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Evaluation of Crosslinking Reaction in Adhesive Based Styrene-Butadiene Elastomers Using Infrared Spectroscopy

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1. Introduction

An adhesive is a material that is applied to the surfaces of articles to join them permanently by an adhesive bonding process, and is capable of forming bond to each of the two parts and only a small quantity is required compare to weight of final materials [1]. Since antiquity, the use of adhesives has been very important for humanity, Greeks and Egyptians were the first to use glue to bond surfaces.

Adhesion refers to a complicated set of inter-connected phenomena that is not easy to understand, and by means several semi-empirical tests try to be predicted the strength of an isolated adhesive joint or the strength of a more complex structure, such a laminate, of a fiber-reinforcer of particle-filled composite [2].

Adhesives are classified according with common characteristics to facilitate their understanding and use, although no one classification is universally recognized. Classifications include source, function, chemical composition, physical form and application. Within the most used adhesive are natural or synthetic rubber-based materials, usually due its good properties.

Based solvent technology in adhesive is one of the most used for wood industry, mainly Polychloroprene, which has high temperature resistance and good paste strength. However, for halogenated compounds generated and for marketing strategy, this material is intended to be replaced by Styrene-Butadiene rubber (SBR) and Styrene-Butadiene-Styrene (SBS) copolymers, and Styrene-butadiene-Ethylene-Styrene (SEBS).

The formulation of Pressure-sensitive adhesives (PSA) consists of elastomers, tackifiers, and various additives have been widely used as tapes in stationery and for electric and medical purposes. Elastomers are widely used, however and additional crosslinking is needed to increase cohesive strength. The use of polydiene-based triblock copolymers (for instance, SBS, SIS) have increase due to higher cohesive strength resulting from the physical network of polystyrene (PS) blocks [3].

PSA is aggressive and permanently tacky, adheres without the need of more than finger or hand pressure, requires no activation by water, solvent or heat, exerts a strong holding force and has sufficient cohesiveness and elasticity that it can be removed from smooth surface without leaving a residue [2].

Styrene-butadiene (S-B) copolymers appeared in 1947, as an option as a raw material for adhesives. Block styrene-butadiene copolymers have applications as: shoe soles, impact modifiers, asphalt modifiers, adhesives and sealants. SB copolymers used in adhesives are A-B-A type, where A is styrenic block and B represents elastomeric block, which can be insaturated, as SIS and polybutadiene (SBS), or saturated as ethylene butylene, which promote stickiness and ability to wet the adhesive, further allowing viscosity variations which can be strengthened by adhesive resins of low molecular weight. Polystyrene block shows a good adhesion to wood, but not to plastics, except itself. For bonding polystyrene, a low-molecular weight styrene polymer with peroxide catalyst is used. Resistance to high temperature is limited, Copolymers of SBR, are much less brittle and more valuable as adhesives [1].

In general, a synthetic adhesive consists of: a synthetic based resin (homopolymer, copolymer or blend of polymers); one or more secondary resins and auxiliar polymers to improve adhesive characteristics; additives (plasticizer, hardener, antioxidants and bactericide); fillers and pigments, and solvent for blend substances.

Adhesive resins are generally, rosins and derivatives, terpene and modified terpene, aliphatic, cicloaliphatic and aromatic; the addition of resins on depends of compatibility with polymeric base that affects final adhesive properties [4]. To achieve this bond there are two procedures, one involving crosslinking mechanisms (vulcanization) and the other using an unvulcanized adhesive. Usually, both procedures are used, adding in the adhesive formulation promoting additives of adhesion and vulcanization, and in some cases, applying an external adhesive onto the substrates to be bonded.

The resins are used in thermoplastic rubbers to carry out one or more functions. Resins are low molecular weight materials, compatible or partially compatible with copolymers, show a higher T_g than polymer o copolymer, and help to improve wetting kinetic. The adhesive resins allow the adhesive to enter more closely contact with substrate which results in an increase in bond strength.

