

## Some Coating Studies on Phenolic Epoxy/Poly (Vinyl Acetal), Resins

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**Abstract:** Two types of epoxy resins namely, epoxy novolac phenol formaldehyde (Epoxy N-PF) and epoxy novolac bisphenol formaldehyde (Epoxy N-BF) were prepared and characterized by hydroxyl group content, epoxy group content, specific viscosity and FTIR spectroscopy. Curing behavior of these epoxy resins with different weight ratios of different types of prepared phenolic resins namely, resol phenol formaldehyde (R-PF), resol bisphenol formaldehyde (R-BF), novolac phenol formaldehyde (N-PF) and novolac bisphenol formaldehyde (N-BF) were carried out at 180 °C for 20 min. The cured samples was applied and evaluated as metal coatings. Mechanical properties of the cured epoxy metal coatings indicated that the optimum ratio of curing agent was 30% by weight on basis of epoxy resin weight. Modification of epoxy resins with different ratios of poly (vinyl formal) (PVF) or poly (vinyl butyral) (PVB) in presence of 30% of different types of curing agents was carried out. It was found that 20% PVF and PVB is the suitable ratio for epoxy resin modification. Non-modified as well as modified epoxy resins were evaluated as metal coatings by measuring mechanical properties, thermal stability and chemical resistance. Modification of epoxy resins with PVF or PVB improves the mechanical properties combined with decrease in the thermal stability, while all coating samples had good chemical resistance towards all used media.

**Key words:** Epoxy Novolac Phenol Formaldehyde resin, Epoxy Novolac Bisphenol Formaldehyde resin, Poly (Vinyl Formal), poly (vinyl butyral), Metal Coatings, Mechanical Properties, Thermal Stability, Chemical Resistance.

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### INTRODUCTION

Epoxy resins are of the most important thermosetting polymers. They are currently used in advanced composites<sup>[9]</sup>, nanocomposite, coatings<sup>[18]</sup>, structural adhesives<sup>[5]</sup>, matrices for fibre composite and microelectronics<sup>[2]</sup>, due to their high stiffness, high strength, good chemical resistance and dimensional stability<sup>[17]</sup>. The primary requirement for high-temperature performance necessitates the selection of polyfunctional epoxy resins and curing agents are capable of creating high crosslink densities. Thus, novolac epoxy resin, can produce a more tightly crosslinked three-dimensional network compared to epoxy diglycidyl ether of bisphenol A (DGEBA) and hence can give better adhesive strength retention at elevated temperatures<sup>[8]</sup>.

The traditional phenolic resins have many advantages<sup>[13]</sup>, such as heat resistance, good electronic properties and flame retardance. Phenolic resins have been used as a crosslinker for epoxy resins<sup>[7]</sup>. Resole phenolic resins are used in various types of coatings as cross-linker, for adjusting flexibility and improving

surface contact<sup>[12]</sup>. Resol type phenolic resins have the ability to cure either by heating only or by the use of a curing agent<sup>[14]</sup>.

Although the importance of the phenolic resins has waned, they still have significant uses. To enhance their flexibility and adhesion, they can be blended with low molecular weight poly (vinyl butyral). They are also blended with epoxy resins in thermosetting coatings for applications such as primers and can coatings. The compatibility of alcohol-soluble resole resins with epoxy resins can be improved by partial conversion of the methylol groups to ethers. Poly (vinyl acetal)s compatibility with other resins is due largely to their unique chemical compositions, permit blending with other resins, resulting in properties not achievable with either component alone<sup>[10]</sup>.

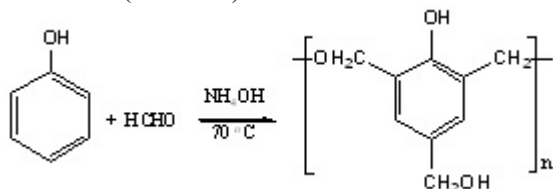
In a previous study<sup>[14]</sup>, we prepared phenolic resins such as resole phenol- and cresol-formaldehyde, as well as low-molecular-weight epoxy resin based on bis (4-hydroxy phenol) cyclohexane and modified with various types of the prepared poly(vinyl acetal)s. Poly(vinyl formal), poly(vinyl isobutyral) and poly(vinyl propional) were used.

In this work, it was reported that the synthesis of epoxy novolac phenol formaldehyde resin (Epoxy N-PF) as well as epoxy novolac bisphenol formaldehyde resin (Epoxy N-BF) and their curing behavior with different types of prepared phenolic resins. Modification of these epoxy resins with different ratios of poly (vinyl formal) (PVF) or poly (vinyl butyral) (PVB) and their evaluation as metallic coatings were also described.

