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Water-based adhesive formulations for rubber to metal bonding developed by statistical design of experiments

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ABSTRACT

Waterborne adhesives for rubber to metal bonding have been available since 1990. However, published information about their formulation has been limited, as proprietary restrictions are exercised by companies. As a consequence, the way these adhesives interact with substrates has not been studied extensively. With the aim of investigating the effect the components of a waterborne adhesive have on rubber to metal bonding, fractional factorial and surface response methodologies of design of experiments were employed in this study. Twenty six formulations were prepared with a polychloroprene latex as the adhesive polymer. Viscosity, wettability and non-volatile solids content were measured with each liquid adhesive, while the mechanical strength was evaluated by applying a tensile mechanical stress over cured solid adhesive films. Adhesion properties were evaluated by using a single lap-shear test on metal to metal joints and a pull-out test on rubber to metal joints. The results showed that the components with the largest relative influence on cohesive and adhesives forces were tackifier resin, silicon dioxide and polychloroprene latex type. In order to better understand the contributions of these variables, mathematical models correlating them with the response variables were obtained. This study is valuable in explaining how, through statistical methods, a waterborne adhesive for rubber to metal bonding can be formulated with a reasonably low number of experiments.

1. Introduction

Rubber to metal adhesives are used in diverse industries including auto-motive, rail, off-highway and construction, health, recreation, aerospace and military. The first commercialized adhesive in 1956, and still in use today, was Chemlok 205/220 manufactured by Lord Company. This system bonds a wide variety of elastomers with metals, while enabling substantial improvements in service performance [1,2]. However, this adhesive uses organic solvents that are harmful [3]. Waterborne adhesives are made from materials that can be dispersed or dissolved in water. The use of water eliminates problems of flammability and toxicity associated with organic volatile solvents. Additionally, these adhesives cost less than their organic solvent-based counterparts. The first waterborne adhesive for rubber to metal bonding became available in 1990 [1]. There are two general types of waterborne adhesives: solutions and latices [4].

Polychloroprene or chloroprene latex (CR) systems are available as adhesives. Contact adhesives based on CR exhibit several performance advantages compared to other adhesives in a wide variety of applications where the quick production of joints, high strength and permanent adhesion are needed [5]. Crystallinity percentage and gel content affect adhesion with CR latices. The degree of crystallization controls the rate of accumulation of strength and the cohesive strength of the polymer.

Adhesives containing polymeric components comprising high levels of crystallinity generally exhibit greater cohesion and high elastic modulus values at room temperature. Similarly, adhesives from polymers with high gel contents show higher cohesive strength, modulus of elasticity and heat resistance. An important difference between gel content and crystallinity is that the effects caused by the former do not disappear when the polymer is heated [3].

There are five key areas to consider when choosing a suitable adhesive: type of rubber, surface preparation of substrates, adhesive preparation, adhesive application, and molding process to perform the

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bonding [2]. Waterborne adhesives for rubber to metal bonding must be capable of resisting heat and mechanical stresses simultaneously. From this, it can be inferred that there are complex relationships between the substrates to be joined and the adhesive formulation. Consequently, this phenomenon is not generally well understood. Choosing a suitable adhesive for rubber to metal bonding is more demanding than in other kinds of joints, because it is necessary to know the surface mechanisms and interfacial variables responsible for the expected mechanical and thermal properties of the adhesive bond. Frequently, adhesives are chosen empirically because the influences of process variables and adhesive ingredients on the properties of the resulting rubber to metal bond are not well known.

An adhesive for this kind of joint must contain at least an adhesive polymer, atackifier resin, a crosslinking agent, and fillers or formulation reinforcements [6,7]. This is why, formulating a waterborne adhesive that fulfills the specific performance requirements for rubber to metal bonding [3,8–10] is not an easy task.

Nowadays research is conducted by changing one variable at the time while keeping the remaining variables constant (OVAT). This approach requires a large number of experiments, especially when studying the influence of multiple factors on the dependent variables and ignores the possibility of interaction of independent variables. Statistical design of experiments (DOE) is a tool to study the individual effects and interactions of a set of factors on a complex system. In DOE, deliberate changes in the multiple input variables (factors) are made so as to determine which tests should be performed, to obtain data that after statistical analysis provides objective evidence to answer the questions raised beforehand, and thus clarify uncertain aspects of a process, solve a problem or achieve improvements [11,12]. With this statistical analysis of the experiments, modeling a system to understand the relationship between adhesive formulation components and mechanical and thermal properties of the bond is easier, quicker and with a reasonable number of experiments [13].

Published information is limited to studies that have been undertaken on understanding how a rubber to metal joint occurs, and how to improve the bonding properties by modifying the rubber to be joined [14–17]. Although there is a long history of research and development of rubber to metal solvent borne adhesives, there are voids in the scientific literature pertaining to the formulation of waterborne adhesives. There are only a few reports about how to improve an adhesive's performance by modifying its formulation, because this know-how belongs predominantly to industries that protect their intellectual property by patents and industrial trade secrets [18–21].

Very few articles relating to the statistical design of experiments approach to the assessment of adhesives and adhesion both generally and with water-borne adhesive formulations exist [12,13,22–25]. To the best of our knowledge, there are no published works that explore relationships between elastomeric substrates and waterborne adhesive formulations for rubber to metal bonding, using DOE.

Taking into account the lack of studies regarding the formulation of waterborne adhesives applied to rubber to metal bonding, and the application of DOE in waterborne adhesives formulation, this article contributes to the field of adhesives formulation by (1) developing systematically formulations for waterborne adhesives for rubber to metal bonding by DOE and (2) identifying the influence of formulation ingredients on the mechanical and adhesion properties.

