Adhesives and Coatings Based on Poly(vinyl acetal)s

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ABSTRACT: Phenolic resins such as resole phenol– and cresol–formaldehyde, as well as low-molecular-weight epoxy resin based on bis(4-hydroxy phenol) cyclohexane were prepared and modified with various types of the prepared poly(vinyl acetal)s. Poly(vinyl formal), poly(vinyl isobutyral), and poly(vinyl propional) were used. This study indicated that the optimum conditions for curing phenolic or epoxy resin–poly(vinyl acetal)s adhesive compositions are of an equal weight ratio or a 2 : 1 weight ratio in the presence of phthalic anhydride (10 or 20 wt %) of resin content as a curing agent at 150°C for 20 or 60 min, respectively. The effect of acetal type on the tensile shear strength values of resin samples, cured under the previously mentioned optimum conditions for different times, was investigated. The effect of structure of cresol–formaldehyde and epoxy resins was also studied. Metallic and glass coatings from the previous pure resins and their formulated mixtures were also prepared and evaluated as varnishes or paints. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1769–1777, 1998

Key words: adhesives; coatings; poly(vinyl acetal)s; phenolic resins; epoxy resins

INTRODUCTION

Phenolic adhesives manifest very good adhesion to materials such as wood, leather, rubber, plastics, synthetic fibers, glass, ceramics, cements, and metals.^{1–3} Phenolic varnishes offer many excellent coating properties, and they also have good adhesion to wood.⁴

Poly(vinyl acetal)s acquire a unique combination of the following properties: adhesion to a wide variety of surfaces, chemical and solvent resistance (especially when crosslinked), good electrical properties, heat stability, film clarity, and physical toughness. These properties, alone or in combination, make these polymers useful in certain coating and adhesive formulations as the principal or as a minor constituent. Their compatibility with other resins, due largely to their unique chemical compositions, permits blending with other resins, resulting in properties not achievable with either component alone.⁵ The use of poly(vinyl formal) as electrical wire insulation permits the decrease of the volume and weight of the electrical motors and the increase of their output.⁴ Poly(vinyl formal)-modified phenol-formaldehyde resin compositions are also used as adhesives and in the coatings field for floor tiles and wood.^{6,7} Poly(vinyl butyral) forms transparent, colorless films that are used in the fabrication of safety glass. It has good adhesion properties to glass and metals. The adhesives made of this polymer are used in the construction industries for metals, plastics, wood, and concrete.^{4,8-11} The viscoelastic properties of the phenolic resin-poly(vinyl butyral) system were studied over a wide range of temperatures.¹²

Cured epoxy resins exhibit excellent adhesion to a variety of substrates; outstanding chemical and corrosion resistance; excellent electrical insulation; high tensile, flexural, and compressive strengths; thermal stability; a wide range of curing temperatures; and low shrinkage upon cure.¹³ Poly(vinyl acetal)¹⁴ or phenolic resins-based¹⁵ epoxy resin adhesive compositions are useful in electric insulation field and electronic parts.

The main objective of this work is the preparation of adhesives and coatings based on the pre-

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Polymer	Specific Viscosity in Acetic Acid (0.1 g/10 mL) at 25°C	Hydroxyl Group Content (%)	Acetal Group Content (%)	Acetate Group Content (%)
PVA	0.5665^{a}	96.60	_	3.55
PVF	0.3561	20.40	74.55	4.32
PVB	$0.3450^{ m b}$	19.10	62.30	12.00
PVP	0.4530	17.10	52.12	15.23

Table I Specifications of the Prepared Polymers

^a In water.

^b In pyridine.

pared phenolic or epoxy resin-poly(vinyl acetal)s systems with high tensile strength values, good adhesion to wood, and excellent coating properties for metallic and glass plates. The effect of the acetal type on the tensile shear strength values of resin samples cured under the optimum conditions is studied. The effect of methyl group in cresol-formaldehyde resin and the effect of oxirane ring in epoxy resin are also studied.