Solvent-based adhesives, also called, pressure sensitive adhesives (PSA), are adhesives that bonding when pressure is applied to bond adhesive between two substrates. There are two type failures in PSA: adhesive and cohesive failure, adhesive failure occurs in interphase between adhesive and substrate and cohesive failure occurs in the adhesive. Used materials for PSA process must have:

- Viscous properties that promote the flow
- Must be able to dissipate energy by adhesion
- Must have a partially elastic behavior

The PSA formulation includes solvents, the selection of adequate solvent allows a more effective bonding of polymers having low intermolecular forces. The solubility parameters theory developed by Hildebrand and Scott [5, 6, 7, 8, 9], contributed to development of these parameters, specially focused on the concept to formulation of solvent-based coatings. The solubility parameters cannot be measured directly due polymers are not volatile. That can be calculated by small molar attractions constants, but generally are inferred to maximum solubility or it swelling power [1]. In other words, PSA must be viscoelastic, the materials that constituting PSA adhesive listed in decreasing order of volume and increasing cost: natural rubber, SBS copolymers, functionalized polymers, neoprenes, nitrile-butadiene copolymers (NBR), thermoplastic elastomers, polyacrylates, polyvinyl acrylates and silicones.

The crosslinking (vulcanization or curing) is a bond that links one polymer chain to another by means covalent or ionic bonds, creating a three-dimensional network structures. The term crosslinking is often used in synthetic polymers, it refers to the use of crosslinks to promote a difference in the polymers' physical properties, as flexibility that decreases, the hardness that increases and the melting point that increases as well.

The sulfur was the first crosslinker to be discovered and together with activators and accelerators is still by far the most frequently used curing system [10]. The crosslinking is used in several technologies of commercial and scientific interest to control and enhance the properties of the resulting polymer system or interphase, such as thermosets and coatings, and can be initiated by heat, pressure, change in pH or radiation [11].

Organic peroxides are compounds of the general structure. $RO-OR'$. The relatively weak oxygen-oxygen bond breaks easily leading to the formation of two oxygen centered radicals: $RO\cdot$, and initiates the free radical processes. The use of peroxide as crosslinking agent of rubber dates from 1914, when Ostromislensk crosslinked for first time natural rubber with benzoyl peroxide. However, use of peroxides had not the success because it led to formation of vulcanized with resistance to traction and to curing lower than crosslinked materials with sulfur. The introduction of Polyethylene in 30's increased the use of free radical donors as crosslinking agents. Afterwards, in 1950, was discovered that di-*t*-butyl peroxide allowed to obtain better quality vulcanized than benzoyl peroxide, but had the disadvantage of high volatility. Shortly after, was discovered that dicumyl peroxide (DCP) shows a good combination of physical and chemical properties.

In absence of other additives, vulcanization with peroxides consists exclusively in creation of a carbon-carbon bond between polymer chains. The polymer crosslinking reaction with peroxide carries out in 3 steps, first one homolytic rupture, formation of cumyloxy radical and the third one gives as product dimethyl benzyl alcohol (DMBA), or acetophenone plus a methyl radical. This crosslinking reaction is rather complex, because of numerous side reactions that

compete with crosslinking mechanism. Main side reactions are: addition of radical to double bond, cleavage reaction of polymer radical, radical transference and oxygenation.

Thermal decomposition of peroxide is a first order reaction that only depends of temperature and time. Although in general peroxides decompose in radicals, its stability varies considerably. Some peroxides are instable at room temperature, while others show no evidence of decomposition when heated at 100°C for several hours. In general, all peroxides used in rubber vulcanization are stable by at least reached temperatures during preparation compound. Peroxide stability is determinate by chemical groups bonded to oxygen atoms of peroxide.

After DCP homolytic rupture, radical fragments can suffer rearrangements that change its initial identity. This response can decrease radical efficiency. Cumiloxy radical can experiment beta cleavage to form acetophenone and methyl radical (figure 1).

Figure 1. β -cleavage of cumiloxy radical to form acetophenone.

Some reports have use IR for evaluation of grafting surface and evaluation of curing reaction in adhesives reporting that is a useful tool for that kind of studies [12, 13]. Also is possible with IR to identify decreasing of peaks attributed to double bonding in polybutadiene backbone when crosslinking process is carry out [14]. In this case, radical energy does not reduce significantly, then peroxide efficiency is not alterated, with advantage that methyl radical is not estericly hindranced as initial cumiloxy radical and can participate more effectively in reactions where esteric limitations or diffusion are a limitation. Formed radical from peroxide decomposition react with hydrogen atoms found in the surrounding. Figure 2 shows heterolytic decomposition of DCP where peroxide radicals are obtained.

Peroxide radicals can react potentially by addition to double bonging or by allylic hydrogen abstraction. Double bondings can act as reaction points. In general, results indicate both mechanisms can be carry out in insaturated elastomer vulcanization, prevailing hydrogen abstraction.

