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Bisphenol-A Resole Resins in Preparation Aqueous Adhesives for Bonding Silicon Rubber-to-Metal

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An aqueous adhesives composition of bisphenol-A resoles resins as adhesion promoter, in combination with a silane compound were prepared useful for bonding silicon rubber to metal surfaces. Silicon rubber-metal joints were prepared and tested according to ASTM D 429 before and after the unloaded specimens were kept in boiling water to find their mechanical properties. All results showed good adhesion to metal surfaces and the rupture was in silicon rubber body.

Key Words: Bisphenol A, Resole, Silane, Mechanical, Metal, Adhesion.

INTRODUCTION

Bisphenol-A resins are important material used in many applications in industry, as adhesives, coatings systems and binders for organic and inorganic material[1]. They have a good adhesion properties to many substrates, such as metals, ceramics, *etc*., where there is a need for silicon rubber-to-metals joints that are a commonly used in medicaments and foods production process lines[2]. Previous adhesive compositions utilized for bonding silicon rubber- to- metal are solvent borne, for this reason are becoming gradually less favourable, increasingly circumscribing with each passing time from government regulations to reduce or eliminate the use of volatile organic compounds in adhesives and coating systems[3]. Therefore, preparation of aqueous dispersion of heat reactive phenolic resin (*e.g*. bisphenol-A resole) and use it as a mixture with silane compounds to produce adhesive formulation are suitable to reduce the need for solvents for both ecological and economic reasons.

To obtain a stable water based bisphenol-A resoles dispersion was used the polyvinyl alcohol (protective colloid or emulsion stabilizing agent), co-solvent (coupling solvent) and water[4].

Several silane adhesive solvent borne compositions have earlier been prepared and used for bonding elastomeric materials to metals especially silicon rubber[5] and didn't contain adhesion promoters such as phenolic resins. Therefore, they have a weakness in withstanding environment conditions.

Silanes compounds are the most commonly used as bonding agents to improve the adhesion between the polymeric materials with inorganic substrates or materials[6-8]. Silanes have a formula (1), as follows:

$$(RO)_3SiCH_2CH_2CH_2\text{-}X \qquad (1)$$

where, RO-: is a hydrolyzable group, like alkoxy group (methoxy-, ethoxy-, acetoxy); X: is the organofuntionality, like vinyl-, amino-, methacrylate-, epoxy-, mercapto-, *etc*. this portion bonds with the organic material (silicon elastomer in our joint).

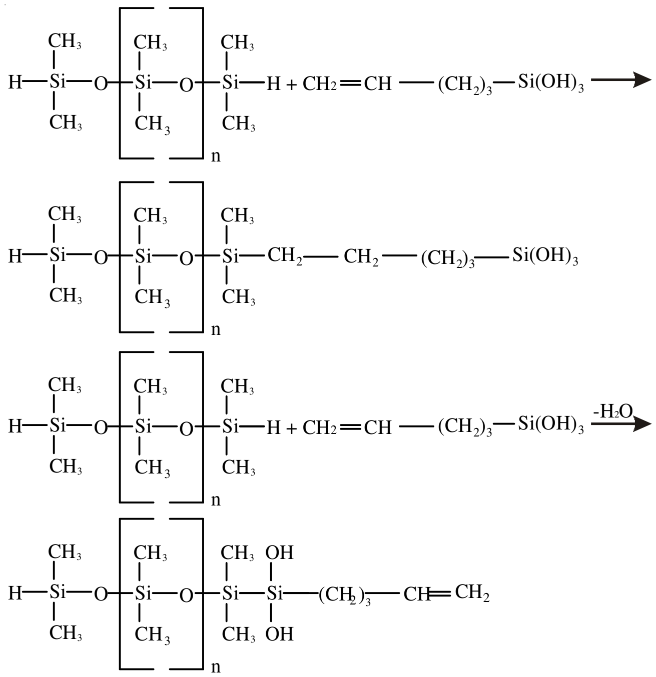
The silane portion reacts with hydroxyl groups that available on bisphenol-A resole resins or on the substrate surfaces. Consequently, it results a chemical bridge between the organic polymers, or between the polymer and metallic substrate[1].

