MECHANISMS OF INTERACTION BETWEEN THE COMPONENTS IN ADHESIVE COMPOSITIONS BASED ON CHLOROPRENE RUBBER
D. Zheleva

ABSTRACT

The aim of this study is to investigate the mechanisms of interaction between the components in adhesive compositions based on chloroprene rubber (CR) during the formation of an adhesive joint.

Investigations are made on the influence of the phenol-formaldehyde resin amount, of the rubber compounds processing regime, of reaction conditions, and of interactions occurring between the rubber and the other components within the adhesive compositions, on the adhesive properties of the polychloroprene adhesives. A comparison between the data from mechanical tests and the data from FTIR and rheological studies of these adhesives is provided.

The IR spectroscopic results prove that adding the resin to the rubber on the rolls during the mixing process favors the creation of physical and chemical interactions between the resin and the rubber and the rest of the components of the adhesive composition. The necessary minimum resin amount as an agent improving the compatibility between the associates of the oxides and the chloroprene rubber, and the associates of the rubber itself, is determined.

Keywords: chloroprene adhesives, resin, mechanisms, IR spectroscopy, bond strength.

INTRODUCTION

Polychloroprene solvent based contact adhesives play a substantial role in bonding the different substrates in the shoe, due to some specific features of the structure of the chloroprene rubber. The process of the bonding is accompanied by a lot of separate effects, which are not explained enough and most of the factors influencing the process are still not established [1 - 6]. As modifying additives for chloroprene base adhesives phenol formaldehyde and coumarone-indene resins, improving the adhesion and the viscosity of the adhesive, are commonly used. According to the authors of [6] the optimum amount of the aforementioned resins is 20 phr per 100 phr rubber.

According to J. Martinez [4, 5], p-tert-butyl phenol resins are used as modifiers for polychloroprene base adhesives, which achieve higher adhesion and heat resistance of the adhesive. He described the reaction of this type of resin with MgO in solution to obtain an infusible resinate (4 phr MgO to 40 phr resin). The recommended amounts of the resin are as follows: from 35 to 50 phr, optimum properties are obtained at 40 phr resin.

For an explanation of the reinforcement mechanism of the rubber with thermosetting resins, it is necessary to take into account the high reactivity and the polyfunctionality of the resins [2]. Various rubber-resin structures at the molecular and over-molecular level are formed. Great influence on the mechanism of reinforcement has the rubber type and the method of mixing [2, 3, 6]. For the reinforcement of rubbers with thermoplastics, thermosetting resins, in most cases, they are incompatible and form a two-phase heterogeneous system. Between the modified rubber and the resin fillers can occur inter-
molecular physical and chemical bonds, leading to an effect of reinforcement of the rubber. For the formation of chemical bonds between the rubber and the resin the amount of functional groups in the phenolic resins has a significant influence. The nature of the bonds between the rubber and the resin is not yet understood, but the values of the tensile strength of this system are sharply reduced on the mixing rolls, suggesting physical connections on the surfaces of the globules [2, 5]. It is considered that a major impact on the bond strength between the resin and the rubber have the hydrogen bonds, formed at the expense of the residual moisture. It was found that prevailing the physical bonds, while a very small part of the resin forms chemical bonds with the rubber. The main quantity of the resin is in a separate phase [2].

As the literature review shows the basic research is directed to various methods to modify the adhesives based on chloroprene rubber. To achieve tight gluing to the materials used in shoe technology which are very heterogeneous in nature, it is necessary to have a universal adhesive that can bond all details. Because of incompatibility of some of the substrates it is important to introduce specific additives in the adhesive composition that improve particular properties (for example, resins, polyisocyanates, chlorfluorolignin, etc.) [2 - 13]. The resins are the most commonly used additives for these adhesives. There are many studies on the optimization of adhesive compositions, but the reaction mechanism of the resin with the rubber and the other components of the composition and the types of interactions that occur during the mixing process of elastomer with the resin are still not fully elucidated.

The aim of this study is to investigate the mechanisms of interaction between the components in adhesive compositions based on chloroprene rubber (CR) during the formation of an adhesive joint.

EXPERIMENTAL

Objects of investigation

Polychloroprene solvent based adhesives prepared in laboratory: PHL1, PHL2, PHL3, PHL4, PHL5, PHL6 and PHL7:

Varying of the p-tret.phenol-formaldehyde resin amount (Resin 2402), respectively: 0, 16, 30, 40 and 60 phr resin per 100 phr rubber in different mixing regimes.

