from DSC isotherms.

From **Table 3** the order reaction is $1 \leq n \leq 2$. The reaction order value, n, affects the reaction rate of the formulation allowing to determine the proper period of crosslinking of materials. On the other hand, the reaction order is indicative of molecule number that can react in crosslinking reaction, so that the resin affects in predominant way the crosslinking kinetic process [2].

About the activation energy values from **Table 3**, it can be observed that resin content decreases the E_a values, and the zinc oxide causes an increase in E_a values compared with adhesives without zinc oxide.

The generous concentration of reactive sites and low viscosities in the initiation stage of crosslinking reaction contribute to increasing the degree of conversion after a time interval decelerates showing changes in the time reaction due the decreasing of availability of active sites and the increasing of viscosity, so the decreasing on reaction rate carry to the crosslinking reaction pass from chemical to diffusion control [21].

The physical properties of thermoplastics and elastomers used for crosslinking depend on the crosslinked structure, grade, time and crosslinking temperature; these parameters are related to network formation that provides substantial information about network structure and properties and processability [23].

3.4. FTIR characterization

FTIR technique was used to evaluate the crosslinking at different times (0, 20, 40 and 60 min, shorter times do not show significant effect), identifying the main functional groups that form or disappear when crosslinking reaction was carried out.

The crosslinking process is carried out by means of reaction of methylol and hydroxyl groups with unsaturations of polybutadiene [2]. Initially, the decomposition reaction of resin by thermal effect generates active sites (methylol and hydroxyl) that stimulate the reaction to the formation of benzocarbenium ions with the double bond of the polybutadiene units to form cromane ring (**Figure 7**). Previous works [24, 25] prepare thermoplastic vulcanizate from natural rubber and high density polyethylene with and without compatibilizer, using an octyphenol formaldehyde resin using a compatibilizer obtaining good tensile strength and high elongation values, besides lower deformation compared with thermoplastic vulcanized without compatibilizer, which can be attributed to the formation of cromane ring of reaction. SBS copolymer and phenolic resin are present in an adhesive formulation.
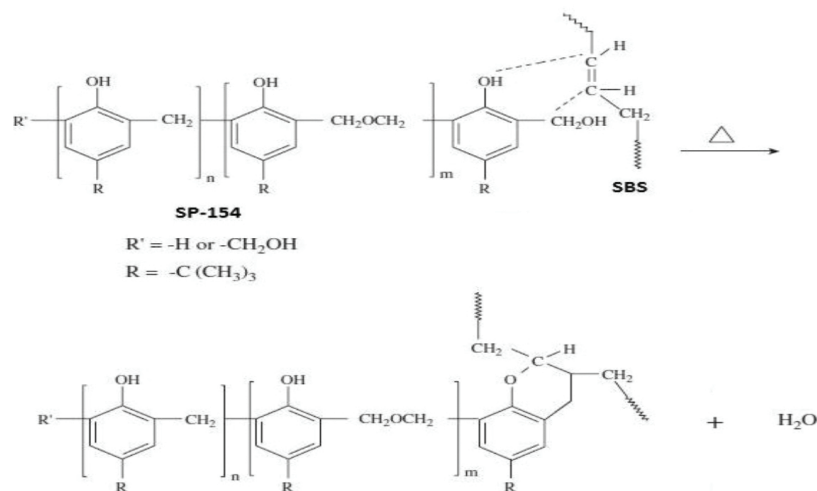

Figure 7. Crosslinking reaction for phenolic resin and SBS elastomer [25, 26].