The reactions that happen during the bonding and vulcanization step of silicon rubber and adhesive can be shown as follows:

$$CH_2 = CH\text{-}(CH_2)_3\text{-}Si(OCH_3)_3 + 3H_2O \rightarrow CH_2 = CH\text{-}(CH_2)_3\text{-}Si(OH)_3 + CH_3OH$$

$$\text{resole -OH} + HO\text{-}Si(OH)_2\text{-}(CH_2)_3\text{-}CH = CH_2 \rightarrow [\text{resole-OHHO-}Si(OH)_2\text{-}(CH_2)_3\text{-}CH = CH_2] \rightarrow \text{resole -O-}Si(OH)_2\text{-}(CH_2)_3\text{-}CH = CH_2 + H_2O$$

$$\text{surface -OH} + HO\text{-}Si(OH)_2\text{-}R \rightarrow [\text{surface -OHHO-}Si(OH)_2\text{-}(CH_2)_3\text{-}CH = CH_2] \rightarrow \text{surface -O-}Si(OH)_2\text{-}(CH_2)_3\text{-}CH = CH_2 + H_2O$$



Water has relatively a complex effect on rubber-to-metal bonds. Hence, the adhesion becomes dynamically critical when water enters the joint at bond line, because of hydration of the adherents.

EXPERIMENTAL

Bisphenol-A (BPA) (99.9 %), formaldehyde (37 % solution in water), sodium hydroxide (99.9 %) and phosphoric acid (85 %), polyvinyl alcohol, isopropyl alcohol, acetic acid, vinylpropyltrimethoxy silane.

Adhesives preparation procedure

Synthesis of bisphenol-A formaldehyde resoles using sodium hydroxide as a catalyst: Resole-type bisphenol-A resins were prepared at varying formaldehyde-bisphenol-A molar ratios (F/BPA: 1.5, 2.0 and 2.5, R1, R2 and R3 respectively) in the presence NaOH (0.017 mol per 1 mol of bisphenol-A), where the pH was kept at 8.2.

Bisphenol-A formaldehyde solution and catalyst were placed in glass reactor with magnetic stirrer, thermometer and reflux condenser. The mixture was stirred and heated to 90 ºC (heating rate: 2.5- 3.5 ºC/min). The reaction was stopped after 2 h, cooled to 70 ºC and neutralized with a solution of phosphoric acid 41 % until the pH reached 6. The contents of the reactor were then subjected to a vacuum to stripe the water from the reaction mixture at 75- 80 ºC until total extraction of water. The characteristic of Bisphenol A resoles resins are listed in Table-1.

TABLE-1
CHARACTERISTIC OF THE RESINS

	R1	R2	R3
F/BPA molar ratio	1.50	2.00	2.50
M_n	524.24	536.3	612.0
M_w	674.27	701.36	905.7
M_w/M_n	1.286	1.25	1.48
Ea (kJ/mol)	49.98	57.807	61.723

M_n: number– average molecular weight, M_w: weight- average molecular weight, calculated by GPC and DSC instruments in a previous work[9].

Aqueous bisphenol-A resole resins dispersions preparation: Bisphenol-A resole resins 50 % in isopropyl alcohol (as coupling solvent) solution were prepared. Polyvinyl alcohol (8 %) solution in deionized water. Where, the solvent is miscible with water completely.

Resole solution was put in a mixer. Polyvinyl alcohol solution was added slowly in portions with increasing the speed of agitation and was maintained until a temperature of 50-55 ºC. At this step smooth emulsion had formed.

Adhesives preparation: The quantity of vinyltrimethoxy silane are blended into the dispersion of a phenolic bisphenol -A resole in water stabilized with polyvinyl alcohol, and it was rapidly emulsified by the resole dispersed. In the final, the pH of medium was adjusted to *ca.* 4 by glacial acetic acid.

Adhesive emulsions of the above resins were prepared according to the formulations shown in Table-2.