Substrates:
- standard rubber vulcanizates (based on styrene-butadiene rubber);
- natural leather.

Ingredients, formulations and compounding of rubber blends

The quantities of the ingredients used for the rubber compounds are given in Table 1:

Chloroprene rubber (CR) Baypren 210 (LANXESS), characterized by [14]: poly(2-chloro-1,3-butadiene), mercaptan modified; of medium crystallization rate; ρ=1,23 g/cm³; Tν ~ 86°C; Tg ~ - 40 °C, Mooney viscosity UHL(1+4)100°C = 43±4; Mm = 120000.

Zink oxide (ZnO) (Brüggemann) was used as vulcanizing agent for CR [14]. White, solid, powder with particles size 0,8÷2,0 μm, moisture content < 0,2 %; ρ = 4,9 g/cm³.

Magnesium oxide (MgO) grade Elastomag 100 (Morton) was used as a scorch retarder in a variety of elastomers and adhesives [14]. White, crystalline powder with particles size > 150 μm; ρ = 3,2 g/cm³; pH 10,3; BET surface area 104-141 m²/g.

Table 1. Ingredients for rubber compounds.

<table>
<thead>
<tr>
<th>Ingredients code</th>
<th>Adhesives code</th>
<th>PHL1</th>
<th>PHL2</th>
<th>PHL3</th>
<th>PHL4</th>
<th>PHL5</th>
<th>PHL6</th>
<th>PHL7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesives code</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroprene rubber</td>
<td>CR (Baypren 210)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>p-tret.phenol-formaldehyde resin (Resin 2402)</td>
<td></td>
<td>0</td>
<td>16</td>
<td>30</td>
<td>60</td>
<td>16</td>
<td>30</td>
<td>40</td>
</tr>
</tbody>
</table>
p-tret. Phenol-formaldehyde resin, grade Resin 2402 (Meyors Chemicals) was used as a tackifying resin for chloroprene base adhesive, improving the heat resistance and adhesive force. It is especially applicable to the adhesive for shoes [14]. It is light an yellow to amber transparent lumpish solid; \( M_m = 500 - 1000 \); methylol groups more than 7 %; \( \rho = 1,04 \text{ g/cm}^3 \); softening point 75 – 85°C.

The compounding of rubber compositions was performed with open laboratory mixing rolls: size L/D 320х360, revolutions of the slower roll 25 min\(^{-1}\) and friction 1,27 [1, 15].

**Methods for preparation of the polychloroprene adhesives in laboratory conditions**

**Adhesive PHL1 (no resin):** The rubber compound was used (see Table 1) for preparation of adhesive PHL1. This compound is dissolved in a mixed solvent in a ratio: acetone: toluene: benzine = 1:1.1:1.3, with concentration of 25 % [1, 15].

**Adhesive PHL2:** The same rubber compound was used for the preparation of PHL2. Two separate solutions with concentration 25 % were prepared: 1) solution of the rubber compound and 2) solution of the resin. The solvents were the same and the quantity of the resin was 16 g. The two solutions were mixed and homogenized by stirring continuously.

**Adhesive PHL3:** For the preparation of PHL3 the same method as for PHL2 was used, but the quantity of the resin was 30 g.

**Adhesive PHL4:** For the preparation of PHL4 the same method was used, but the quantity of the resin was 60 g.

**Adhesive PHL5:** To the rubber compound was added 16 g resin during the mixing of the rubber on the rolls. A solution of the rubber compound was prepared in the presence of the resin in the rubber blend.

**Adhesive PHL6:** The same mixing procedure (see PHL5) was used for the preparation of PHL6, but the quantity of the resin was 30 g.

**Adhesive PHL7:** The same mixing procedure (see PHL5) was used for the preparation of PHL7, but the resin was 40 g.

All adhesives were analyzed after preparation [1, 15].

**Methods for investigation**

**Determination of the concentration of solid substance**

This is a mass method applied for control during the preparation, when the adhesives are used. The samples are dried to complete evaporation of the solvents [15].