2. Experimental

2.1. Materials

The components and preparation methods for the waterborne polychloroprene adhesive (WPCA) were chosen based on a literature review. Two different types of polychloroprene latices (Dispercoll C84 and Dispercoll C74 from Bayer Material Science (Germany) were used to form the adhesive polymer matrix. Dispercoll C84 exhibits a high degree of crystallization and Dispercoll C74 a medium degree of crystallization Table 1 presents all components used in the adhesive formulation, their respective manufacturer, trade name and order of addition in the preparation procedure. All materials were used in the commercially available form without further purification.

Table 1
Formulation and order of addition of components of WPCA.

Order of addition	Component	Manufacturer
1	Dispercoll C84	Bayer Material Science, Germany
2	Dispercoll C74	Bayer Material Science, Germany
3	Dispercoll S4020	Bayer Material Science, Germany
4	Bostex 422	Akron Dispersions, USA
5	HRJ 11112	SI Group, USA
6	Permutex XR 28-404	Stahl, Italy
7	Darvan WAQ	R.T. Vanderbilt Company, USA
8	Bostex 346	Akron Dispersions, USA

2.2. Methods

2.2.1. Waterborne polychloroprene adhesive preparation

WPCA formulations were prepared using a mechanical stirrer model RZR 2020, with a radial ow impeller (diameter 50 mm) (Heidolph Instruments GmbH & Co, Germany). All components were mixed following the order of addition described in Table 1, at 23 ± 2 °C with a constant stirring rate of 40 rpm. Formulations were kept in hermetic containers, away from UV light rays in a dry place at 23 ± 2°.

2.2.2. Waterborne polychloroprene adhesives characterization

Viscosities of WPCA samples were measured using a Brookfield viscometer RVDV-I-Prime (Brookfield Engineering Laboratories, USA) at 25 ± 2 °C over 200 mL of WPCA using the spindles 2, 3, 4, 5 and 6, at 20, 30, 50, 60 and 100 rpm. The value of Brookfield viscosity for each adhesive sample was calculated as the average of the measured viscosities with each spindle at 100 rpm.

The non-volatile solids content of the WPCAs were obtained by thermal gravimetric analysis carried out in a TGA Q500 instrument (TA Instruments, USA). Samples were heated from 30 °C to 800 °C at a rate of 20°C/min under nitrogen blanketing. The non-volatile solids content was calculated as the remaining mass percentage after 180 °C, according to ASTM D4758-92 standard.

Wettability was evaluated by contact angle measurements using a Ramé-Hart 100 goniometer (Ramé-Hart Instrument Co., USA) and five drops (5 μL per drop) of each sample of WPCA located over different places of a standard surface of polytetrafluoroethylene (PTFE). Previously, the standard surface was cleaned with methyl ethyl ketone (MEK) and placed into the hermetic isothermal chamber of the goniometer at 26 °C, saturated with twice distilled and deionized water. Contact angle values were measured 10 min after placing the drops over the standard surface. The contact angle reported for each WPCA was the average of the five measurements.

2.2.3. Waterborne polychloroprene adhesive films preparation

Solid films were generated by placing about 50 ml of each sample of WPCA over a glass sheet and allowing water evaporation at room temperature over a 72 h period to avoid air bubble formation. The WPCA solid films were then cured in a vacuum oven at 150 °C for 15 min Cured films were about 0.5 to 1 mm thick.

2.2.4. Waterborne polychloroprene adhesive film characterization

Tensile strength and strain at break of the cured films were measured using an Instron 3366 universal testing machine (Instron, USA). All experiments were carried out using dog bone test pieces from each cured film, following ASTM D412-06 standard, and using a crosshead speed of 100 mm/min at 20 ± 2 °C.

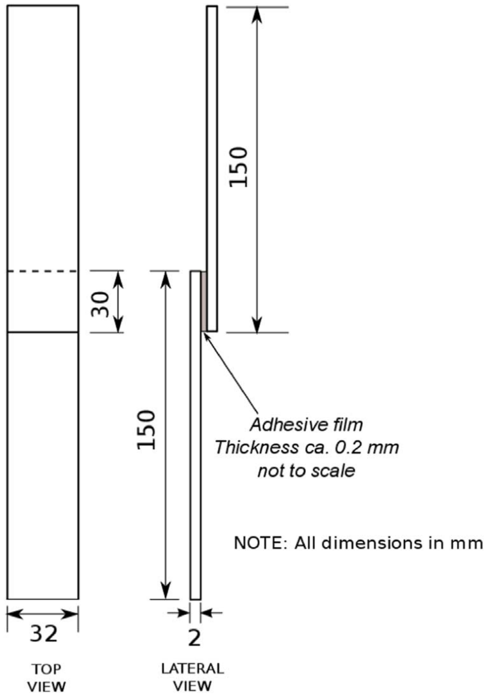

Fig. 1. Schematic of single lap-shear test specimen.

To better understand the mechanical behavior of the cured films, each one of the polychloroprene latices used in the formulations was evaluated by calorimetric analysis in a DSC Q200 (TA Instruments, USA). Samples were heated from −90 °C to 150 °C at a rate of 20 °C/min under nitrogen blanketing.