TABLE-2
AQUEOUS ADHESIVE FORMULATIONS

Chemical names	Formulations			
	F1	F2	F3	F4
Bisphenol-A resole 50 %	R1	R2	R3	-
	10.0	10.0	10.0	-
Isopropyl alcohol	5.00	5.00	5.00	47.5
Vinyltrimethoxy	5.00	5.00	5.00	5.00
Polyvinyl alcohol 8 %	37.5	37.5	37.5	-
Water	-	-	-	5.00
Glasical acetic acid	To pH *ca.* 4			

Joints preparation: The metal surfaces were cleaned by physical and chemical treatment before application of adhesive such as grit blasting and solvent degreasing. The adhesive compositions prepared were typically applied to the metal surfaces and allowed to dry completely. The coated metal surface and silicon rubber are then brought together under heat (170 ºC) and pressure (150- 200 kg/cm^2) to complete the bonding procedure[2].

The assembly should remain under the applied pressure and temperature for a period depending on the cure rate and thickness of the rubber substrate. After the moulding process is completed, the joints were fully vulcanized and ready for use in final application or test them after vulcanization and adhesion, the specimens were stored at temperature of 23 ± 2 ºC for at least 16 h before test them.

RESULTS AND DISCUSSION

Joints testing: The adhesives formulations prepared were tested by preparation specimens according to ASTM 429 methods A, B and C[10], by using testometric apparatus made in England. All the specimens were tested under normal condition and withstand to boiling water for 2 h (for method B).

Method A- Rubber part assembled between two parallel metal plates: The standard test specimen dimensions are cylinder of rubber 3.2 ± 0.1 mm thick and diameter 39.9 ± 0.1 mm attached to the faces of two metal plates each at least 9.5 mm in thickness and of the same diameter as the rubber cylinder. The extension rate was 24 mm/min. Fig. 1 showed the specimens according to method A.

Table-3 shows the mechanical results. Fig. 2 shows the mechanical test curve as method A.

Fig.1. Test specimen according to method A

TABLE-3
TENSILE STRESS RESULTS AND RUPTURES TYPES FOR SPECIMENS ACCORDING TO METHOD A

		F1	F2	F3	F4
Tensile stress (N/mm^2)		1.66	2.53	1.68	1.53
Types of break (%)	R[1]	95	100	85	70
	RC[2]	5	0	15	15
	M[3]	0	0	0	15

R[1] indicates the failure is in the rubber. RC[2] indicates the failure is at the rubber-cover cement interface. M[3] indicates the failure is at the metal-prime cement interface

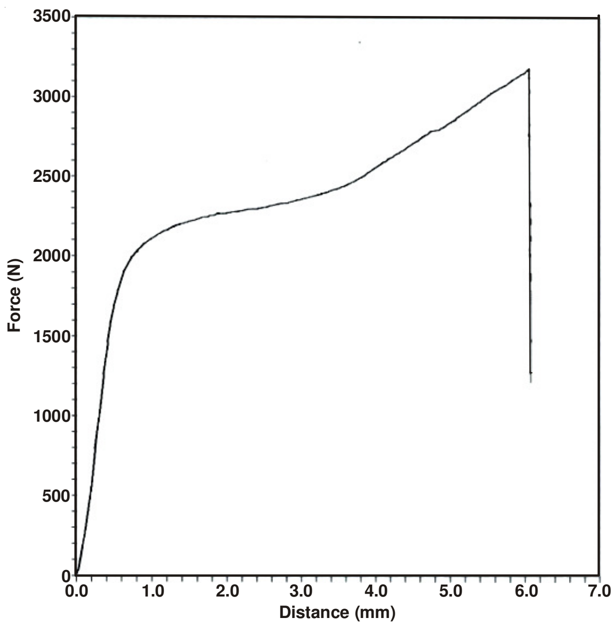


Fig. 2. Curve of specimen failure during tensile stress is applied (F2)

Method B 90º stripping test-rubber part assembled to one metal plate: The data obtained indicate the strength of adhesion along a line across the width of the rubber strip being separated from metal plate at a 90º angle. The bond area of 25 mm × 25 mm. The extension rate was 50 mm/min.