EXPERIMENTAL

Preparation of Poly(vinyl alcohol)

Poly(vinyl acetate) (PVAc) (Resemul 9013) produced by Emulsion Polymer Ltd., Limassol, Cyprus, is used. PVAc solution (30 g in 45 mL of methyl alcohol) was added dropwise in a period of 1.5 h at 25 ± 5 °C to an alkaline alcoholic solution (9 g of NaOH in 100 mL of alcohol). The experiment was carried out according to the method described in Motawie et al.¹⁶ Specifications of the prepared PVA are given in Table I.

Preparation of Poly(vinyl acetal)s

Poly(vinyl formal) (PVF), poly(vinyl isobutyral) (PVB), and poly(vinyl propional) (PVP) were synthesized by condensation of the prepared poly(vinyl alcohol) (10 g) and a suitable aldehyde. Formaline solution 40% (10 g) or isobutyraldehyde (6 g) or propionaldehyde (7 g) was treated at 80°C in

aqueous media containing hydrochloric acid (0.5 g) as an acid catalyst to obtain the required polymers respectively. The experiment was carried out according to the method described in Nakajima.¹⁷ Specifications of the prepared polymers are given in Table I.

Preparation of Resole Phenol–Formaldehyde PF and Cresol–Formaldehyde CF Resins

Phenol (17.5 g) or tricresol (122 g) was mixed with formaline solution (40%, 17.75 g for preparation of PF) or (30%, 109.5 g for preparation of CF) and then liquid ammonia (25%; 1.50 g) or (12.5 g) was added as a catalyst to prepare PF or CF, respectively. The reaction mixture was heated in a water bath at 90°C. The experiment was carried out according to the method described in Motawie et al.¹⁸ Specifications of the prepared resins are given in Table II.

Preparation of Low-Molecular-Weight Epoxy Resin E Based on Bis(4-hydroxy phenyl) Cyclohexane

Phenol (80 mL) was condensed with cyclohexanone (15 mL) in the presence of dry hydrochloric gas to give bis(4-hydroxy phenyl) cyclohexane with an average molecular weight of 270 and a melting point of 175 °C. This bisphenol (270 g) was converted into low-molecular-weight epoxy resin by the action of epichlorohydrin (280 g) in the presence of sodium hydroxide. The experiment

Table II Specifications of the Prepared Resins

Resin	Color	pH at 20°C	Specific Gravity at 20°C	Specific Viscosity $(C_p s)$ at 20°C
PF CF	Yellow liquid Dark brown liquid	12.0 12.5	$\begin{array}{c} 1.05\\ 1.18\end{array}$	650 930

was carried out according to the method described in Motawie et al.¹⁹ Specifications of the prepared epoxy resin are given in Table III.

Preparation and Evaluation of Adhesive

Viscous adhesive was prepared by dissolving formulated mixtures of PF or CF or E and poly(vinyl acetal)s in methanol (10 mL). Phthalic anhydride (PA) as a curing agent was added (according to formulations given in Table VIII), stirring until a homogeneous solution was obtained. The prepared adhesives were applied on wooden samples according to the method described in the literature.^{20,21} Finally, the wooden samples were placed in an oven at different temperatures for different times. Tensile shear strength T_s s values were determined on Instron testing machine (Model 1026) at 23 \pm 2°C, with cross head speed 100 mm/min, a chart speed 200 mm/min, and a load cell range of 0-500 Newton according to ASTM D 2240.

Preparation and Evaluation of Coatings

Coatings were prepared by dissolving pure PF, CF, E, PVF, PVB, PVP, or their formulated modified mixtures, and the calculated amount of curing agent in methanol (0.4 g resin/100 mL solvent) (according to formulations given in Table IX). The mixture was stirred until a homogeneous solution was obtained. The solution was sprayed on metallic or glass plate and left in air for 3 h, and the sample was placed in an oven at the determined optimum curing time for each adhesive. The physicomechanical and chemical resistance tests were carried out according to ASTM D 543-78 and ASTM G 20-72.