2.2.5. *Characterization of adhesion properties*

The adhesive strength (under shear stress) of WPCAs were evaluated from single lap-shear test pieces of 1020 steel/ WPCA/ 1020 steel. Before application of the WPCA to the steel adherends, the 1020 steel surfaces were roughened with a scotch brite sponge and wiped with isopropanol at 99% to remove grease and other forms of surface contamination. Removal of isopropanol from the adherend surfaces was achieved by heating the surface treated adherends at 150 °C for 10 min. Subsequently three layers of WPCA were then applied by brush and a hand coating bar used to guarantee a wet film of 200µm thickness covering an area of 30×32 mm on each of the test pieces. The 1020 steel strips were immediately placed in contact and a static weight of 5 kg applied for 72 h to achieve a suitable joint. The shear strength was measured 72 h after joint formation on an Instron 3366 universal testing machine (Instron, USA), following ASTM D1002-10 standard, and using a crosshead speed of 1.3 mm/min. Fig. 1 shows the joint configuration.

The adhesion properties of the WPCAs in the presence of the rubber and steel materials were evaluated under pull out stress, using the pull out tests pieces suggested by method B of ASTM D429-08 standard (i.e., rubber part assembled between two parallel 1020 steel plates). The rubber part was a disc with 39.9 ± 0.1 mm diameter and thickness of 3.2 ± 0.1 mm, based on a compound comprising natural, chloroprene and nitrile rubbers in equal parts. Before the WPCA sample was applied, the surfaces of the metal plates were sand-blasted and cleaned with isopropanol. After isopropanol evaporation, plates were heated at 80 °C for 30 min, and sprayed with approximately 30 g of WPCA in two layers. The 1020 steel pieces were immediately placed in contact with the rubber piece and vulcanized in a mold suggested by ASTM D429-08 standard at 150 ± 2 °C for 15 min. The pull out strength was measured 48 h after joint formation in an Instron 3366 universal testing machine (Instron, USA), following ASTM D1002-10 standard, and using a crosshead speed of 0.83 mm/min. Fig. 2 shows the joint configuration.

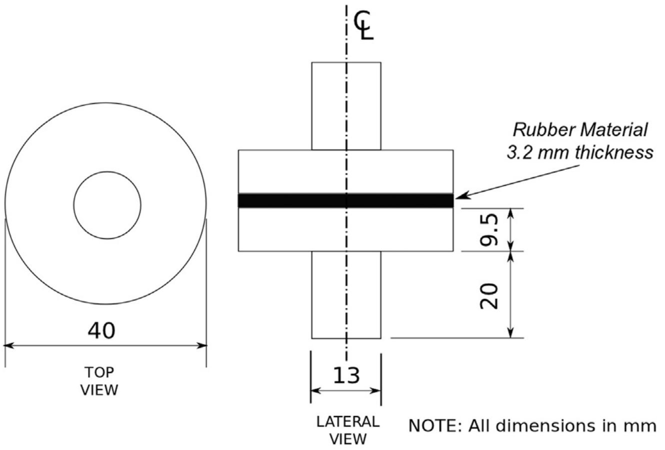

Fig. 2. Schematic of pull out test specimen.

2.2.6. *Design of experiments (DOE)*

Due to the large number of components in the WPCA formulation, a fractional factorial design of experiments 2^{6-2} with 16 runs was initially used to identify the adhesive components that most impact on performance and also to define under which vulcanization process conditions the resulting adhesive material promotes rubber to metal adhesion. Four of the factors stemmed from the components of the formulation: Tackifier resin (A), crosslinking agent (B), silicon dioxide (C) and latex type ratio (D). The remaining factors were vulcanization process conditions: Time (E) and temperature (F). Table 2, shows the design 170 matrix with factors and the experimental runs carried out.

The information gathered from fractional factorial DOE is not complete as a response surface DOE, but identifies the most significant factors with a minimum number of runs [24]. Thereafter, the factors that had the largest impact on the properties and performance of the adhesive formulation were chosen to optimize the formulation by using a central composite DOE. A mathematical model was obtained by multivariable second order regression for each response variable with this DOE. Table 3, shows the design matrix with factors and the experimental runs carried out.

R- statistical software (R version 3.1.3) was used to analyze the results and to determine the most suitable correlations between factors and measured variables, as well as to estimate the main effect of each particular factor, calculated over the entire range of levels for all other factors. Once the effects were calculated, these were graphed in Daniel plots, to identify the most influential variables.

A multivariable regression analysis was also performed. In addition, significance tests on the factors and their interactions, by analysis of variance (ANOVA) were done.

3. Results and discussion

3.1. 2^{6-2} *Fractional Factorial DOE*

This type of DOE allows discriminating the most significant factors for each response variable. Each factor was evaluated at two levels (high and low). Table 2 presents the design matrix for this DOE with the experimental runs carried out and the results obtained.

The main effects of the factors and their interactions on the response variables were found using linear regression models and plotted in Daniel Plots to find those that deviate the most from the normal distribution (i.e., the most significant ones).

The most significant factors were: Tackifier resin (A), Cross-linking agent (B), Silicon dioxide (C) and Latex type ratio (D) (see Fig. 3). Since

Table 2
Design matrix and response variables of 2^{6-2} factorial design of experiments.