Figure 8 shows the IR spectra for adhesive formulations with 30 phr resin without zinc oxide at different times. According to crosslinking reaction proposal, double bond of polybutadiene block has to decrease. The characteristic peak of C=C is at 1639 cm^{-1} and does not show a significant change with time; however, there is another peak attributed to =C—H trans and =CH$_2$ vinyl at 963 and 910 cm^{-1}, which present a decrease in intensity. The peaks from =C—H cis at 727 cm^{-1} also show a decrease in intensity with time, which is indicative that crosslinking reaction of phenolic resin and SBS copolymer is carried out, mainly in cis structures. The polystyrene peaks at 1602 and 697 cm^{-1} do not show significant changes, which implies that crosslinking is not taking place in that polymer block. On the other hand, peaks attributed to phenolic resin are present at 3319, 1450, 1210 and 1026 cm^{-1}, which present significative changes in intensity corroborating that crosslinking reaction is carried out with elastomer compared with elastomer without curing.
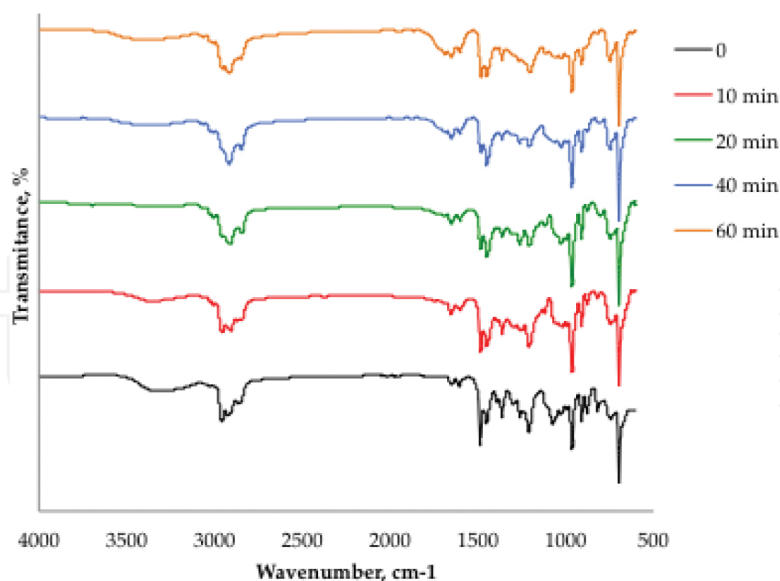
Figure 8. FTIR spectra of adhesive formulation with 30 phr resin at different times.

The peak at 1450 cm^{-1} corresponding to CH$_2$ group increases due to the formation of methylene bonding between methylol groups of phenolic resin and some double bonds from polybutadiene block. At 1210 cm^{-1} peak attributed to C—O of phenols presents a decrease in intensity due to the influence of phenol in the crosslinking reaction. **Figure 9** shows the IR spectra for adhesive formulations with zinc oxide. The changes in peaks are similar to those observed when zinc oxide is not added to adhesive formulation, which is indicative that it does not affect the crosslinking reaction. There are reports about the appearance of symmetric bands of OH groups that indicate breaking of hydrogen bonds and that over 200°C the OH group peak is indistinguishable [19, 26].
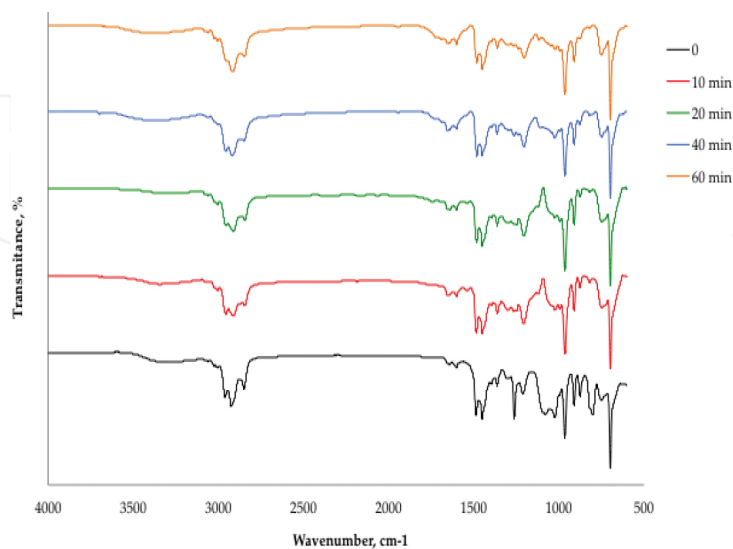

Figure 9. FTIR spectra for adhesive formulations with 30 phr resin and zinc oxide at different curing times.