## MATERIALS AND METHODS

**Experimental:** Preparation of Phenolic Resins<sup>[1,15]</sup>:

**Preparation of Resole-Phenol Formaldehyde Resin (R-PF):** R-PF resin was prepared by condensation reaction between phenol and formaldehyde under alkaline conditions (Scheme I)

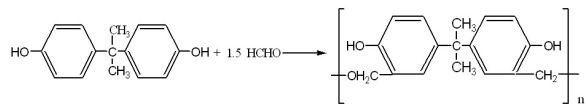


**Scheme I:** Preparation of R-PF.

In a 250 ml three-necked round bottom flask fitted with condenser, stirrer and thermometer, 0.5 mol phenol, 0.72 mol 37% aqueous formaldehyde solution and 1.5 g 25% ammonia solution were placed. Reflux and stir for 2 h at 70°C. The pH value of the reaction mixture was then adjusted to 6-7 by addition of 10% sulfuric acid. The aqueous phase was allowed to separate and the water distilled off at  $\leq 70^\circ\text{C}$ .

The characteristics of the prepared R-PF resin are tabulated in Table (1). The IR spectrum of the prepared R-PF exhibited absorption bands of group C=C aromatic at 1594  $\text{cm}^{-1}$ ,  $\text{CH}_2$  at 1465  $\text{cm}^{-1}$ , C-O ether at 1173  $\text{cm}^{-1}$  and C-H aromatic at 2923  $\text{cm}^{-1}$ .

**Preparation of Resol-Bisphenol A Formaldehyde Resin (R-BF):** R-BF resin was prepared by condensation reaction between bisphenol A and formaldehyde under alkaline conditions (Scheme II).



**Scheme II:** Preparation of R-BF.

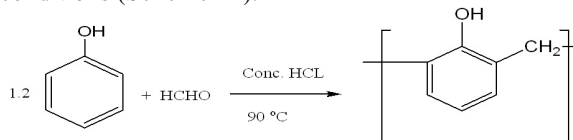
In a 250 ml three-necked round bottom flask fitted with condenser, stirrer and thermometer, 0.093 mol bisphenol A, 0.14 mol 37% aqueous formaldehyde solution and 2 g of 25% ammonia solution were used. The experiment was completed as the same method described before.

**Table 1:** The Characterization of the Prepared Resins

Resin Type	Hydroxyl Group Content	Epoxy Group Content	Acetal Group Content	Specific Viscosity ( $\eta_{sp}$ )
R-PF	23.2	-	-	0.032
R-BF	21.8	-	-	0.023
N-PF	13.3	-	-	0.034
N-BF	18.5	-	-	0.028
Epoxy N-PF	9.2	8.3	-	0.030
Epoxy N-BF	12.8	12.4	-	0.028
PVF	22.7	-	44	0.053
PVB	20.6	-	40.4	0.049

The characteristics of the prepared R-BF resin are tabulated in Table (1). The IR spectrums of the prepared R-BF exhibited absorption band of group OH at 3318  $\text{cm}^{-1}$ , CH aromatic at 2967  $\text{cm}^{-1}$ , CH alkane at 2876  $\text{cm}^{-1}$ , C=C aromatic at 1509  $\text{cm}^{-1}$ ,  $\text{CH}_3$  at 1365  $\text{cm}^{-1}$ ,  $\text{CH}_2$  at 1437  $\text{cm}^{-1}$  and C-O ether at 1178  $\text{cm}^{-1}$ .

**Preparation of Novolac Phenol Formaldehyde Resin (N-PF):** N-PF resin was prepared by condensation reaction between phenol and formaldehyde under acidic conditions (Scheme III).

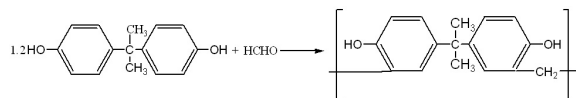


**Scheme III:** Preparation of N-PF.

In a 250 ml three-necked round bottom flask fitted with condenser, stirrer and thermometer, 0.69 mol phenol, 0.57 mol 37% aqueous formaldehyde solution and 0.4 g conc. HCl were placed. Reflux and stir for 1.5 h at 90°C. 100 ml water was then added, stirred briefly and allowed to cool, whereby the condensation polymer settles out. The aqueous layer was separated and the residual water was distilled off while slowly raising the temperature to 150°C.

The characteristics of the prepared N-PF resin are tabulated in Table (1). The IR spectrum of the prepared N-PF exhibited absorption bands of group C=C aromatic at 1601  $\text{cm}^{-1}$ ,  $\text{CH}_2$  at 1400  $\text{cm}^{-1}$  and OH at 3132  $\text{cm}^{-1}$ .

**2.1.4. Preparation of Novolac-Bisphenol A Formaldehyde Resin (N-BF):** N-BF resin was prepared by condensation reaction between bisphenol A and formaldehyde under acidic conditions (Scheme IV).



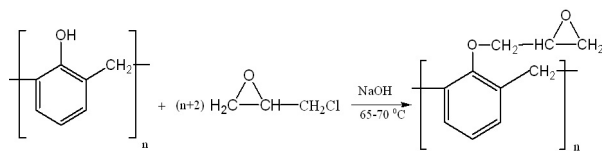
**Scheme IV:** Preparation of N-BF.

In a 250 ml three-necked round bottom flask fitted with condenser, stirrer and thermometer, 0.1 mol of bisphenol A, 7.8 g of a 37% aqueous formaldehyde solution, 4 g 1N oxalic acid and 0.4 g of conc. HCl were placed. Reflux and stir for 1.5 h at 90°C. The experiment was completed as the same method described in earlier.