Design matrix							**Response variables**				
Run	A (PHR[a])	B (PHR)	C (PHR)	D (PHR/PHR)	E (min)	F (°C)	Viscosity (mPa*s)	Non-volatile solids (%)	Contact Angle (°)	Tensile strength (MPa)	Total strain after break (%)
1	-1(30)	-1(1)	-1(10)	-1(0.11)	-1(20)	-1(150)	324.8	56.46	34.50	5.75	40.68
2	1(50)	-1(1)	-1(10)	-1(0.11)	1(40)	-1(150)	632.00	60.06	58.33	2.94	20.39
3	-1(30)	1(5)	-1(10)	-1(0.11)	1(40)	1(170)	353.20	59.89	32.00	6.43	49.22
4	1(50)	1(5)	-1(10)	-1(0.11)	-1(20)	1(170)	348.50	57.34	38.25	5.65	47.55
5	-1(30)	-1(1)	1(30)	-1(0.11)	1(40)	1(170)	1807.00	56.73	31.67	4.63	36.34
6	1(50)	-1(1)	1(30)	-1(0.11)	-1(20)	1(170)	2002.00	54.47	33.00	2.88	13.19
7	-1(30)	1(5)	1(30)	-1(0.11)	-1(20)	-1(150)	2222.00	57.39	45.25	2.77	8.33
8	1(50)	1(5)	1(30)	-1(0.11)	1(40)	-1(150)	1511.00	52.42	39.17	2.88	6.31
9	-1(30)	-1(1)	-1(10)	1(9)	-1(20)	1(170)	224.40	53.15	19.33	5.37	164.11
10	1(50)	-1(1)	-1(10)	1(9)	1(40)	1(170)	359.60	52.28	27.75	2.47	30.68
11	-1(30)	1(5)	-1(10)	1(9)	1(40)	-1(150)	151.00	53.25	30.63	9.13	224.01
12	1(50)	1(5)	-1(10)	1(9)	-1(20)	-1(150)	205.40	52.10	30.63	3.45	13.73
13	-1(30)	-1(1)	1(30)	1(9)	1(40)	-1(150)	1410.00	53.95	35.13	5.10	127.60
14	1(50)	-1(1)	1(30)	1(9)	-1(20)	-1(150)	1577.33	53.27	35.13	2.54	16.07
15	-1(30)	1(5)	1(30)	1(9)	-1(20)	1(170)	1629.33	54.10	35.83	3.48	40.26
16	1(50)	1(5)	1(30)	1(9)	1(40)	1(170)	1169.33	56.15	44.17	3.15	2.00

[a] PHR: parts per hundred of rubber, in this cases latex

contact angle was not affected significantly by the factors studied, its Daniel Plot is not included.

Tackifer resin (A) reduced viscosity and mechanical properties. Crosslinking agent (B) reduced viscosity and increased tensile strength. Silicon dioxide (C) increased viscosity and non-volatile solids content, and reduced mechanical properties. Latex type ratio (D) reduced viscosity and non-volatile solids content, and increased mechanical properties. Finally, time (E) and temperature (F) of vulcanization were not statistically significant and became fixed parameters in the central composite DOE.

3.2. Central composite DOE

This DOE adds 10 runs more to the fractional factorial DOE, which corresponds to the central points of each evaluated factor. Table 3 presents the design matrix and the experimental results obtained with this DOE. These results were analyzed using rsm's package from R statistical software to obtain second order models that best fit the response of each measured variable. Table 4 presents the mathematical equations that best model each one of the response variables.

These equations can be used to evaluate formulations where specific properties are sought in a new waterborne adhesive. For instance, an

Table 3
Design matrix and response variables of central composite design of experiments.

Design matrix					**Response variables**				
Run	A (PHR[a])	B (PHR)	C (PHR)	D (PHR/PHR)	Viscosity (mPa*s)	Non-volatile solids (%)	Contact Angle (°)	Tensile strength (MPa)	Total strain after break (%)
1	-1(30)	-1(1)	-1(10)	-1(0.11)	324.80	56.46	34.50	7.48	64.98
2	1(50)	-1(1)	-1(10)	-1(0.11)	632.00	60.06	58.33	4.25	22.78
3	-1(30)	1(5)	-1(10)	-1(0.11)	353.20	59.89	32.00	5.63	21.04
4	1(50)	1(5)	-1(10)	-1(0.11)	348.50	57.34	38.25	3.35	12.85
5	-1(30)	-1(1)	1(30)	-1(0.11)	1807.00	56.73	31.67	3.73	32.24
6	1(50)	-1(1)	1(30)	-1(0.11)	2002.00	54.47	33.00	3.12	28.88
7	-1(30)	1(5)	1(30)	-1(0.11)	2222.00	55.83	45.25	3.22	8.90
8	1(50)	1(5)	1(30)	-1(0.11)	1511.00	52.56	39.17	4.12	22.01
9	-1(30)	-1(1)	-1(10)	1(9)	224.40	53.95	19.33	12.12	59.64
10	1(50)	-1(1)	-1(10)	1(9)	359.60	52.28	27.75	2.49	69.59
11	-1(30)	1(5)	-1(10)	1(9)	151.00	53.25	30.63	10.24	62.56
12	1(50)	1(5)	-1(10)	1(9)	205.40	52.10	30.63	3.46	8.24
13	-1(30)	-1(1)	1(30)	1(9)	1410.00	53.95	35.13	6.15	67.13
14	1(50)	-1(1)	1(30)	1(9)	1577.33	53.27	35.13	3.12	9.78
15	-1(30)	1(5)	1(30)	1(9)	1629.33	54.10	35.83	7.43	78.41
16	1(50)	1(5)	1(30)	1(9)	1169.33	56.15	44.17	3.91	10.06
17	0(40)	0(3)	0(20)	0(1)	1102.00	64.62	32.38	4.66	28.99
18	-1(30)	0(3)	0(20)	0(1)	805.00	55.06	42.00	7.47	46.52
19	1(50)	0(3)	0(20)	0(1)	1104.00	55.18	48.83	4.32	25.22
20	0(40)	-1(1)	0(20)	0(1)	1097.00	56.02	41.33	4.54	37.83
21	0(40)	1(5)	0(20)	0(1)	899.00	54.55	36.13	6.29	44.57
22	0(40)	0(3)	-1(10)	0(1)	562.00	57.11	37.50	5.70	41.74
23	0(40)	0(3)	1(30)	0(1)	1234.00	57.30	40.50	4.97	35.94
24	0(40)	0(3)	0(20)	-1(0.11)	1434.67	59.92	32.17	4.36	20.65
25	0(40)	0(3)	0(20)	1(9)	375.50	54.71	30.00	5.57	41.52
26	0(40)	0(3)	0(20)	0(1)	1019.00	57.39	33.33	4.76	32.46[a]