Infrared (IR) is one of oldest technique useful for surface analysis, and to probe the surface compositions of polymers that have been surface-modified by an etching process or by deposition of a film. IR has numerous characteristics that make it useful in adhesion science, mainly because is sensitive to functional groups and provides information about curing reactions of adhesives and about other chemical reactions that are relevant in adhesion [2].

Figure 2. Heterolytic decomposition of DCP.

Although it is important to understand the crosslinking process, there is a few literature on the subject, so in this work a study of the crosslinking reaction in pressure sensitive adhesives (PSA) based styrene-butadiene copolymer (SBS) using as crosslinking agent dicumyl peroxide (DCP) was carried out, using infrared spectroscopy to evaluate crosslinking reaction and possible side reactions, and progress of crosslinking reaction according with preparation. Effect of DCP, crosslinking time, total styrene content in elastomer, molecular weight of elastomer and resin type in adhesive formulation were evaluated variables in crosslinking process. Also effect of crosslinking on mechanical properties of adhesive was evaluated.

2. Methodology

2.1. Materials

Adhesives formulations based solvent, also called pressure sensitive adhesives (PSA), consist of elastomer, resin, crosslinking agent and solvents. In this case two block copolymers styrene-butadiene-styrene (SBS) were used: (E1) 33% and (E2) 31% styrene content, linear structure,

provided by Dynasol Elastomers S.A. de C.V. plant Altamira; two resins were used, one compatible to polybutadiene segment (ester, R1) and other one compatible to polystyrene segment (styrenated R2), as crosslinking agent dicumyl peroxide (DCP) was used, which was provided by Retilox Co.; and a mix of solvent consisting of toluene, acetone and n-hexane (all ACS grade), which were selected according with compatibility of all adhesive components.

Components	Amount (phr)
Polymer (SBS)	100
Resin	40
Dicumyl peroxide	3.5 - 0.81
Toluene	150
Hexane	150
Acetone	150

Table 1. Formulation amount used for Adhesive preparation

2.2. Adhesives preparation

Adhesives preparation consists in mixed all components in a glass reactor using a mechanic stirrer at high shear rate. The addition sequence was established according to several experimentations, based on solubility, dispersion, color, viscosity and mixing time. First, elastomer in corresponding amount was added at low shear rate (500 rpm), after that, shear rate was increased until 1500 rpm and then resin was added, finally DCP (3 concentration levels, 0.81 phr [1], 2.19 phr [2], 3.6 phr [3] and 0 phr) was added until complete dispersion was reached. Final mixture was poured in glass container closed and storage in room conditions. Table 1 show amounts used according with Roebeson [15] and Bohwmoick [16]. Table 2 show the codes used for adhesives formulations prepared.

Resins		R1		R2	
Polymer		E1	E2	E1	E2
DCP (phr)	0		0	0	0
	1		1	1	1
	2		2	2	2
	3		3	3	3

Table 2. Codes for adhesive formulations. For instance formulation E1-R1 2 means Elastomer with 33% styrene content, ester resin and 2.19 phr DCP concentration.

Adhesive films were prepared pouring specific amount of adhesive mixture in a manufactured container with siliconated paper, and were evaporating until complete solvent remotion, at room conditions. The films were cured in convection oven at 180°C for 90 minutes.

2.3. Infrared spectroscopy

IR analysis was carried out to evaluate crosslinking reaction, by means monitoring typical functional groups of this kind of reaction. IR spectra were recorded with a Perkin Elmer Spectrum 100 model spectrophotometer, using for analysis the Attenuated Total Reflectance (ATR) technique, with a diamond/KRS-5 plate, using 12 scans and resolution of 4 cm⁻¹, in a wavenumber range from 4000-400 cm⁻¹.

2.4. Fracture mechanical test

The necessity of fracture analysis in adhesives applied in wood, helps to estimate internal forces (cohesion) and interphase forces of adhesive line. Adhesive mixtures were impregnated in pine wood substrates of 4*1*0.064 in dimensions. Specimens were conditioning at 50±2% relative humidity and 23±1°C temperature until equilibrium. Substrates surface was cleaned with acetone to remove any residue. Measurements were carried out according with ASTM D1002. Impregnation process consists in the addition of adhesive on two wood specimens trying to maintain a constant thickness of adhesive film. Contact area was 1 in² and two wood specimens were pressed and allowed to cure for 24, 48 and 72 hrs at room temperature and constant DCP concentration. The method consists in a 0.2 mm thickness, a 10 KN load and 0.5 in/min displacement. It was necessary 5 repetitions of each specimen.