The characteristics of the prepared N-BF resin are tabulated in Table (1). The IR spectrum of the prepared N-BF exhibited absorption band of group OH at 3286 cm<sup>-1</sup>, CH alkane at 2871 cm<sup>-1</sup>, CH<sub>2</sub> at 1434 cm<sup>-1</sup>, CH<sub>3</sub> at 1385 cm<sup>-1</sup> and C=C aromatic at 1511 cm<sup>-1</sup>.

**Preparation of Epoxy Resins<sup>[14]</sup>:**

**Preparation of Epoxy Novolac Phenol Formaldehyde (Epoxy N-PF):** Epoxy N-PF was prepared by condensation reaction between novolac phenol formaldehyde resin and epichlorohydrine in presence of sodium hydroxide (Scheme V).



**Scheme V:** Preparation of Epoxy N-PF.

A solution of 11.8 g the prepared N-PF in methanol and 12.5 g epichlorohydrine were mixed in a three-necked round bottom flask equipped with a stirrer, condenser and dropping funnel. A solution of 0.05 mol sodium hydroxide in 10 ml water was prepared, 60% of this solution was added in a period of 2 h. The second portion 22% of the solution was added during 15-20 min. The third portion (18%) was added at once and stirring continued for another 30 min at 65-70°C. At the end of the reaction water was added and the mixture was stirred for 20 min at 60-70°C, then resin was precipitated. The upper layer was decanted and then the resin was washed several times with distilled water at 40-60°C, until the water gave no color with phenolphthalein or any precipitate with silver nitrate. The obtained resin was dissolved in acetone and filtrated. The acetone was removing from the resin solution by heating in oven at 60°C and then dried.

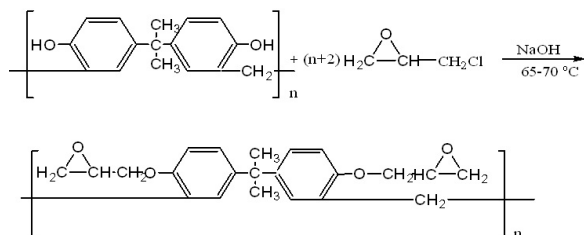
The characteristics of the prepared Epoxy N-PF resin are tabulated in Table (2). The IR spectrum of the prepared Epoxy N-PF exhibited absorption bands of group CH alkane at 2932 cm<sup>-1</sup>, C=C aromatic at 1504 cm<sup>-1</sup>, CH<sub>2</sub> at 1456 cm<sup>-1</sup>, C-O at 1168 cm<sup>-1</sup> and epoxy group at 909 cm<sup>-1</sup>.

**Table 2:** Mechanical Properties for Epoxy Metal Coatings.

Formulation						
Epoxy Type	Hardener		Mechanical Properties			
	Type	%	Adhesion	Hardness	Impact	Elongation
Epoxy N-PF	R-PF	10	2B	F	Fail	14
		20	2B	H	Fail	11
		30	2B	2H	Pass	9.7
		40	2B	H	Fail	7.7
		50	2B	H	Fail	7.5
R-BF		10	1B	HB	Fail	18
		20	1B	F	Fail	14
		30	2B	2H	Pass	10.4
		40	2B	F	Pass	8.25
		50	2B	HB	Fail	8
N-PF		10	0B	3B	Fail	35
		20	1B	3B	Fail	35
		30	1B	2B	Pass	28.1
		40	1B	3B	Fail	26
		50	1B	2B	Fail	25
N-BF		10	1B	3B	Fail	27
		20	1B	3B	Fail	22
		30	2B	HB	Pass	17.2
		40	2B	B	Fail	14
		50	2B	HB	Fail	12
Epoxy N-BF	R-PF	10	3B	2H	Fail	12.5
N-BF		20	4B	3H	Fail	8
		30	5B	4H	Pass	4.9
		40	4B	3H	Pass	3.7
		50	4B	4H	Fail	3.7
	R-BF		10	3B	H	Fail
		20	4B	2H	Fail	9
		30	5B	3H	Pass	6.7
		40	4B	2H	Fail	5.75
		50	4B	2H	Fail	5.5
N-PF		10	2B	2B	Fail	27.5
		20	2B	HB	Fail	23
		30	3B	F	Pass	18.1
		40	3B	F	Pass	16.5
		50	2B	HB	Fail	15
N-BF		10	2B	HB	Fail	23
		20	3B	H	Fail	19
		30	4B	2H	Pass	12.0
		40	2B	H	Pass	10.75
		50	2B	H	Fail	10.75

5B: No peeling or removal  
 4B: Trace peeling or removal along incision or at their intersection,  
 3B: Jagged removal along incisions up to 1/16 in. (1.6 mm) on either side,  
 2B: Jagged removal along most incisions up to 1/8 in. (3.2 mm) on either side,  
 1B: Removal from most of the area under the tape and  
 0B: Removal beyond the area.  
 These symbols were according to ASTM D 3359-95 (B).