To examine the specimens as withstood toward boiling water, the specimens buffed on the edges with a grinding wheel. The rubber for each specimen was bent backwards 180º to stress the bonded area. This exposed the bond line to the environment. The specimens placed in a beaker and kept unloaded in boiling water, for 2 h. After drying in air at room temperature, the specimens were tested according to ASTM D 429[9], method B the stripping angle was 90º. The Fig. 3 shown the specimens as method B. Table-4 shows the mechanical results according of method B.

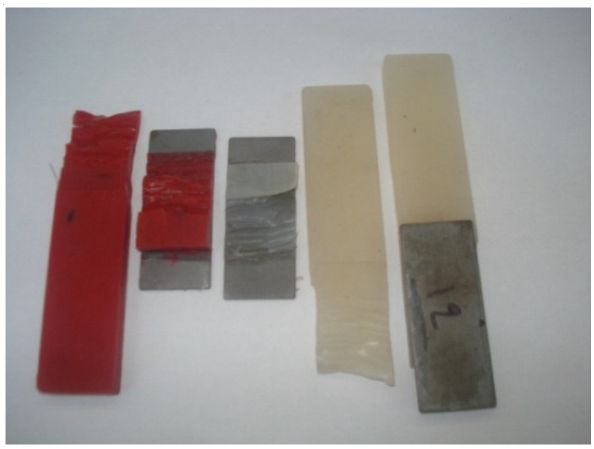


Fig. 3. Test specimen according to method B

Fig. 4 shows the mechanical test curve according to method B.

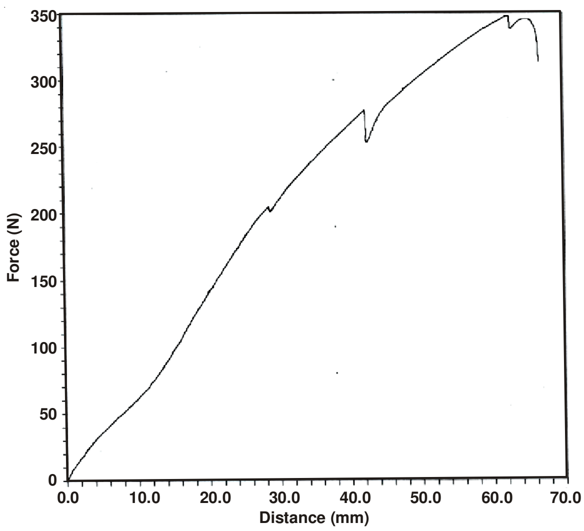


Fig. 4. Curve of specimen failure during peel tensile F2

TABLE-4
PEEL TENSILE AND RUPTURE TYPES ACCORDING TO METHOD B

		F1		F2		F3		F4	
		Normal	Boiling water	Normal	Boiling water	Normal	Boiling water	Normal	Boiling water
Stripping force (N/mm^2)		14.48	13.79	12.0	11.00	9.37	8.5	8.3	7.34
Types of break(%)	R	100	100	100	100	90	80	80	60
	RC	5	0	0	0	10	10	20	10
	M	0	0	0	0	0	10	0	30

Method C measuring adhesion of rubber-to-metal with a conical specimen: This test provides data for development and control for bonding system and their components such as cements, or special rubber compounds. The dimension of the test specimen are the diameter 25 ± 0.5 mm, the distance between the opposed conical end pieces is 11.5 ± 1.2 mm, the height of each conical end piece is 23.4 ± 0.5 mm. Fig. 5 shows the specimens as method C. Table-5 showed the mechanical results of tensile strain for method C.