3. Results and discussion

3.1. Monitoring crosslinking reaction by means IR

There are different variables that play an important role during the crosslinking reaction, between the most important are: crosslinking agent concentration, reaction time, resin type, temperature. By means IR it is possible identify functional groups associated to crosslinking reaction so useful information about the process can be obtained.

Figure 3 shows IR spectra of adhesive mixture E1-R1 with DCP high concentration at different times. From the spectra 3 important regions draw attention due are associated to crosslinking reaction: 3400, 1724 and 724 cm⁻¹. It is possible identify signals at 966, 911 and 721 cm⁻¹ attributed to out-of-plane bendings of γ (=CH) trans, ω (=CH₂) vinyl and γ (=CH) cis groups respectively, present in polybutadiene domains Those peaks decrease with time which is associate to crosslinking that occurs in double bonding. In the other hand, typical signals from polystyrene domains (1601, 1492, 1450, 699 and 540 cm⁻¹), remain without significative changes [17, 18]. That is indicative that crosslinking reaction carries out preferably in double bonds of polybutadiene domains.

Figure 3. IR spectra of E1-R1-3 adhesive mixture at different times @170°C, 0 min (black), 30 min (blue), 60 min (red), 90 min (green), 120 min (yellow).

Crosslinking reaction consist in first step DCP homolytic rupture, after hydrogen abstract from polymer chain, and then bonding of two polymer chain forming a three dimensional structure. In DCP rupture, the cumyloxi radical can stabilize forming α,α , dimethyl bencyl alcohol or acetophenone.

Curing effect in adhesive E1-R1 with DCP was monitored by means IR spectroscopy. Figure 4 shows main regions in IR spectra for adhesive: 3400 cm^{-1} for α,α , dimethyl bencyl alcohol, 1725 cm^{-1} for acetophenone and $724\text{ cm}^{-1}=\text{C-H cis}$, at 0, 30, 60, 90 and 120 min. It is evident decreasing in intensity according with time for signals attributed to double bonding of elastomer (720 cm^{-1}) due these groups participate in crosslinking reaction. In the other hand, an increasing of signals assigned to carbonyl and hydroxyl groups confirm abstraction reaction and beta cleavage reaction in crosslinking with peroxides. As consequence methyl radical is obtained, which present the advantage that is less esterical hindrance compared with Cumyloxi radical. Wu et al [17], Ellul et al [19] report the same behavior and that polystyrene characteristic peaks (1601 , 1492 , 1450 , 699 and 540 cm^{-1}) remain with not significative change.

Figure 4. IR spectra for main peaks in adhesive E1-R1 formulation at different times.

The same analysis was carried out for adhesive formulations E1-R2, E2-R1 and E2-R2, with different DCP content, and a similar behavior was observed for these 3 peaks at 3400, 1725 and 724 cm⁻¹.

DCP concentration on crosslinking reaction was evaluated in figure 5. The presence of side reactions can be identified when thermal decomposition is carry out. The 3 main signals plus peaks at 866 and 1452 cm⁻¹, attributed to out of plane bending of $\gamma(=C-H)$ *cis*, were monitored to evaluate crosslinking effect. It is observed that adhesive with high DCP concentration show increasing on peaks at 3400, 1725 and 725 cm⁻¹ compared with adhesive with low DCP concentration, which was expected due high DCP concentration may cause crosslinking reaction between SBS chains because an important requirement for this reaction to be successful is that the amount of free radicals is high enough to be able to abstract the active hydrogens on the polymer. Evidence of side reactions was not found. Wu et al [17] reports that a high peroxide concentration in adhesive formulation causes the free radical concentration in the system increase and because there are lots of double-bonds in the SBS macromolecule structure, excessive peroxide may cause crosslinking reaction between SBS molecule chains. Dlezniski [20] reports a high DCP concentration increase the possibility of side reactions that compete with crosslinking reaction and then decrease crosslinking points in polymer backbone.

Figure 5. IR spectra of E2-R1-1 (blue) and E2-R1-3 (red), at 90 min @ 170°C.