**Preparation of Epoxy Novolac-Bisphenol A Formaldehyde (Epoxy N-BF):** Epoxy N-BF was prepared by condensation reaction between novolac-bisphenol A formaldehyde resin and epichlorohydrine in the presence of sodium hydroxide (Scheme VI)



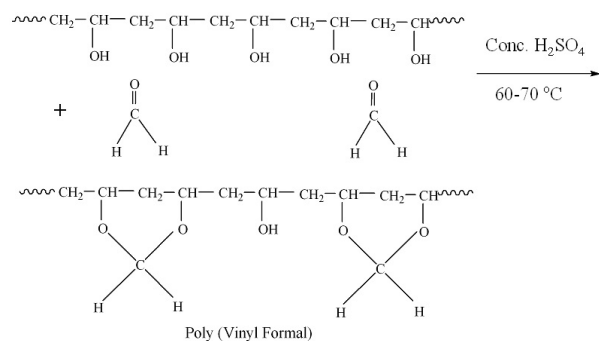
**Scheme VI:** Preparation of Epoxy N-BF.

Prepared novolac bisphenol A formaldehyde resin (9.5 g in methanol) and epichlorohydrine (6 g) were mixed in a three-necked round bottom flask equipped with a stirrer, condenser and dropping funnel. The experiment was completed as the same method described in before.

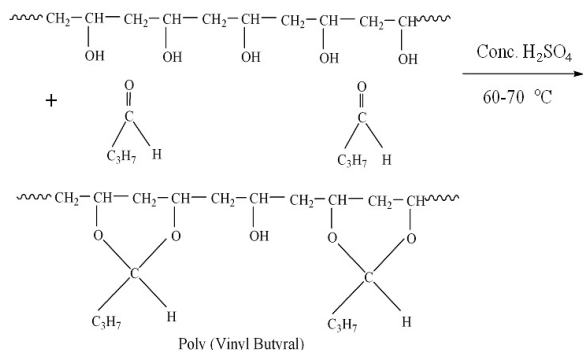
The characteristics of the prepared Epoxy N-BF resin are tabulated in Table (2). The IR spectrum of the prepared Epoxy N-BF exhibited absorption bands of group CH alkane at  $2967\text{ cm}^{-1}$ , C=C aromatic at  $1541\text{ cm}^{-1}$ ,  $\text{CH}_3$  at  $1400\text{ cm}^{-1}$ , C-O at  $1246\text{ cm}^{-1}$  and epoxy group at  $940\text{ cm}^{-1}$ .

**Preparation of Some Poly (Vinyl Acetal)s<sup>[6]</sup>:**

**Preparation of Poly (Vinyl Formal) PVF or Poly (Vinyl Butyral) PVB:** Poly (vinyl formal) and Poly (vinyl butyral) were prepared by dissolving a suspension of poly vinyl acetate (PVAc) in acetic acid and reacting it with formaldehyde or butyraldehyde in the presence of a catalytic amount of a mineral acid (sulfuric, hydrochloric or phosphoric); c.f. Schemes VI and VIII; respectively.



**Scheme VII:** Preparation of PVF.



**Scheme VIII:** Preparation of PVB.

Into a three-necked round bottom flask equipped with reflux condenser, stirrer and thermometer, 20 g poly vinyl acetate (PVAc), 80 g glacial acetic acid, 0.6 g concentrated sulphuric acid, 80 ml formalin 40%, or 80 ml butyraldehyde and 1 ml distilled water were introduced. The mixture was stirred at (60-70°C) for 16 or 24 h. The water was added drop wise for the precipitation of PVF or PVB, respectively. It was washed by hot water, followed by 1% solution of ammonia solution then again by water till neutralization. The polymer was dried at 40°C and pressure 400-500 Hg.

The characterizations of the prepared PVF resin are tabulated in Table (3). The IR spectrum of the prepared PVF exhibited absorption bands of group OH at  $3500\text{ cm}^{-1}$ , CH alkane at  $2900\text{ cm}^{-1}$ ,  $\text{CH}_2$  at  $1465\text{ cm}^{-1}$  and C-O at  $1150\text{ cm}^{-1}$ .

The characterizations of the prepared PVB resin are tabulated in Table (3). The IR spectrum of the prepared PVB exhibited absorption bands of group OH at  $3490\text{ cm}^{-1}$ , CH alkane at  $2961\text{ cm}^{-1}$ ,  $\text{CH}_2$  at  $1435\text{ cm}^{-1}$ ,  $\text{CH}_3$  at  $1382\text{ cm}^{-1}$  and C-O at  $1140\text{ cm}^{-1}$ .

**Characterization of the Prepared Resins:** Specific Viscosity ( $\eta_{sp}$ ) of resins was carried out using Ostwald viscometer<sup>[15]</sup>. Hydroxyl group content was carried out using pyridine-acetic anhydride solution method<sup>[15]</sup>. Epoxy group content was carried out using HCl/pyridine solution<sup>[9]</sup>. Acetal group content was based upon the ability of hydroxylamine hydrochloride to react with acetal in alcoholic solution. The reaction leads to the formation of poly (vinyl alcohol) oxime and the evolution of HCl, which titrated against alkali<sup>[14]</sup>. IR-spectra of the prepared resins were recorded using ATI Mattson-Genesis Series FTIR<sup>TM</sup> infrared spectroscopy.