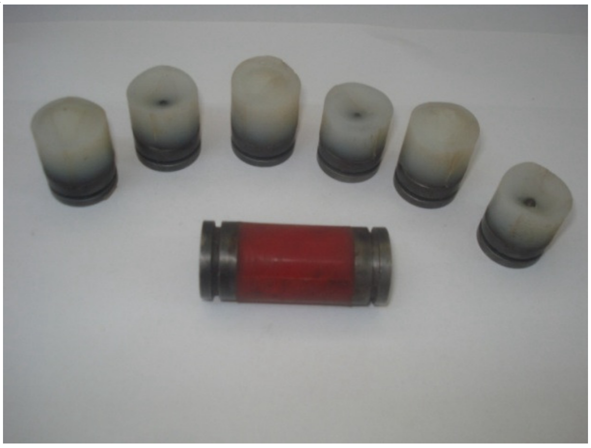


Fig. 5. Test specimen according to method C

Fig. 6 shown failure curve of specimen of method C.

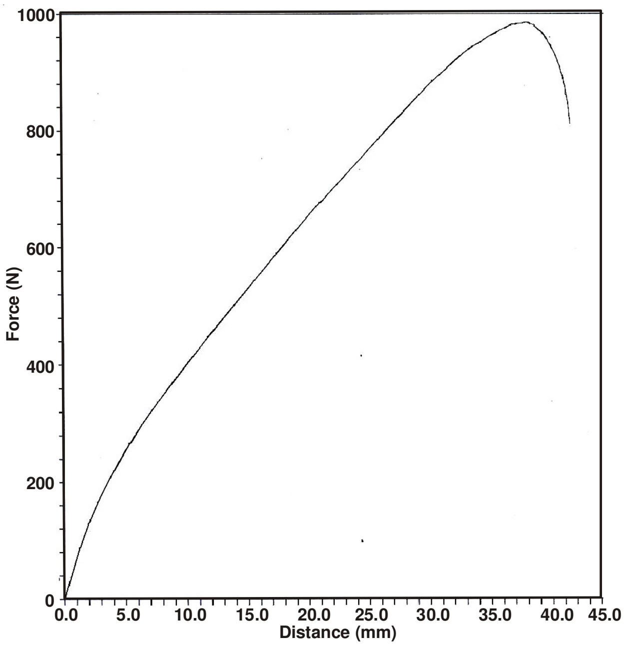


Fig. 6. Curve of specimen failed during tensile stress is applied F2

TABLE-5
TENSILE STRESS AND FAILURE TYPES
ACCORDING TO METHOD C

		F1	F2	F3	F4
Tensile stress (N/mm^2)		2.00	2.03	2.07	1.35
Types of break (%)	R	90	100	80	70
	RC	10	0	20	10
	M	0	0	0	20

Conclusion

From the adhesive composition formulations and mechanical tests the following conclusion can be drown: (1) It in possible to reduce the volatile organic compounds by using adhesive formulations based on water; (2) Comparison of (F1, F2, F3 and F4), it is found that the series (F1, F2 and F3) showed resistance toward boiling water environment at bonding line according to results of method B, while was noted the failure in large percentage on metallic surfaces in joints were using adhesive of formulation F4; (3) Bisphenol-A resole resins are good adhesion promoters for these applications.

REFERENCES

1. E.M. Petrie, Handbook of Adhesives and Sealants, p. 880 (2000).
2. B. Crowther, The Handbook of Rubber Bonding, p. 373 (2001).
3. J.S. Fry, H. Towinship and S. County, U.S. Patent No. 4124554 (1978).
4. K.A. Bourlier, N.J. Randolph, P.S. Mulrenin and G. Tucker, U.S. Patent No. 5548015 (1996).
5. K. Khoudary, G. Salloum and S. Gharibe, Adhesive Preparation for Bonding Silicon Rubber-to-metal, R.J. of Aleppo University Basic Science, Series No. 52, 233 (2007).
6. E.P. Plueddemann, Silane Coupling Agents, (New York) (1991).
7. G.L. Witucki, A Silane Primer: Chemistry and Application of Alkoxy-silanes, Dow Corning Corporation, Chicago, (1992).
8. K.L. Mital, Silane and Other Coupling Agents, Utrecht, VSP (1992).
9. K. Khoudary, N. Sarkis, G. Salloum and S. Gharibe, *Arabian J. Chem.*, (2012) (In press).
10. ASTM D429-73 Rubber Property - Adhesion to Rigid Substrates.