**Determination of the viscosity**

The rheo-viscometer Höpppler was used. The adhesive is poured into a test tube and at 20°C above it is mounted a glass ball, which is loaded with different weights [15]. The time for passing the ball through the solution in the tube is measured and the dynamic viscosity was calculated using the following formula:

\[ \eta = k \cdot p \cdot t \]

\( \eta \) – viscosity \([\text{cP}]\); 
\( k \) – constant of the used tube; 
\( p \) – shear stress \([\text{g/cm}^2]\); 
\( t \) – time for passage the ball \([\text{s}]\).

**Infrared spectroscopy**

Infrared spectroscopy is a method of molecular absorption spectroscopy [16]. As one of the main instrumental methods Infrared Spectroscopy is used for qualitative determination of chemical structure and crystallinity of elastomers and ingredients. The IR transmission spectra of the samples were recorded with a Bruker Tensor 27 spectrometer with scanner velocity 10 kHz, using an MCT detector, with 64 scans and 1 cm\(^{-1}\) resolution. Liquid samples (as liquid adhesives) were sandwiched between two plates of a salt (typically potassium bromide).

**Determination of peel resistance**

To determine the strength of adhesive joint by peel resistance tests, samples by the same standard material with thickness 2 mm were prepared [15]. The dimensions of samples are 150x20 mm. The samples were joined and pressed and then separated. On a dynamometer scale at a speed of 100 mm/min the load (power) causing breaking of the bond in each of the zones (the sample is pre-divided into 10 zones in length) was recorded and the peel strength \([\text{N/mm}]\) of the investigated samples was calculated.

**RESULTS AND DISCUSSION**

**Determination the solid content**

The results for the solid content in the adhesive compositions are presented in Table 2.

The observed decrease of the dry mass content in the adhesive compositions is due to incorporation in the
samples of resin, which is a low molecular mass product, in increasing concentrations.

**Determination of the viscosity of the investigated adhesives**

In order to determine the viscosity of polychloroprene adhesives we used Höppler Reo-viscometer. Measurements were performed at the same temperature (20°C), but under different shear stresses. The rheological characteristics are presented in Table 3.

The rheological studies established the flow regimes and predicted the optimal properties of the adhesive composition. This is very important for technological processes. For example, an optimum amount of the resin of 30 phr and the method of mixing on rolls ensure good adhesion properties.

**Results from the infrared spectroscopy**

The influences of phenol-formaldehyde resin amount, of rubber compounds processing regime, of reaction conditions, and of interactions occurring between the rubber and the other components within the adhesive compositions, on the adhesive properties of the polychloroprene adhesives were studied. The data from the IR spectroscopy allows understanding the mechanism of the reactions between the ingredients of the mixture and estimating the chemical structure of the product obtained.

The following phenomena were observed:

- In the mechanical mixing of the rubber solution with the solution of the resin separation of into two phases over time was observed, indicating incompatibility between the polymers;
- When rubber, resin and the other ingredients (ZnO, MgO) were mixed on the rolls, the rubber compound was dissolved. The resulting solution was homogenous and did not separate into two phases. Therefore, applying the conclusions of Sloninskii [17] there is reason to assert chemical grafting of the polymers.

Due to the multifunctional nature of the phenolic resins, various interactions under heating or in a rubber compound might occur [3, 4, 13]. To ensure good dispersion of the resins in the rubber blend, they should be introduced into it at a temperature higher than the softening point of the resin [14].

The data from infrared spectra (Fig. 1) indicate that there is a reduction of the intensity of certain absorption bands for PHL1, as compared to CR. This is most probably due to the depletion of these groups at the expense of the formation of others, e.g. at 2917 cm⁻¹, 1430 cm⁻¹; 1117 cm⁻¹. They might to participate in the curing process or in the formation of other bonds.

### Table 2. Solid content in the investigated adhesives.

<table>
<thead>
<tr>
<th>Adhesives</th>
<th>Solid content, [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHL1</td>
<td>33.2</td>
</tr>
<tr>
<td>PHL2</td>
<td>32.4</td>
</tr>
<tr>
<td>PHL3</td>
<td>27.2</td>
</tr>
<tr>
<td>PHL4</td>
<td>25.8</td>
</tr>
<tr>
<td>PHL5</td>
<td>31.5</td>
</tr>
<tr>
<td>PHL6</td>
<td>30.0</td>
</tr>
<tr>
<td>PHL7</td>
<td>25.8</td>
</tr>
</tbody>
</table>