**Preparation of the Metal Coating Samples:** 1 g of the prepared epoxy resins (Epoxy N-PF or Epoxy N-BF), was dissolved in 28 ml acetone at room temperature. Ethanolic solution of prepared phenolic resins (R-PF, R-BF, N-PF

**Table 3:** Mechanical Properties for Epoxy Metal Coatings Modified with PVF.

Formulation			Mechanical Properties		
Epoxy Type	Hardener Type 30%	PVF %	Adhesion	Hardness	Elongation
Epoxy	R-PF	0	2B	2H	9.7
		5	2B	2H	9.4
		10	2B	3H	9.1
		15	3B	3H	8.8
		20	3B	3H	8.2
		25	3B	3H	8.0
		30	3B	3H	7.9
N-PF	R-BF	0	2B	2H	10.4
		5	2B	2H	10.0
		10	2B	2H	9.8
		15	3B	2H	9.7
		20	3B	2H	9.5
		25	3B	2H	9.4
		30	3B	3H	9.4
N-PF	N-PF	0	1B	2B	28.1
		5	1B	2B	26.0
		10	1B	2B	25.3
		15	1B	2B	24.2
		20	2B	2B	23.5
		25	2B	2B	23.2
		30	2B	2B	23.0
N-BF	N-BF	0	2B	HB	17.2
		5	2B	HB	15.8
		10	2B	HB	15.4
		15	2B	F	15.1
		20	2B	F	14.7
		25	3B	F	14.6
		30	3B	F	14.5
Epoxy	R-PF	0	5B	4H	4.9
		5	5B	4H	4.6
		10	5B	4H	4.4
		15	5B	4H	4.1
		20	5B	5H	4.0
		25	5B	5H	3.9
		30	5B	5H	3.8
N-BF	R-BF	0	5B	3H	6.7
		5	5B	3H	6.3
		10	5B	3H	6.0
		15	5B	3H	5.8
		20	5B	4H	5.5
		25	5B	4H	5.4
		30	5B	4H	5.3
N-PF	N-PF	0	3B	F	18.1
		5	3B	F	17.0
		10	3B	F	16.1
		15	3B	F	15.4
		20	3B	H	14.7
		25	3B	H	14.5
		30	3B	H	14.3
N-BF	N-BF	0	4B	2H	12.0
		5	4B	2H	11.4
		10	4B	2H	10.5
		15	4B	2H	9.3
		20	4B	3H	7.7
		25	4B	3H	7.6
		30	4B	3H	7.5

and N-BF) was added as curing agents with different ratios (10, 20, 30, 40 and 50% weight) on the basis of epoxy resin weight. The mixture was stirred with gentle heating till a homogenous solution was obtained. The solution was applied on metallic plates by flow coating method and left in air for 3 h to evaporate the solvent. The coating samples were thermally cured in an oven for 20 min at 180°C to have a uniform coating thickness of about 20-30 μm measured in accordance with ASTM D4138-94.

**Modification of the Metal Coating Samples:** Modification of each type of prepared epoxy resin samples were carried out by adding different ratios 5, 10, 15, 20, 25 and 30% weight of the prepared PVF or PVB (dissolved in chloroform). The modified epoxy resins were then cured using 30% weight of each type of prepared phenolic resins.

**Testing of the Metal Coating Samples:** Adhesion by tape test was carried out according to ASTM D 3359-95 (B). Impact test was carried out according to ASTM D2794-93. Scratch hardness was carried out according to ASTM D3363-92a. Elongation test was carried out according to ASTM D 522-93a, thermal stability based on the weight loss for the samples after heating at 200°C for different time intervals and chemical resistance was carried out according to ANSI/ASTM D543-67.

## RESULTS AND DISCUSSION

**Curing Process of Epoxy Resins Coated Films:** Metallic coating samples of the prepared epoxy resins (Epoxy N-PF and Epoxy N-BF) that cured with different percentage weight (10, 20, 30, 40 and 50%) of the prepared phenolic resins (R-PF, R-BF, N-PF and N-BF) at 180 °C for 20 min were applied. The prepared metal coating samples with thickness approximately 20-30 μm, were evaluated by measuring the mechanical properties to get the optimum ratio of curing agent leads to highest values.

**Mechanical Properties of Metal Coatings:** The mechanical properties involved adhesion by tape test, scratch hardness by pencil test, impact test and elongation test. The data were given and tabulated in Table (2). This data indicate that the mechanical properties of the prepared epoxy samples depend on the type of epoxy used and the type of phenolic resin hardener added and its ratio.