RESULTS AND DISCUSSION

For the past 15 years, phenolic resin mixed with poly(vinyl acetal)s and cured at high temperature has been in general use as a coating material for metal sheets and magnetic wires. It is known that poly(vinyl butyral) mixed with phenolic resin increases the flexibility and adhesiveness of this resin.¹² As the useful properties of this system appear only as a result of curing, it seems desirable to understand the structure resulting from curing.

In the work reported here, PF, CF, and E resins are prepared for study the optimum conditions of formulation and curing process of each of these resins and/or poly(vinyl acetal)s system. The effect of curing time at 150°C on T_s s values of pure resin samples is studied (Table IV). Results given in Table IV show the following.

- 1. For PF, CF, and poly(vinyl acetal)s samples without curing agent, T_s s values increase with increasing time, and the optimum curing time is 60 min at 150°C, while it is 80 min for E resin at the same temperature in the presence of PA (20 wt %) of the resin content as a curing agent. Beyond these times, T_s s values begin to decrease. This can be attributed to the fact that a long heating time at high temperatures may lead to destruction of pure resins so that T_s s values appreciably decrease.
- 2. The optimum T_s s values for pure resin samples cured at 150°C for 60 min can be arranged in the following order: PVF > PVB > PVP > PF > CF. Increasing acetal or hydroxyl group contents may lead to an increase in the rate of crosslinking formation so that T_s s values appreciably increase, while incorporation of alkyl phenol into the resin reduces hardness and the crosslink density, leading to a decrease in T_s s values of CF, as compared with those of PF.⁵ The mechanism of curing process of resoles is complex. Heat curing of resoles is obtained at 130–200°C. In the first stage, methylene and ether bridges are produced. At temperatures above 210°C, the ether linkage is converted to a methylene bridge and oxidation occurs. 5,22

On the other hand, the highest T_s s values for pure E resin samples cured at 150°C for 80 min can be attained only by treating the resin with a curing agent. The curing agent can react with epoxy and pen-

Table III Specifications of the Prepared Epoxy Resin

Average	Dropfalling Temp	Viscosity at	Epoxy Group	Hydroxyl Group
Molecular Weight	(°C)	50°C (mPa s)	Content (%)	Content (%)
360-400	67	400	24-25	12.12

							C	uring Pro	ocess at 1	L50°C			
]	Formula	tion (pbw	7)					Curing I	Sime (mir	1)		
	Resins		Poly	(vinyl ac	etal)s	Curing	10 20 40 60 80				80	100	
PF	\mathbf{CF}	Е	PVF PVB PVP (wt %)			$T_s s ~(kg/cm^2)$							
100						_	4	10	24	32	28	22	
	100					_	8	12	20	24	18	12	
		100				20	81	163	432	505	611	573	
			100			_	61	82	100	146	94	80	
				100		_	40	77	97	122	83	70	
					100		32	55	85	103	30	20	

Table IV	Effect of Curing	Time at 150°C on	T_s Values	of Pure	Resin Sam	ples
			8			L

dent hydroxyl groups on the resin backbone by way of either an anionic or cationic mechanism, giving a three-dimensional insoluble and infusible network.⁵

Throughout the study of the optimum conditions of formulation and curing process of PF– PVF resins, the effect of their different weight ratios is investigated in the presence of PA (10 wt %) of the resin content at different temperatures for different times (Table V). Formulation results in Table V reveal the following.

- 1. At relatively low temperatures, the curing time is very long. Raising the temperature enhances the process of curing and leads to an increase in T_s s values.
- 2. For all ratios of PF–PVF resin samples, the optimum curing time at 150°C is about 20 min, giving maxima T_s s values, as com-

Presence of PA (10 wt %) of the Resin Content at Different Temperatures for Different Time	s
Table V Effect of Different Weight Ratios of PF-PVF Resins on T _s s Values of Samples Cure	d in the