### Table 3. Viscosity of the investigated adhesives in dependence of the shear stress.

<table>
<thead>
<tr>
<th>Shear stress, [g/cm²]</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>100</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity of PHL1, [cP]</td>
<td>1912</td>
<td>1695</td>
<td>1590</td>
<td>1416</td>
<td>1361</td>
</tr>
<tr>
<td>Viscosity of PHL2, [cP]</td>
<td>2496</td>
<td>2080</td>
<td>1893</td>
<td>1770</td>
<td>1496</td>
</tr>
<tr>
<td>Viscosity of PHL3, [cP]</td>
<td>425</td>
<td>359</td>
<td>341</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity of PHL4, [cP]</td>
<td>319</td>
<td>266</td>
<td>248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity of PHL5, [cP]</td>
<td>834</td>
<td>758</td>
<td>701</td>
<td>634</td>
<td>587</td>
</tr>
<tr>
<td>Viscosity of PHL6, [cP]</td>
<td>365</td>
<td>319</td>
<td>310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity of PHL7, [cP]</td>
<td>165</td>
<td>155</td>
<td>155</td>
<td></td>
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</tbody>
</table>
The depletion of the C-Cl bond at 825 cm\(^{-1}\) and 1693 cm\(^{-1}\) (= C - H) indicates crosslinking of the elastomeric macromolecules exactly in those places. This is an indication of chemical interactions. We have observed the following for PHL2 (quantity of the resin is 16 g) in comparison to PHL1: appearance of new bands of absorption at 2954 cm\(^{-1}\) (C-H), which show changes during the modification of the rubber with the resin [18-21]. The band at 1693 cm\(^{-1}\) disappeared, which was most likely due to reaction of the CR and the resin during the curing process. The most intense chemical reactions were observed for PHL3 (30 g of resin). Almost no differences were observed for PHL4 in comparison with PHL3, although the amount of the resin is extremely high (Fig. 1).

A difference was observed between PHL6 and PHL5 (adding the resin during the mixing process), e.g. reduction of basic bands at 1445 cm\(^{-1}\) and 1658 cm\(^{-1}\) (C=C) for PHL6, indicating depletion of the bonds at the expense of interaction of the resin with the rubber, when the resin amount is larger (30 g). No changes of bands for PHL7 were observed, indicating that the resin in a quantity larger than 30 g did not enter into additional interactions (Fig. 2).

Fig. 1. IR spectra of the chloroprene rubber (CR), the resin and the adhesives: PHL1, PHL2, PHL3 and PHL4.

Fig. 2. IR spectra of the chloroprene rubber (CR), the resin and the adhesives: PHL5, PHL6 and PHL7.
When comparing PHL2 and PHL5 (different regimes of mixing and the same amount of resin 16 g), no additional interactions between the rubber and the resin, as well as with the oxides, during the mixing process on the rolls were observed (Fig. 3).

Comparing the spectra of PHL3 and PHL6 (resin of 30 g, but different regimes of mixing), it can be concluded that the mixing conditions and the optimum concentration of 30 g favor chemical interactions (Fig. 4). In PHL6 weakening of the bands at 1605 cm\(^{-1}\) (depletion of C=C as a result of interactions on the rolls), 1362 cm\(^{-1}\) and 879 cm\(^{-1}\) was observed. The resin in an amount of more than 30 g does not lead to additional interactions (PHL7).

**Results for the peel resistance**

The reported results of the initial and final bond strength are shown in Figs. 5 and 6:

The physico-mechanical tests have also shown that the resin in an amount of 16 g is not improving the adhesion properties, i.e. this amount is not enough to spread throughout the rubber matrix. The most optimal
amount is 30 g. Quantities of the resin exceeding 40 g deteriorates the adhesive properties. These results support the data from rheological and spectroscopic studies.

**CONCLUSIONS**

Investigations are made on the influence of the preparation method and the phenol-formaldehyde concentration of adhesive polychloroprene compositions on their properties. The plasticizing and dispersing influence of the resin when it is in certain amount and added to the rubber compound on the rolls is proved to lead to obtaining adhesives of high quality. By infrared spectroscopy the appearance of physical interactions, chemical grafting of polymers, and chemical interactions between the components in the rubber compound was found. It was established that when the resin was in an amount of 30 g and added on the rolls, the mixing conditions and its optimal concentration favored the chemical interactions. The compounds with a quantity of resin greater than 30 g do not favor the interactions.

**REFERENCES**

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