Generally, the adhesion values were increased in the majority of epoxy samples with increasing hardener ratio tell up to 30%. More than this ratio most samples give higher peeling behavior. This behavior due to complete curing for epoxy samples was reached using 30%

phenolic resin hardener and any other addition of phenolic resin not be reacted as curing agent, but cured by heat to crosslinked structure. The samples varying from softer to harder according to the order of; 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H; which given in ASTM D3363-92a. The hardness values in Table (2) increased for all samples with increasing the ratio of phenolic resin hardeners from 10, 20, till 30%, where complete network formation for all epoxy takes place. The hardness values decreased with very small values again beyond 30% with increasing the ratio of phenolic resin hardeners from 40 to 50%. It is due to presence of non-reacted phenolic resins, where all epoxy were consumed in the curing process with 30% phenolic resin hardener. All prepared samples with the ratio of 30% and some prepared samples with 40% hardener give pass impact where all other prepared samples give fail impact. In the other hand the sample with pass impact from standard weight (1.8 kg) was dropped from a distance of 1 m; according to ASTM D2794-93. The elongation values, given according to ASTM D 522-93a, were decreased with increasing the ratio of hardener for all epoxy and phenolic resins types used. The rates of decreasing give lower slop beyond 30% phenolic resin hardener. These results confirm that the optimum ratio of the phenolic resin added to the epoxy resin to give complete hardening is 30%.

The mechanical properties of the prepared samples were also affected with the type of epoxy used. The samples prepared from epoxy N-BF give more adhesion, hardness and pass impact with lower elongation than those samples prepared from epoxy N-PF. This is due to the presence of higher epoxy group content, higher hydroxyl group content and more aromatic rings in bisphenol epoxy resin than phenol epoxy resin. That is means that epoxy N-BF give more preferable mechanical properties than epoxy N-PF.

The type of the phenolic resin curing agent used was affect on the mechanical properties of the prepared samples. The samples cured with same ratio of curing agent give different values with different curing agent. The prepared epoxy samples cured with resol phenolic resins give more adhesion, hardness and pass impact combined with lower elongation than those prepared samples cured with novolac phenolic resins. This can be attributing to the difference in the chemical structure between the two types of phenolic resins, larger molecule of resol phenolic resins with presence of more active methylol groups, CH<sub>2</sub> bridges and higher hydroxyl group content of resol phenolic resins than novolac phenolic resins. The presence of methylol groups in the resol which can react with the epoxy groups of the epoxy resin and get three dimensional structures<sup>[3]</sup>.

That is means that resol phenolic resins are more effectible for curing of epoxy resins than novolac phenolic resins. The prepared epoxy samples cured with

**Table 4:** Mechanical Properties for Epoxy Metallic Coatings Modified with PVB.

Formulation			Mechanical Properties		
Epoxy Type	Hardener Type	PVB %	Adhesion	Hardness	Elongation
Epoxy N-PF	R-PF	0	2B	2H	9.7
		5	2B	2H	9.5
		10	2B	2H	9.3
		15	2B	2H	9.2
		20	3B	2H	9.0
		25	3B	2H	8.9
		30	3B	2H	8.8
Epoxy R-BF	R-BF	0	2B	2H	10.4
		5	2B	2H	10.4
		10	2B	2H	10.3
		15	2B	2H	10.3
		20	3B	2H	10.2
		25	3B	2H	10.2
		30	3B	2H	10.2
Epoxy N-PF	N-PF	0	1B	2B	28.1
		5	1B	2B	27.6
		10	1B	2B	26.9
		15	1B	2B	26.2
		20	1B	2B	25.5
		25	1B	2B	25.4
		30	1B	2B	25.4
Epoxy N-BF	N-BF	0	2B	HB	17.2
		5	2B	HB	16.8
		10	2B	HB	16.3
		15	2B	HB	15.9
		20	2B	F	15.5
		25	2B	F	15.5
		30	2B	F	15.4
Epoxy N-BF	R-PF	0	5B	4H	4.9
		5	5B	4H	4.7
		10	5B	4H	4.6
		15	5B	4H	4.5
		20	5B	5H	4.4
		25	5B	5H	4.4
		30	5B	5H	4.3
Epoxy R-BF	R-BF	0	5B	3H	6.7
		5	5B	3H	6.3
		10	5B	3H	6.1
		15	5B	4H	5.9
		20	5B	4H	5.7
		25	5B	4H	5.6
		30	5B	4H	5.5
Epoxy N-PF	N-PF	0	3B	F	18.1
		5	3B	F	17.5
		10	3B	F	16.8
		15	3B	F	16.1
		20	3B	F	15.2
		25	3B	F	15.1
		30	3B	F	15.0
Epoxy N-BF	N-BF	0	4B	2H	12.0
		5	4B	2H	11.1
		10	4B	2H	10.3
		15	4B	2H	9.5
		20	4B	3H	8.8
		25	4B	3H	8.7
		30	4B	3H	8.6