					Cu	ring Pro	ocess							
						Т	'ime (mi	n)						
Form (p	ulation bw)		10	20	40	60	80	100	120	130	140	160		
PF	PVF	Temp (°C)		$T_s { m s}~({ m kg/cm}^2)$										
		40	125	150	180	197	210	232	240	250	253	250		
		70	340	350	390	456	480	510	490					
50	50	100	569.5	589.6	629.8	670	600	514						
		130	700.8	734.4	800	700	580	360						
		150	817	860	740	590	318	290						
		40	70	85	125	162	190	219	225	231	220	218		
		70	240	260	282	300	320	340	330					
100	50	100	400	445	515	610	530	480						
		130	561	601.8	680	612	481	245						
		150	667	710	640	500	210							
		40	60	80	100	120	130	148	159	163	165	163		
		70	80	100	160	208	254	236	200					
50	100	100	280	309	340.7	380	340	260						
		130	398.69	429.62	491	350	312	220						
		150	483.6	520	490	334	190							

				Curing Pro	ocess						
					Time (min))					
Form (p	(pbw) Curing 10 Agent PA		10	20	40	60	80				
PF	PVF	(wt %)		$T_s s ~(kg/cm^2)$							
		5	510	580	632	410	240				
50	50	10	817	860	740	590	318				
		15	700	780	695	530	285				
		20	62	690	661	482	260				

Table VI Effect of PA % on T_s s Values of Equal Weight Ratios of PF-PVF Resin Samples Cured at 150°C for Different Times

pared with 40 and 60 min at temperatures of 130 and 100°C, respectively. This can be attributed to the fact that when the mixture of PF–PVF is heated to high temperature, then, during the course of the curing reaction, some grafted crosslinked structure would be produced by the condensation between the hydroxyl groups of the PVF and the methylol groups of the PF resin.¹²

3. Accordingly, it is clear that for wood adhesives based on the PF-PVF resins, the optimum formulation is equal weight ratio of mixed resins.

The effect of PA (wt %) on T_s s values of equal weight ratio of the PF–PVF resin samples, cured at 150°C for different times, was then studied (Table VI). Results given in Table VI indicate that T_s s values increase with increasing PA and reach their maxima when the weight is about 10% of the resin content, beyond which (for example, 15– 20%), some excessive weight may be found in the reaction medium, leading to a decrease in T_s s values. When PA is 5%, its quantity is insufficient to make complete network structure, leading to destruction of the adhesive composition with an appreciable decrease in T_s s values.

Thus, the previous results indicate that the optimum conditions of curing process of PF–PVF resins are equal weight ratios of formulated resins and 10% PA of the resin content, cured at 150°C for 20 min. Under these conditions, the aldehyde group of the curing agent may react with the methylol groups of PF resin, as follows.



The methylene bridging group in the produced crosslinked structure may be converted to a hydroperoxide, which partially decomposes at high temperature into alcohols and a ketone, as follows.



Concerning the previous work,²³ E–PVF resins are formulated at weight ratio of 2 : 1, cured in the presence of 20% PA at 150°C, and T_s s values are recorded and compared with those of PF–PVF resin system cured at an equal weight ratio in the presence of 10% PA at 150°C (Table VII). Formulation results in Table VII indicate that for wood adhesives based on E–PVF resins, the optimum formulation is 2 : 1 of mixed resins, cured in the presence of 20% PA at 150°C for 60 min. The

					Curing P	rocess at 15	0°C		
						Curing T	ime (min)		
For	Formulation (pbw)		Curing	10	20	40	60	80	100
PF	Ε	PVF	(wt %)			T_s s (k	g/cm ²)		
50	100	50	10	817	860	740	590	318	290 790

Table VII T_ss Values of Cured PF or E-PVF Systems at 150°C for Different Times

curing agent may react with the epoxy and pendent hydroxyl groups on the resin backbone; both esterification and etherification occur.¹³ The curing mechanism is as follows. Secondary alcohols from the epoxy backbone react with the anhydride to give a half ester, which reacts with an epoxy group to give the diester. A competing reaction is that with a secondary alcohol, either on the resin backbone or formed during the esterification, resulting in a B-hydroxy ether, as follows.



In the present work, the effect of acetal type on the T_s s values of resin samples, cured under the previously mentioned optimum conditions for different times, is investigated. Also, it is interesting to investigate the effect of substituted phenol like cresol, and the effect of oxirane rings into the E resin. PF–PVF samples are also formulated at an equal weight ratio and cured without PA at 150°C for the purpose of comparison (Table VIII).