4. Conclusions

According to results, it is possible to obtain an adhesive formulation using solvents as an alternative for less environmental impact based on the solubility parameter that depends on the polymer used; in this case, solubility parameter found favours the polystyrene and polybutadiene blocks. The use of a reactive resin is an option to prepare adhesive formulations based on SBS elastomers. The inclusion of reactive resin affects the viscoelastic properties, due to the crosslinking process that was carried out as DMA results demonstrate; the best viscoelastic properties were observed for adhesive formulation with 30 phr of resin, and addition of zinc oxide was not favourable for adhesives. The results of kinetic study of crosslinking process indicate that addition of reactive resin is favourable for decreasing the E_a values. Also, it is evident that polymeric structure with available insaturations at the end of chain favours the reduction in E_a values. FTIR demonstrates that crosslinking reaction carried out in metylol and hydroxyl groups presents in resin and double bonds of polybutadiene block of elastomer.

Acknowledgements

Author details

Tzeitel Hernández-Martínez, Beatriz Adriana Salazar Cruz, José Luis Rivera-Armenta[*], María Yolanda Chávez-Cinco, María Leonor Méndez-Hernández and Ulises Paramo-García

*Address all correspondence to: jlriveraarmenta@itcm.edu.mx

Secondary Petrochemical Research Center, Instituto Tecnologico de Ciudad Madero, Ciudad Madero, Tamaulipas, Mexico

References

[1] Packham DE, editor. Handbook of Adhesion. 2nd ed. Addison-Wesley Longman Ltd; 1992. 17 pp. 10.1002/0470014229

[2] Salazar-Cruz BA, Mendoza-Martínez AM, Esquivel-de la Garza AC, Moctezuma Espíricueto SA, Rivera-Armenta JL. Evaluation of crosslinking reaction in adhesive based styrene-butadiene elastomers using infrared spectroscopy. In: Theophanides

Theophile, editor. Infrared spectroscopy-anharmonicity of biomolecules, crosslinking ofbiopolymers, food quality and medical applications. InTech; 2015. p. 117-135. DOI 10.5772/58911.ch7.

[3] Salazar-Cruz BA, Rivera-Armenta JL, García-Alamilla R, Mendoza-Martínez AM, Esquivel de la Garza A, Moctezuma Espiricueto S. Evaluación térmica del curado de adhesivos base SBR usando peróxido de dicumilo. Quimica Nova. 2015;38:651-656. DOI 10.539/0100-4042.20150067.

[4] Zielinska AJ. Cross-linking and Modification of Saturated Elastomers Using Functionalized Azides [Thesis]. Eindhoven, The Netherlands, University of Twente; 2011.

[5] SI group, technical data sheet [Internet]. 2009. Available from: https://www.pharosproject.net/uploads/files/sources/1828/SP-154-1.pdf [Accessed: 2016-03-31].

[6] Kim J, Kim WH, Lee DH. Adhesion properties of UV crosslinked polystyrene-block-polybutadiene block-polystyrene copolymer and tackifier mixture. Polymer. 2002;43:5005-5010. DOI: 10.1016/S0032-3861(02)00327-0.

[7] Navarro-Bañón MV, Pastor-Blas MM, Martín-Martínez JM. Elimination of the reactivation process in the adhesion of chlorinated SBS rubber with polychloroprene adhesives. eXPRESS Polymer Letters. 2007;1:236-244. DOI: 10.3144/expresspolymlett.2007.36.

[8] Sturiale A, Vazquez A, Cisilino A, Manfredi LB. Enhancement of the adhesive joint strength of the epoxy–amine system via the addition of a resole-type phenolic resin. International Journal of Adhesion and Adhesives. 2007;27:156-164. DOI: 10.1016/j.ijadhadh.2006.01.007.

[9] Simal F, Jeusette M, Leclère PH, Lazzaroni R, Roose P. Adhesive properties of a radial acrylic block co-polymer with a rosin ester resin. Journal of Adhesion Science and Technology. 2007; 21:559-574. DOI:10.1163//156856107781192355.