In order to determinate how the resin nature affect the crosslinking reaction, two resins were studied. Main functional groups of two resins are listed: R1 (ester resin) present peaks under 3000 cm^{-1} , 1755 cm^{-1} , due insaturations and ester group, which make it compatible with polybutadiene block in SBS backbone, helping to curing process with DCP; and R2 (styrene resin) present an assignation at 2945 attributed to methylene group, overtones in $2000\text{--}1750\text{ cm}^{-1}$ attributed to aromatic group, which contribute to compatibility with polystyrene block in SBS.

Figure 6 shows IR spectra of E2-R1-3 and E2-R2-3 where is evaluated effect of resin in crosslinking process for. It can observe that due polarity R1 generates a high electronic density that helps to crosslinking process in adhesive mixture, in spectrum is observed in range from 1500 to 100 cm^{-1} where the presence of some peaks and complexity are indicative of crosslinking effect. In the other hand, the crosslinking effect it is observed in peaks at 1725 and 3450 cm^{-1} from carbonyl and carboxyl groups respectively. The resin nature is important according with functional groups and type of reaction that can be carry out.

Styrene content in the elastomer becomes important because certain functional groups present in resin having affinity with the vinyl bonds and it is of interest to determine the effects that has styrene content in crosslinking reaction. E1 has 33% and E2 31% of total styrene content, respectively, both elastomers generate similar structures but styrene content can produces steric hindrance of Polystyrene block. Signal at 1725 and 3400 cm^{-1} are related with crosslinking, also peaks in $1500\text{--}1000\text{ cm}^{-1}$ region indicate gel formation which is associated with a reticulated structure.

Figure 6. IR spectra of adhesive mixtures E2-R1 (green), E2-R2 (blue) and without resin (red) @170°C.

The formation of macrophase-separated resin domains and the tack strength of the adhesive are significantly changed by the presence of the microphase structure when either the mid or end block domains are saturated. Considering the near-surface morphology of the block copolymer, the chain connectivity in block copolymer imposes limitations on the degrees of freedom of molecules, avoiding the crosslinking reaction [21].

Also resin type and molecular weight were evaluated. Resin R1 was identified compatibility to PB segment and R2 was compatible to PS segment. Due the polarity a high electronic density is present in region 1500-100 cm^{-1} , where several signals are attributed to crosslinking effect. Resin R2, signal at 1725 cm^{-1} and 3450 cm^{-1} corresponding to carbonyl and carboxyl groups are related to crosslinking effect.

About effect of molecular weight, figure 7 shows spectra of E1-R1-3 and E2-R1-3 adhesive mixtures, E1 has higher molecular weight than E2. The main differences are identified in: 3400, 1725, and 1400 cm^{-1} , peaks associated to hydroxyl groups, carbonyl groups which are from thermal decomposition of DCP, and to double bond respectively. High molecular weight can cause steric hindrance to generated radicals from DCP decomposition by thermal effect generate abstraction process of unsaturated segments in SBS backbone, then minimizing crosslinking between polymeric radicals. However, crosslinking is carrying out, because some peaks are identified in range from 1500 to 1000 cm^{-1} that indicates crosslinking of C-C bonds.

Figure 7. IR spectra of E1-R1-3 (blue) and E2-R1-3 (red) adhesive mixtures @170°C.

For a deep analysis of DCP decomposition, thermal analysis was carried out, in inert atmosphere of nitrogen, with a heating ramp of 10°C/min from 40 to 600°C. Figure 8 a and b show TGA thermogram where it can observe DCP decomposition start at 145°C and elastomers around 380°C, it is important to be sure elastomers do not experiment thermal degradation at temperatures where DCP decompose (150-200°C). Derivative curves show that the maximum temperature is in 446°C and DCP at 161°C, thus can be sure that any exothermic process observed under 200°C implies activation of peroxide to form radicals to crosslinking.

3.2. Fracture mechanical test

The necessity of a fracture analysis to evaluate adhesive applied in wood, help to estimate internal forces (cohesive area) and interphase forces of adhesive line. Figure 9 shows type of forces when an adhesive is applied in wood. For this test some criteria were established:

- Superposition that in adherent region shear stress is constant.
- Wood specimens were from pine wood and the same batch.
- The substrates were conditioned for a week.
- The substrate surface was cleaned with acetone to eliminate any residual dust or grease.

Figure 8. Loss weight (left) and weight derivative (right) from TGA thermogram of E1, E2 and DCP.

Figure 9. Analysis of tension force (a) and fracture analysis (b) in adhesives on wood substrate.