[a] parts per hundred of rubber, in this cases latex

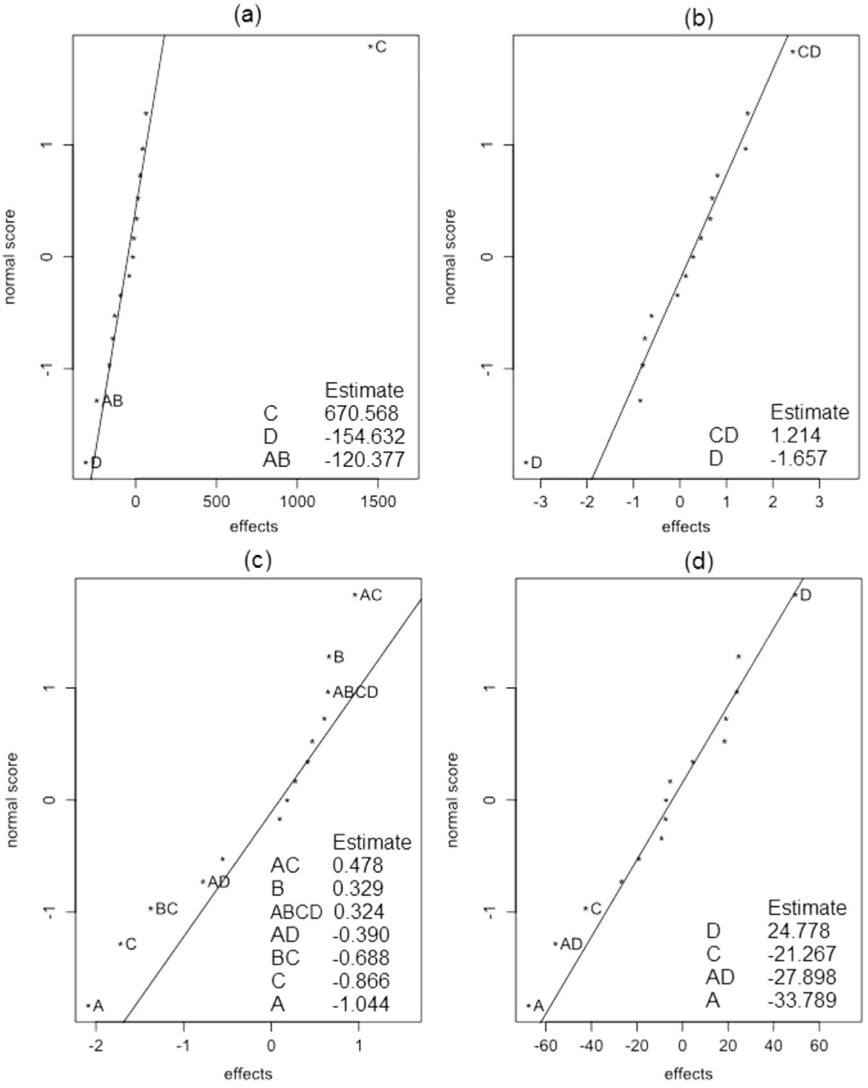

Fig. 3. Daniel's Plots for discriminating the significance of evaluated factors on: (a) Viscosity, (b) Non-volatile solids content, (c) Tensile strength and (d) Total strain after break.

Table 4
Model equations obtained for each one of the response variables.

Response	Units	Model Equation	R^2
Tensile strength	MPa	$T = 5.22 - 1.74{*}A - 0.83{*}C + 0.85{*}D + 0.98{*}A{*}C - 1.11{*}A{*}D$	0.96
Viscosity	mPa*s	$V = 964.19 + 633.39{*}C - 196.29{*}D$	0.93
Total strain after break	%	$TSB = 34.98 - 12.89{*}A + 9.59{*}D$	0.71
Contact angle	°	$CA = 36.85 + 3.49{*}C{*}D - 3.09{*}D$	0.71
Non-volatile solids content	%	$NVS = 57.93 - 1.62{*}D - 1.79{*}A^2$	0.61

A: Tackifier resin content (PHR); B: Cross-linking agent content (PHR); C: Silicon dioxide content (PHR); D: Latex type ratio (PHR/PHR)

adhesive formulation with desired specific tensile strength and viscosity can be postulated by using the equations shown in Table 4. Afterwards, total strain after break, contact angle and non-volatile solids content can be predicted. All properties for the formulations must be measured and compared to predicted values by the equations. Since the determination coefficients (R^2) of tensile strength and viscosity are reasonably high, predicted property values approach better the experimental values. On the other hand, low determination coefficients of the remaining properties indicate that the correlation is not as good and that total strain after break, contact angle and non-volatile solids content need to be measured experimentally. This is shown in the graphs depicting predicted values vs. experimental values for each property (see Fig. 4).