[10] Fink JK. Reactive Polymers Fundamentals and Applications: A Concise Guide to Industrial Polymers. 2nd ed. William Andrew. 2013. 29pp.

[11] Skeist I, editor. Handbook of Adhesives. 3rd ed. International Thomson Publishing; 2011. 556 p.

[12] Reghunadhan Nair CP, Bindu R L, Ninan KN. Thermal characteristics of addition-cure phenolic resins. Polymer Degradation and Stability. 2001;73:251-257.DOI:10.1016/S0141-3910(01)00076-3.

[13] Pilato L. Phenolic resins: 100 Years and still going strong. Reactive and Functional Polymers. 2013; 73:270-277. DOI:10.1016/j.reactfunctpolym.2012.07.008.

[14] Scheneberger, G.L. editor. Adhesives in Manufacturing. 1st ed. Marcel Dekker. 1983. 353pp.

[15] Tan D, Wang Y, Li Z, Xing H. Synthesis and cure kinetics of diphenyl (diphenylethynyl) silane monomer. Research on Chemical Intermediates. 2013;39:3427-3440. DOI: 10.1007/s11164-012-0855-8.

[16] Pérez JM, Oliet M, Alonso MV, Rodriguez F. Cure kinetics of lignin–novolac resins studied by isoconversional methods. Thermochimica Acta. 2009;487:39-42. DOI: 10.1016/j.tca.2009.01.005.

[17] Ginic-Markovic M, Choudhury NR, Dimopoulos M, Williams DR, Matisons J. Characterization of elastomer compounds by thermal analysis. Thermochimica Acta. 1998:316:87-95. DOI: 10.1016/S0040-6031(98)00290-1.

[18] Feng S, Yuan Z, Leitch M, Xu CC. Thermal degradation performance of bark based phenol formaldehyde adhesives. Journal of Analytical and Applied Pyrolysis. 2015;115:184-193. DOI: 10.1016/j.jaap.2015.07.015.

[19] Mangal R, Srivastava S, Archer LA. Phase stability and dynamics of entangled polymer-nanoparticle composites. Nature Communications. 2015:6:1-9. DOI:10.1038/ncomms8198.

[20] Rahul R, Kitey R. Effect of cross-linking on dynamic mechanical and fracture behavior of epoxy variants. Composites Part B: Engineering. 2016;85,336-342. DOI: 10.1016/j.compositesb.2015.09.017.

[21] Ren R, Xiong X, Ma X, Liu S, Wang J, Che P, Zeng Y. Isothermal curing kinetics and mechanism of DGEBA epoxy reins with phtalide-containing aromatic diamine. Thermochimica Acta. 2016; 623:15-21. DOI: 10.1016/j.tca.2015.11.011.

[22] PerkinElmer Instruments LLC. Pyris Kinetics Software User Guide. 2002. Part Number 0996-6500, Release A.

[23] Cai H, Li P, Sui G, Yu Y, Li G, Yang X, Ryu S. Curing kinetics study of epoxy resin/flexible amine toughness systems by dynamic and isothermal DSC. Thermochimica Acta. 2008;473:101-105. DOI: 10.1016/j.tca.2008.04.012

[24] Nakason C, Nuansomsri K, Kaesaman A, Kiatkamjornwong S. Dynamic vulcanization of natural rubber/high-density polyethylene blends: effect of compatibilization, blend ratio and curing system. Polymer Testing. 2006;25:782-796. DOI: 10.1016/j.polymertesting.2006.05.001.

[25] Scagliusi S, Cardoso E, Luga, A. Radiation-induced degradation of butyl rubber vulcanized by three different crosslinking systems. Radiation Physics and Chemistry. 2012;81,991-994. DOI: 10.1016/j.radphyschem.2012.01.011.

[26] Yue S, Juanfeng H, Hong H, Hequing F, Hanwei Z, Huanqin C. Synthesis, properties and application of a novel epoxidized soybean oil-toughened phenolic resin. Chinese Journal of Chemical Engineering. 2007;15:418-423. DOI:10.1016/S1004-9541(07)60101-3.