Results illustrated in Table VIII reveal the following.

- 1. For PF-PVF resin samples, cured in the presence of 10% PA, a maximum T_s s value (860 kg/cm^2) can be attained after 20 min, as compared with that (431 kg/cm^2) after 40 min for these formulated resin samples without PA. While for PF-PVB and PF-PVP, cured in the presence of 10% PA, maxima T_s s values are 731 and 689 kg/ cm², respectively, after 40 min. This sharp decrease in T_s s values as compared with that for PF-PVF cured under the same conditions can be attributed to the fact that increasing the hydroxyl group content of PVF (for example, 20%), as compared with those of PVB and PVP, as well as the presence of curing agent, increase the crosslink density, leading to an appreciable increase in T_s s values.
- 2. Accordingly, it is clear that adhesive samples of all resins (PF, CF, and E) based on PVF have the highest T_s s values for all times as compared with those based on PVB and PVP.
- 3. When alkyl-substituted phenol (for example, cresol) is used instead of phenol in a modified phenolic resin structure, there is a small decrease in T_s s values of adhesive samples. This can be attributed to the fact that incorporation of alkyl phenols into the resin reduces reactivity, hardness, and crosslink density.⁵
- 4. On the other hand it was found that introduction of oxirane rings into the resin increases reactivity, hardness, and crosslink

							Cu	ring Pro	cess at 1	.50°C		
		Formu	lation (pb	w)				(Curing T	ime (mir)	
	Resins		Poly	(vinyl ace	etal)s	Curing	10	20	40	60	80	100
PF	\mathbf{CF}	Е	PVF	PVB	PVP	Agent PA (wt %)			T_s s (k	g/cm ²)		
			50			_	110	200	431	260	205	190
50				50		_	103	329	280	228	203	175
					50	—	169	274	225	165	143	125
			50			10	817	860	740	590	471	400
50				50		10	570	588	731	523	327	300
					50	10	428	573	689	430	318	290
			50			10	743	816	720	580	380	300
	50			50		10	560	580	700	500	300	290
					50	10	417	570	660	400	310	270
			50			20	455	771	840	920	801	720
		100		50		20	380	640	750	780	740	680
					50	20	210	518	695	712	589	543

Table VIII Comparison Between T_s s Values of PF, CF, and E Resins Modified with Different Types of Acetals (PVF, PVB, and PVP) at 150°C for Different Times

density; thus, there is an appreciable increase in T_s s values of adhesive samples based on epoxy resins.

Throughout the present work, coatings on metallic and glass plates from the pure resins and their modified mixtures were prepared and evaluated as varnishes or paints (Table IX).

Results illustrated in Table IX show the following.

- 1. All the prepared coatings pass the scratch hardness measurement. The rocker hardness for unmodified PF, CF, E, PVF, PVB, and PVP are relatively low as compared with that for modified resin samples. Incorporation of alkyl phenols into CF resin decreases rocker hardness values, while oxirane rings in the E resin increase the degree of crosslinking, thus increasing these values, as compared with rocker hardness for modified PF. Also, it is clear that coating samples for all resins (PF, CF, and E) based on PVF have the highest rocker hardness values as compared with those based on PVB and PVP since increasing the acetal or hydroxyl group contents in PVF may lead to an increase in the rate of crosslinking formation so that rocker hardness values increase.
- 2. Unmodified PF, CF, and E resins pass the

flexibility test about only the rod diameter (1 cm). This proves their validity as varnishes. Only their modified samples and poly(vinyl acetal)s pass flexibility tests with the 2 rod diameters (3 mm and 1 cm), making them more suitable as varnishes and paints.

- 3. The surface luster of poly(vinyl acetal)s is lower than that of the standard sample (for example, lower than 80%), and, therefore, pure poly(vinyl acetal)s are unsuitable for glossy paints according to the standard specifications²⁴; whereas for all other formulated coating samples, the surface luster is higher.
- 4. All modified coating samples have better chemical resistance to dilute acids, alkalis, and aliphatic hydrocarbon solvents²⁵ than the pure resins. This makes them more suitable as varnishes and paints.