Equally, these equations are graphed in contour and surface plots in Fig. 5. From Fig. 5(a), it can be observed the relation between the factors silicon dioxide (C) and Latex type ratio (D) added to WPCA's formulation and its viscosity. Silicon dioxide acts as a viscosity modifier, this component is able to increase up to 80% the viscosity values [26–28], as can been seen at contour graphic. This viscosity increase is created by roughly spherical particles with a diameter of 100 nm, these particles form aggregates, which in turn are grouped to make larger agglomerates, which form a gel-type three-dimensional structure when a dispersion of them is allowed to stand [29]. Meanwhile, latex type ratio also acts as a viscosity modifier that increases the viscosity value up to 60%. This rheological behavior affects characteristics such as: processing capacity, dosage, and wettability, which are indicators of product performance and, therefore, of its quality [29]. Viscosity also determines the selection of an appropriate adhesive for industrial scale [12].

Fig. 5(b) shows the non-volatile solids content of WPCA formulations as functions of the factors that have most influence on it: Silicon dioxide (C) and latex type ratio (D). Latex type ratio represents the adhesive polymer, which is the major component and the skeleton of an adhesive formulation, and gives the cohesive properties [30]. Silicon

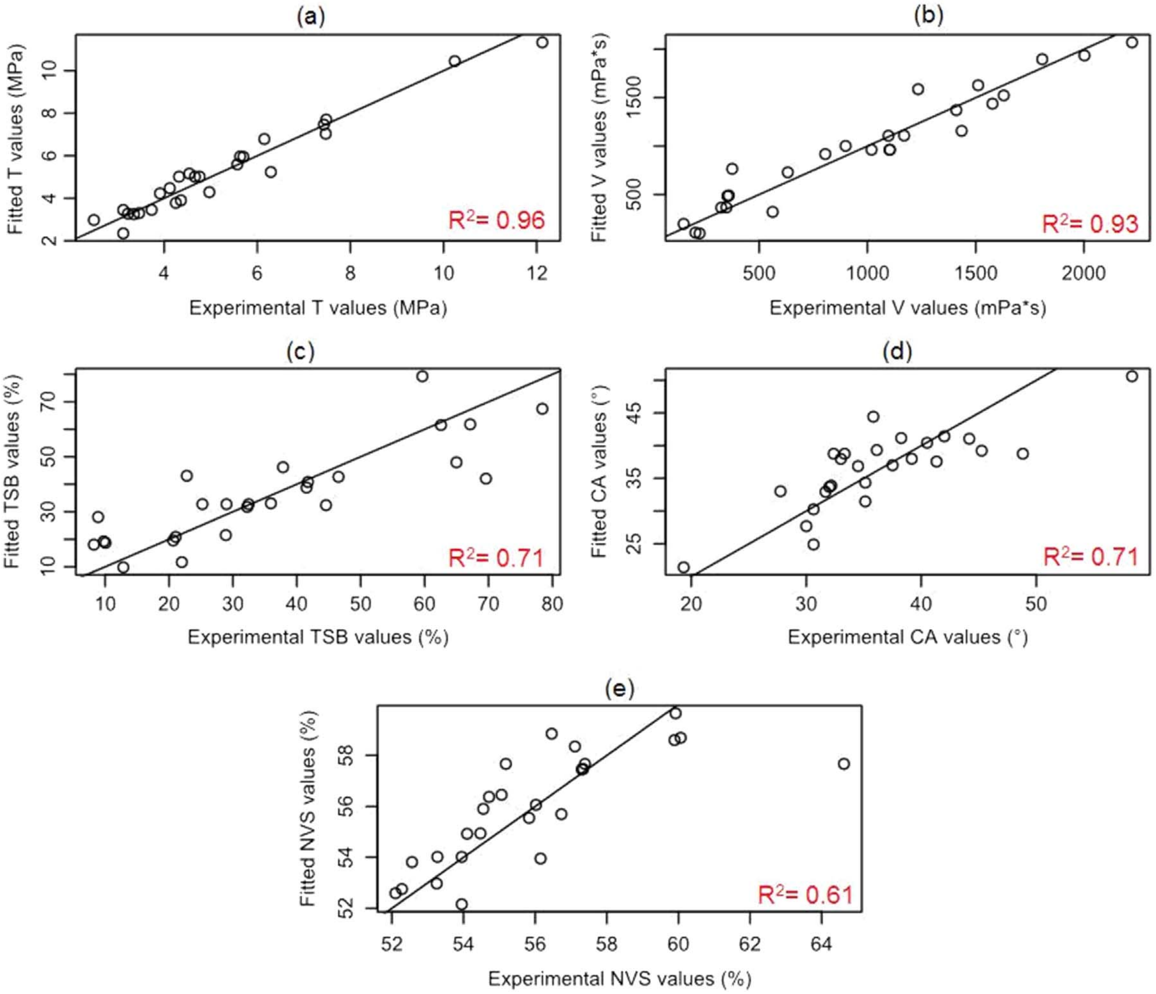

Fig. 4. Predicted values calculated by using the model equations vs. Experimental values for: (a) Tensile strength (MPa), (b) Viscosity (mPa*s), (c) Total strain after break (%), (d) Contact angle (◦), (e) Non- volatile solids content (%).

dioxide is not easily volatized but it aids with the adhesion to metallic substrates. Usually, the non-volatile solids content of a waterborne adhesive is in the range of 40–50%, while the solids content of a solvent borne adhesive is in a range of 20–30% [31]. This is why waterborne adhesives are more efficient than solvent borne adhesives.