**Table 5:** Thermal Stability (Weight Loss %) of Epoxy Metal Coatings.

Formulation			Thermal Stability (Weight Loss %) at 200 °C after Time Intervals (h)												
Epoxy Resin	Hardener 30%	Modifier 20%	2	5	10	20	30	40	50	60	70	80	90	100	
Epoxy N-PF	R-PF	-	1.1	2.5	3.5	4.9	6.5	7.6	8.7	9.1	9.8	10.1	10.1	10.1	
		PVF	3.2	4.3	5.4	6.7	8.0	9.6	10.9	11.8	13.0	13.2	13.2	13.2	
		PVB	2.7	4.0	5.1	6.7	8.0	9.3	10.7	12.5	13.4	15.0	15.0	15.0	
	R-BF	-	1.2	2.4	3.7	4.1	5.2	6.1	6.7	7.0	7.2	7.2	7.2	7.2	7.2
		PVF	3.0	4.0	4.8	5.4	6.5	7.7	8.6	9.4	10.2	10.7	10.7	10.7	10.7
		PVB	2.5	3.4	4.6	6.1	7.6	8.9	10.0	10.7	11.9	12.6	12.6	12.6	12.6
	N-PF	-	1.5	3.2	5.1	5.9	7.0	8.8	9.4	9.8	10.4	10.9	10.9	10.9	10.9
		PVF	3.9	5.6	6.8	8.1	9.2	10.1	11.0	12.2	13.6	14.3	14.3	14.3	14.3
		PVB	3.1	4.3	5.9	7.6	9.1	10.4	11.6	13.2	15.4	16.7	16.7	16.7	16.7
	N-BF	-	1.4	2.9	4.0	4.5	6.1	7.3	7.9	8.1	8.6	8.7	8.7	8.7	8.7
		PVF	3.4	4.1	5.2	6.5	7.8	9.3	10.6	11.4	12.1	12.8	12.8	12.8	12.8
		PVB	2.1	2.8	3.8	4.5	5.6	6.6	7.6	8.4	9.2	9.9	9.9	9.9	9.9
Epoxy N-BF	R-PF	-	1.2	2.4	3.8	4.7	6.4	6.6	7.0	7.7	8.3	8.7	8.7	8.7	
		PVF	2.3	2.8	3.7	5.0	6.2	7.5	8.4	9.2	10.0	10.6	10.6	10.6	
		PVB	2.2	2.9	4	5.1	6.3	7.4	8.6	9.5	10.6	11.5	11.5	11.5	
	R-BF	-	0.8	1.4	3.5	4.4	5.3	5.6	5.9	6.4	6.7	6.8	6.8	6.8	6.8
		PVF	1.9	2.6	4.2	5.1	5.8	7.0	7.9	8.8	9.6	10.0	10.0	10.0	10.0
		PVB	2.1	2.4	3.6	4.3	5.5	6.4	7.3	8.1	8.8	9.8	9.8	9.8	9.8
	N-PF	-	1.5	2.7	4.4	5.7	7.6	8.2	8.4	9.0	9.6	10.0	10.0	10.0	10.0
		PVF	2.8	3.7	4.8	5.4	6.9	8.5	9.7	11.4	12.7	13.4	13.4	13.4	13.4
		PVB	2.7	3.5	4.8	6.2	7.7	9.1	10.3	11.4	12.7	13.5	13.5	13.5	13.5
	N-BF	-	1.3	2.9	4.1	5.1	6.3	7.0	7.3	7.8	8.3	8.3	8.3	8.3	8.3
		PVF	2.1	2.9	3.9	4.7	5.9	7.4	8.3	9.1	10.3	10.9	10.9	10.9	10.9
		PVB	1.9	3.0	3.7	4.8	6.0	6.7	8.0	8.4	9.2	10.0	10.0	10.0	10.0

bisphenol phenolic resins give more adhesion, hardness and pass impact combined with lower elongation than those prepared samples cured with phenol phenolic resins. This is due to presence of higher hydroxyl group content and more aromatic rings in bisphenol formaldehyde resins than phenol formaldehyde resins. That is means that bisphenol formaldehyde resins are more effectible for curing of epoxy resins than phenol formaldehyde resins.

**Modification of Epoxy Resins by Poly (vinyl acetal)s:** Modification of epoxy resins by poly (vinyl acetal)s was carried out before curing process with phenolic resins then applied as metallic coatings. The prepared epoxy resins (Epoxy N-PF and Epoxy N-BF), were cured with

the preferable ratio of curing agent, 30% by weight phenolic resins which was the selected ratio for curing of epoxy resins. Modification was carried out with different ratios by weight poly (vinyl formal) (PVF) or poly (vinyl butyral) (PVB) and cured at 180°C for 20 min. Non-modified and modified epoxy metallic coating samples with thickness approximately 20-30 µm were tested by carrying out the mechanical tests, thermal stability and chemical stability.

**Mechanical Properties of Modified Epoxy/Poly (vinyl acetal)s Coatings:** Mechanical properties of non-modified as well as poly (vinyl formal) or poly (vinyl butyral) modified epoxy metal coatings were carried