CONCLUSIONS

- 1. The optimum conditions of formulation and curing process of phenolic or epoxy resin-poly(vinyl acetal)s are of an equal weight ratio or a 2 : 1 weight ratio in the presence of (10 or 20%) PA at 150°C for 20 or 60 min, respectively.
- 2. Adhesive samples of all resins (PF, CF, and E) based on PVF have the highest T_s s val-

Table IX Physicomechanical and Chemical Resistance Tests of Coated Samples (Film Thickness 130-140 µm)

			aCl 40%	20% 7 days)	Ċ	ტ	되	Ċ	Ċ	Ŀ	되	ы	ы	되	되	되	ы	되	E
		Di	- Na I N	s) (7															
30°C		Crude (75% + Benzo	25% (7 day:	μ	ы	E	ы	ы	ы	IJ	IJ	Ċ	IJ	IJ	IJ	Ы	IJ	E
ance Tests at		H_2SO_4 3% HNO. 10%	HCI 10% CH ₃ COOH	5% (7 days)	Ъ	Р	IJ	Ь	Р	Ь	E	IJ	ŋ	E	Ċ	IJ	IJ	Ċ	Ċ
emical Resist			NaOH 5% NH ₄ OH	10% (7 days)	Ъ	Р	Р	Р	Р	Р	ŋ	IJ	IJ	ŋ	IJ	IJ	IJ	IJ	IJ
Che			C_2H_5OH MEK	CCI ₄ (1 day)	Ŀ	ы	Э	Ч	Ч	F	Ċ	Ċ	Ċ	Ċ	Ċ	Ċ	E	Ċ	Ċ
		Distilled	${ m H_2O}{ m Boiling}$	H_2O (30 days)	IJ	Ċ	E	IJ	Ċ	IJ	E	Э	E	E	E	E	E	E	E
			cations	Varnish	۶	ы	Ы	Р	Р	Ь	ы	ტ	ტ	ы	ტ	ტ	ы	되	Э
			Applic	Paint	Ь	Р	Р	Р	Р	Ь	ы	Ы	E	ы	되	E	ы	E	E
			ē	Glossy (%)	128	129	130	46	40	58	118	120	122	120	121	123	125	126	128
4	212		ty on neter	(1 cm)	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
T looing	Iamcal re		Flexibili Rod Diar	(3 mm)	I	I	Ι	+	+	+	+	+	+	+	+	+	+	+	+
Dhurstonnool	r II ystcollied	Scratch	Hardness (Vertical	= 1000 g	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
			Rocker	Hardness (s)	290	205	312	105	110	118	320	301	298	296	255	234	390	373	340
ng.	2 ar		i	Time (min)	40	40	80	60	60	60	20	20	20	20	20	20	60	60	60
Curi	150°		Curing Agent	PA (wt %)	I		20			I	10	10	10	10	10	10	20	20	20
			tal)s	PVP						100			50			50			50
		(M)	inyl ace	PVB					100			50			50			50	
		tion (pł	Poly(v	PVF				100			50			50			50		
		rmula		Э			100										100		
		Fo	Resins	CF		100								50					
			I	\mathbf{PF}	100						50								

^{+,} pass; -, not pass; E, excellent; G, good; F, fair; P, poor.

ues for all times as compared with those based on PVB and PVP.

- 3. Incorporation of alkyl phenols into phenolic resin structure reduces reactivity, hardness, and crosslink density, while oxirane rings in epoxy resins have the opposite effect with an appreciable increase in T_s s values.
- 4. Coating samples for all resins (PF, CF, and E) based on PVF have the highest rocker hardness as compared with those based on PVB and PVP.
- 5. Unmodified phenolic and epoxy resins can be evaluated as varnishes, while their modified samples can be recommended as varnishes and paints.
- 6. The glossy coatings of poly(vinyl acetal)s paints can be modified by adding PF or E resins under the previously mentioned optimum conditions.

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