Fig. 5(c) shows the wettability of WPCA formulations represented by the contact angle, as a function of the factors that have the most significance. Silicon dioxide (C) and latex type ratio (D) are again the factors that have the major influence. These components tend to increase the cohesive forces of the adhesive, modifying its surface energy and viscosity, and affecting the capacity of the adhesive to wet well the substrate [27]. Together these components may increase up to

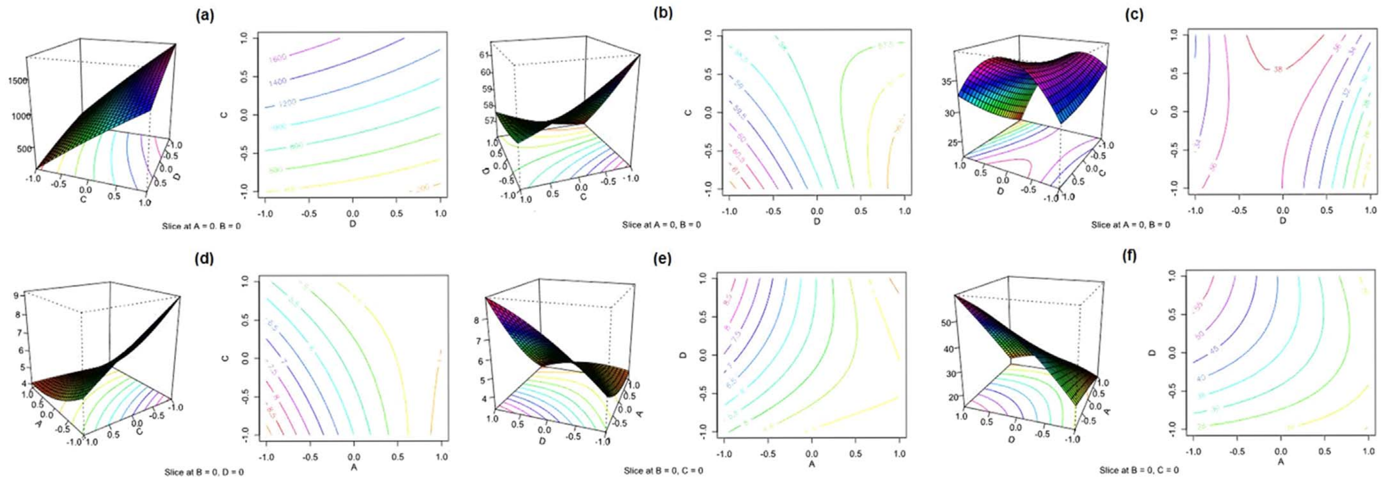

Fig. 5. Surface responses and contour plots obtained with central composite design of experiments and R statistical software, for: (a) Viscosity (mPa*s), (b) Non-volatile solids content (%), (c) Contact angle (°), (d) Tensile strength (MPa) as function of C and A factors, (e) Tensile strength (MPa) as function of D and A factors and (f) Total strain after break (%).

26.31% contact angle values, as shown in the contour graphic. The curvature of the graphic indicates that an excess of each one of the two types of latices affects considerably the response of this variable, latex C84 increases the cohesive forces of the adhesive and reduces its wettability.

Fig. 5(d) and (e), present the behavior of tensile strength of cured adhesive films as a function of the factors that most impact its response: Tackifier resin (A), Silicon dioxide (C) and Latex type ratio (D).

Tackifier resin (A) and silicon dioxide (C) increase the liquid adhesive's viscosity, reducing its wetting capacity and making film formation difficult. Cured films from adhesives with high viscosity usually have pores caused by the formation of bubbles when they are applied. These pores act as stress concentrators and weaken the integrity of the specimen during tensile testing. Both components may reduce tensile strength values up to 50%, as can been seen on the contour plot.

Latex type ratio (D) affects the cohesive and mechanical strength of the cured adhesive's films, because this represents the quantity of each one of the lattices added to the adhesive formulation. Treatments with greater latex C84 content can support more mechanical stresses before rupture, this component may increase by up to 67.82 % the tensile strength values. Treatments with greater latex C74 content do not support such high efforts but recover better their shape after rupture as they are more elastic. To clarify the effect of each type of latex on the mechanical properties of cured adhesive films, differential scanning calorimetry tests for each type of latex were conducted. It was identified that latex C84 has a Tg of -40.20 °C and a Tm of 37.10 °C. On the other hand, for latex C74 a Tg of -38:02 °C was measured. This difference in the thermal behavior elucidates a micro structural difference between these two latices, and explains why treatments with more or less an equivalent content of each latex exhibit different cohesive forces and mechanical behavior. The degree of crystallization of a polymer controls the rate of accumulation of cohesive strength and resistance of the ultimate adhesive. Polymers with higher crystallinity exhibit increased cohesion forces, elastic modulus at room temperature and reduced elongation [10].

Fig. 5(f) shows the total strain after break of cured adhesive's films as a function of the factors that have most influence on it: Tackifier resin (A) and latex type ratio (D). This result was expected because this property also represents the cohesive forces of the cured adhesive. Treatments with less content of tackifier resin and more content of latex C74 are more elastic and recover better their shape after rupture, these components may reduce the strain after break values down to 39.82 %, as can been seen from the contour graphic. If Fig. 5(e) and (f) are compared, it can be noted that curvatures of both response surfaces are inverse, which agrees with the analysis mentioned before.

3.3. Adhesion properties

Results obtained with metal to metal joints with their corresponding types of failures are shown in Fig. 6. Comparing these results with the design of experiments matrix in Table 3, the increase of tackifier resin and silicon dioxide in the adhesive formulation reduces the shear strength of metal to metal adhesive joints down to 74.16%. Otherwise, the increase of crosslinking agent (B) and latex type C84 content increases by up to 61.02% the shear strength of metal to metal adhesive joints.