In table 3 is showed the type of failures that occur in different adhesives after mechanical test. Adhesives that include R1 in its formulation present cohesive failure (adhesive thickness) after mechanical test, while adhesives including R2 in formulation show adhesive failure (substrate interphase), increasing the percentage with time; this behavior is assumed to polarity on R1 that stimulate substrate affinity with adhesive.

In the other hand, an increase of DCP concentration causes a considerable diminishing of the maximum load for adhesive mixtures with R1 and R2, which is indicative that crosslinking reaction is not favored with increasing peroxide radicals. An explanation of this behavior is the competition between side reactions and crosslinking reaction which causes a decrease in crosslink points. Dlezneski [20] reports similar behavior when peroxides are used for crosslink

styrene-butadiene based elastomers. However, Marzocca et al [22] found that an increment of DCP content in cured polybutadiene reflects in a high crosslinking density in materials. Here the difference is use of resins in formulation and presence of polystyrene domains in polymer structure justifying that behavior.

Time, (h).	0	24	48	72
E1-R1-1
	failure	Cohesive	Cohesive	cohesive
E1-R2-1
	failure	Cohesive	Adhesive 60%	Adhesive 70%
			Adhesive 90%	

Table 3. Failure type present in adhesive after single lap shear test in adhesives E1-R1-1 and E1-R2-1.

It is important to detail stickiness in prepared adhesives is higher for adhesive with R1 respect to adhesives with R2, this adhesiveness increase, attributed to a more compatible behavior on wood surface, which also explains the failure type in adhesives with R2 (cohesive). In the other hand, R2 is more compatible to polystyrene block, shows less adhesiveness with substrate, so that cause the interphase failure (adhesive).

The DCP was added to adhesive mixture and cured at 170°C for 120 min. Effect of DCP concentration on adhesives mixtures prepared with R1 and R2 are shown in figure 11 (R1) and 12 (R2). It is evident that adhesives prepared with E2 show higher maximum load compared with adhesives with E1, this behavior is attributed to lower styrene content in E2 generates less steric hindrance in curing process. The selective compatibility of the R1 with polystyrene domains over polybutadiene is important for controlling the ordered structures of SBS-resin blends [21].

According with results, lower DCP content in adhesive mixtures present better mechanical response for E1 and E2, due supports higher stress. Adhesive mixture with E2 present higher maximum load than E1 adhesives, attributed to the less steric hindrance caused by the styrene domains that favoring crosslinking.

Figure 10. Effect of the time for adhesives mixtures E1-R1 (blue) and E2-R1 (red) without DCP on maximum load.

Figure 11. Effect of DCP concentration on maximum load for E1-R1(blue) and E2-R1 (red) adhesive mixture cured @170°C.

The effects discussed are because every component in adhesive mixture play an important role in crosslinking process and each of components in the formulation tend to develop of adhesive or cohesive properties to the adhesive, so it is important to achieve an optimal combination of resin, polymer, additives and solvents used in the preparation of adhesive materials. The success of an adhesive depends on reaching an ideal balance of adhesive and cohesive forces, any imbalance of these cause a failure in the adhesive performance.

Figure 12. Effect of DCP concentration on maximum load for E1-R2 and E2-R2 adhesive mixture cured @170°C.

4. Concluding remarks

From presented results in this research it can be concluded that is possible use infrared spectroscopy to evaluate crosslinking reaction in adhesives based polystyrene-butadiene using as crosslinking agent dicumyl peroxide. It was possible identify effect of diverse variables in crosslinking process, such as crosslinking time, crosslinking agent content, styrene content in elastomer, resin type, molecular weight of elastomer.

By means IR was possible probe that peroxide radical can react in double bonding region of elastomers, mainly by allylic radical abstraction, which can be identified for decreasing of signals at 966, 724 and 911 cm^{-1} attributed to out-of-plane deformation $\gamma(=\text{CH})$ trans, $\gamma(=\text{CH})$ cis and $\omega(=\text{CH}_2)$ of vinyl groups respectively, and the increasing of peaks at 1724 and 3450 cm^{-1} from carbonyl and hydroxyl groups.

Ester resin (R1) was more effective to crosslink reaction because its groups show partial affinity and compatibility with polystyrene domains and polybutadiene domains, compared with R2 that only is compatible with polybutadiene block; so styrene content is also an important parameter for a good adhesive formulation if ester resin is used.

It was found that DCP lower content produces better mechanical properties than higher contents, because there is a competition among crosslinking reaction and side reactions during curing process.

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