**Table 6:** Chemical Resistance for Epoxy N-PF Metal Coatings.

Formulation			Chemical Resistance												
			Water	Acids			Alkalis		Salts	Solvents				Oils	
Epoxy Resin	Hardener 30%	Modifier 20%	Distilled Water	AcOH 10%	HCL 10%	HNO3 10%	NaOH 10%	KOH 10%	Na2CO3 20%	Acetone	Toluene	CCl4	Ethanol	Cotton Seed Oil	
Epoxy N-PF	R-PF	-	E	E	E	G	G	E	E	E	E	E	E	E	
		PVF	E	E	E	G	G	G	E	E	E	E	E	E	
		PVB	E	E	E	G	G	G	E	E	E	G	E	G	
	R-BF	-	E	G	G	G	G	G	G	E	G	G	E	G	
		PVF	E	E	G	F	F	F	G	G	G	G	E	G	
		PVB	E	E	G	G	F	F	G	G	G	E	E	E	
	N-PF	-	E	G	G	F	G	G	G	G	G	G	E	G	
		PVF	E	E	G	G	G	G	G	G	G	G	E	G	
		PVB	E	E	E	G	G	G	G	G	E	G	E	G	
	N-BF	-	E	E	G	G	G	G	G	E	G	G	G	G	
		PVF	E	E	E	G	F	E	G	G	G	G	E	E	
		PVB	E	E	E	G	F	E	G	G	G	G	G	G	
	Epoxy N-BF	R-PF	-	E	E	G	E	G	G	G	E	E	E	G	E
			PVF	E	E	G	G	G	G	E	E	G	E	E	E
			PVB	E	E	G	G	G	E	E	E	E	G	E	G
		R-BF	-	G	G	E	G	G	G	G	G	G	G	E	E
			PVF	E	G	E	G	G	G	G	G	G	G	G	G
			PVB	E	G	E	G	G	G	G	G	E	G	E	G
N-PF		-	E	G	G	G	F	G	G	G	E	G	E	E	
		PVF	E	G	G	G	F	G	E	G	G	G	E	E	
		PVB	E	G	G	G	G	G	G	G	E	G	E	G	
N-BF		-	E	G	F	G	G	G	G	F	E	G	G	G	
		PVF	E	G	G	G	G	G	G	G	E	E	G	G	
		PVB	E	G	G	G	G	G	G	G	E	E	E	G	

E: Excellent, G: Good, F: Fair, P: Poor

out and tabulated in Tables (3) and (4) respectively. Results reveal that addition of each of the both types of poly vinyl acetal (PVF or PVB) increase the values of adhesion and hardness combined with decrease in elongation values. Values of adhesion and hardness were increased with increasing the ratio of poly vinyl acetal added till 20%. No increase in adhesion or hardness values beyond the 20% ratio of poly vinyl acetal. All modified samples with both PVF and PVB give pass impact metallic coating samples. Values of elongation decreased continuously with increase the ratio% of poly vinyl acetal. This behavior was matched with adhesion

and hardness properties of epoxy coating samples were improved by modifying with 20% PVF which could be attribute to good compatibility of (vinyl acetal)s with epoxy resins<sup>[4]</sup>. The type of poly vinyl acetal modifier used was effect on the mechanical properties of the prepared samples. PVB give lower values of adhesion and hardness combined with higher values of elongation than PVF.

**Thermal Stability:** Non-modified as well as 20% PVF or PVB modified epoxy metal coatings previously cured by 30% of different types of curing agents at 180°C for

20 min, film thickness 20-30  $\mu\text{m}$  were placed in furnace at 200 °C and then withdrawn from the furnace after fixed time intervals, cooled till room temperature, weighed and then replaced in the furnace for another fixed time interval and the process was repeated till reaching the whole time of subjecting to heat equal to 100 h. The weight loss for cool samples after each time interval was recorded.

The data obtained in Table (5) indicated that thermal stability of epoxy resins were decreased by modification with 20% PVF or PVB due to incorporation of thermoplastic poly (vinyl acetal) into the epoxy novolac resins which decrease their thermal stability<sup>[16]</sup>. On the other hand, thermal stability of epoxy resins cured with resol resins was higher than that cured with novolac resins due to the presence of methylol groups in the resol that can react with both the hydroxyl and epoxy groups of the epoxy resin<sup>[13,15]</sup>. On the other hand thermal stability varies with different types of epoxy resins due to difference in chemical structure of epoxy resins used. The recorded values (wt. loss, %) generally increased with the time of heating.

**Chemical Resistance:** This method can be applied as a change in weight of the prepared coating film samples after immersion for 7 days in a variety of standard reagents and common industrial products, with specified concentrations, at room temperature (25°C).

The data obtained in Tables (6) indicated that non-modified as well as PVF or PVB modified epoxy metallic coatings previously cured by 30% of different types of curing agents at 180°C for 20 min had chemical resistance to water, solvents, oils and specified concentrations of acids, alkalis and salts for 7 days at room temperature (25°C). This could be attributed to the fact that all the bonds, formed during the reaction of crosslinking agent with epoxide and hydroxyl groups were relatively stable bonds, resulting in highly chemical and solvent-resistant films[4]. Moreover, the films of epoxy resin that cured with phenolic resin were unaffected after 3 months immersion at 25 °C by most alcohols, ethers, acids, bases, water and some ketones. After 1 month's exposure at room temperature the films softened with the following materials: MEK, ethylene dichloride, hydrochloric acid (> 25%), sulphuric acid (> 25%) and hydrogen peroxide (> 15%)[3].

**Conclusion:** Mechanical properties of epoxy metal coatings cured by different types of phenolic resins indicated that the optimum ratio of curing agent is 30% by weight on basis of epoxy resins.

Epoxy coating samples cured by resol phenolic resins had better mechanical properties than those cured by novolac phenolic resins.

Modification of epoxy resins with PVF or PVB improves the mechanical properties combined with decrease in the thermal stability,

All coating samples had good chemical resistance towards all used medias.

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