These effects are produced because each one of these components tends to develop adhesive or cohesive properties in the WPCA samples. Considering that to create an adhesive formulation that bonds well, it is necessary to have a perfect balance between these properties. Also, it can be expected that an excess or lack of any of these components may result in a poorly functioning adhesive.

From lap-shear test results, WPCA treatments selected to test under pull out stress were: 1, 4, 5, 6, 8, 9 and 16. Similarly, the performance of these treatments was compared with that of commercial waterborne (Cilbond 62W from Chemical Innovations Limited, United Kingdom) and solvent borne (Chemlock, from Lord Company, USA) adhesives.

Results obtained with rubber to metal joints with their corresponding types of failures are shown in Fig. 7. Comparing these results with the design of experiments matrix in Table 3, it can be observed that adhesives with a greater tackifier resin (A) content and crosslinking agent (B) have better pull out strength. This agrees with the results obtained from the lap-shear tests. On the other hand, it was found that pull out strength values of rubber to metal joints made with WPCA samples were low compared to those obtained with commercial adhesives, under the same testing conditions. However, treatment 4 reached the highest performance between all WPCA samples, achieving values close to the commercial waterborne adhesive (Cilbond 62W from Chemical Innovations Limited, United Kingdom).

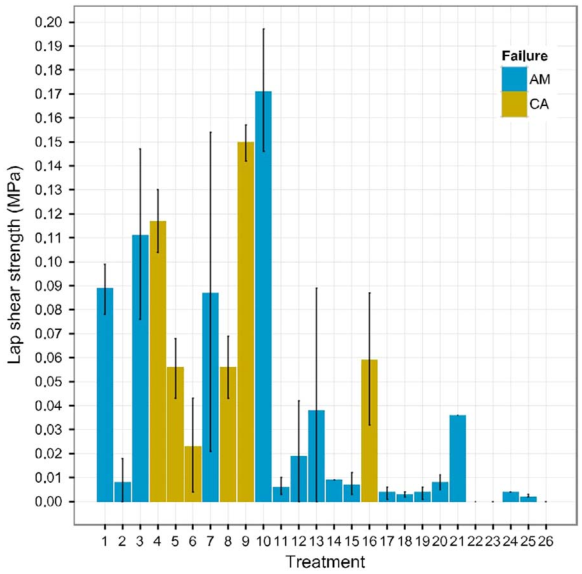

Fig. 6. Single lap-shear strength values of metal/ WPCA /metal joints obtained with each adhesive formulated, and its corresponding type of failure AM for adhesive failure to metal surface, or CA for cohesive failure in the adhesive.

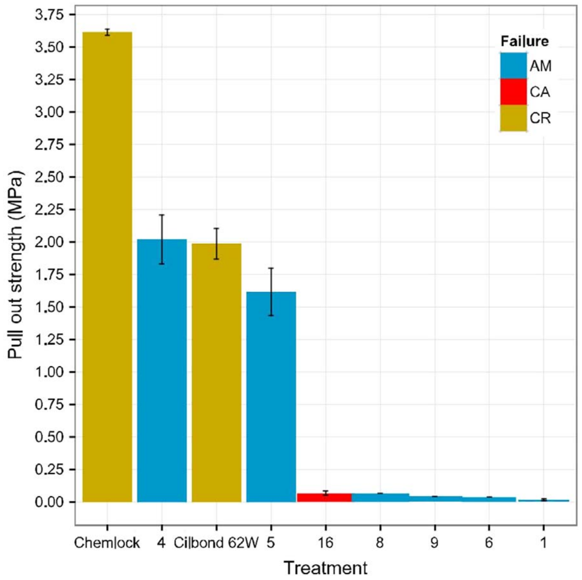

Fig. 7. Pull-out strength values of rubber/ WPCA /metal joints obtained with adhesives selected from metal to metal adhesion analysis and commercial available adhesives, and its corresponding type of failure: AM for adhesive failure to metal surface, CA for cohesive failure in the adhesive, or CR for cohesive failure in the rubber.

4. Conclusions

A complete study of the formulation of a polychloroprene waterborne adhesive for rubber to metal bonding using statistical experimental design was performed. Through this methodology the individual and mixed effects of different factors were determined, for the formulation of the adhesive and the bonding process. Fractional factorial design of experiments approach proved to be a very useful tool to identify critical factors that affect most the response variables. Once these factors were recognized, a central composite design of experiments approach allowed developing mathematical models for each measured variable, which were used to plot surface response and contour graphics to predict the behavior of the formulations. Factors related to adhesive formulation had the most influence on the measured variables: Silicon Dioxide (C) mainly affected the liquid adhesive's properties, tackifier resin (A) allowed more control on cured adhesive's properties, and latex type radio (D) influenced both cohesive and adhesive's forces. The quantity, micro structure and crystallization rate of each type of used latices, affected the mechanical behavior of cured adhesive. Latex type C84 gave strength to the adhesive, while latex type C74 gave elasticity. Crosslinking agent (B) did not show a representative effect as the other components, it was always limited to interactions with them. For WPCA formulations designed in this study it was found that the best conditions that promoted rubber to metal adhesion during vulcanization were cure at 150 °C for 15 min under pressure.

Adhesion results following these cure conditions showed that treatment 4 was the adhesive with the best performance, and the closest to the commercial waterborne adhesive of all those studied (Cilbond 62W from Chemical Innovations Limited, United Kingdom).

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