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High performance water borne coatings from epoxy resin and novel acrylamide based curing agents

Mahendrasinh M. Raj[1*], Hemul V. Patel[2], Niranjan V. Patel[3] and J. S. Parmar[4]

[1]Institute of Science & Technology for Advanced Studies & Research (ISTAR), Vallabh Vidyanagar, Anand, Gujarat, India
[2]Ashok & Rita Patel Institute of Integrated study & Research in Biotechnology and Allied Sciences (ARIBAS), New Vallabh Vidyanagar, Anand, Gujarat, India
[3]I-43, Shiv Sagar Enterprise, Opp. Laxmi Patent, Phase IV, GIDC, V. U Nagar, Anand, Gujarat, India
[4]Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Anand, Gujarat, India

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ABSTRACT

Water borne acrylamide based curing agents were prepared from acrylamide, formalin and methanol. The curing agents were characterized for their various physico-chemical characteristics. High performance coatings based on water compatible epoxies and above curing agent were than prepared by blending them in a various ratio's. The coating compositions were cured at 150°C/15 min and the cured films evaluated for their performance properties. The films were also characterized by thermogravimetric analysis (TGA) and DSC. The comparative evaluation was carried out with the conventional water borne system from epoxy and amino resin. The study reveals that satisfactory performance of the cured film was obtained with certain coating composition. Thus environment friendly water borne epoxy coating prepared as above can be used as high performance coatings.

Key words: water borne, Acrylamide, curing agents and environment friendly.

INTRODUCTION

Epoxy resins have been commercially available for more than forty years and arguably are used in one of the most diverse range of applications in the modern world. The use of epoxy resin not only restricted to the surface coatings industry, they are also used in both thermal and ambient cure applications In industries such as aerospace, civil engineering, automotive, chemical, electrical, marine, leisure and many others[1-5].

Most industrial coatings originate in liquid organic materials. These organic materials (solvent) contribute to air pollution. Due to environmental regulation the use of organic solvent in coating formulations is rapidly being phased out [6-8]. In order to save the environment, conventional organic coating polymers, which are soluble in organic solvents, are being replaced gradually by water soluble polymers, since water is certainly an environmentally favourable solvent or carrier for coatings. Several recent developments are made in the field of water borne epoxy resin [9-10] to use as water thinnable paints.

Novel water borne epoxy resin [11-12] has been developed which offers the most attractive feature of both liquid and water borne epoxy resin systems.
Melamine, urea, benzogunamines and their substitute variants all contain amino functionality, and as such they can be used for curing epoxy resin. Many people refer to these types of resin as amioplasts. The resins are used in their methylolated or alkylated forms for many applications. [13- 14]

In the present work the acrylic grafted epoxy (water borne) resins are used with water borne acrylamide copolymer based curing agent to make water based high performance coating compositions. Thus evaluation of this novel curing agent is done comparatively with the conventional HMMM based curing agents for the higher performance water borne coating applications.

MATERIALS AND METHODS

Materials:
The monomers acrylamide and methyl methacrylate (MMA) as well as formaldehyde used for the preparation of curing agent were of LR grade. Methyl methacrylate was made from free inhibitor by washing initially with 10% NaOH solution followed by distilled water and dried over anhydrous calcium chloride. The solvents methanol, isopropyl alcohol and initiator AIBN were of LR grade, AIBN was twice recrystalized from dry methanol. All the solvents and monomer were used without any further purification.

The hydroxyl functional water borne acrylic grafted epoxy resin used to prepare stoving compositions has been prepared by the reported method [15] and the physical properties of this resin are given in Table No.3.

The conventional water borne Hexa Methoxy Methyl Melamine (HMMM) curing agent used in this study was commercial grade and it was supplied by M/S Pidilite Industries, Limited, Mumbai. The physical properties of this material are given in Table No.2.

Synthesis of water borne acrylamide based curing agent (WACA):
The water borne acrylamide based curing agent used in the present study was prepared by the reported method [16]. The acrylamide-co-MMA copolymer was prepared using azobisisobutyronitrile initiator (1%) and methanol (50%) as solvent by solution polymerization technique. The copolymer thus formed was further reacted (without separating from the system) with formaldehyde at 60^{o}C using methanol as solvent and for 1.5 to 2 hrs, so that up to about 90% methylation was achieved. After that, the etherification of these methylol groups with methanol was carried out in situ during the process (Scheme:1). The reaction was discontinued to predetermined conversion stage to give water borne acrylamide based curing agent (WACA) of viscous consistancy and required percentage of non-volatile matter solubility. The various sets of WACA were prepared with the compositions given in Table No.1; the physical properties of these WACAs are given in Table No.2.

Structure and Characterization of WACA:
IR-spectra of water borne acrylamide based curing agents were recorded on Nicolet Japan FTIR–spectrophotometer in the range of 4000–400 cm^{-1}. Gel permeation chromatography (GPC) was used to determine number and weight average molecular weight of the acrylamide based curing agents. The representative chromatograph is presented in fig. 1. Non-volatile contents [17] of resin systems are evaluated to ascertain the film build and the curing characteristics. Solution viscosity of the curing agents (40% solution in methanol) was determined using Ford-cup [18]. Free formalin (formaldehyde) was estimated by ASTM-1979-97 test method. The results of all the physical properties of acrylamide based curing agents are summarized in Table No. - 2.

Preparation and application of the coating compositions:
The water borne acrylamide based curing agents (WACAs) and hydroxyl functional water borne epoxy resin were mixed in various proportions as per the composition given in Table No.-1. The conventional hexamethoxy methyl melamine (HMMM) resin was also mixed with hydroxide functional water borne epoxy resin in various proportions as per the composition given in Table No.1. The mixed material was thinned to an application viscosity using isopropyl alcohol and then applied on test panels. The coated panels were stoved at 150°C for 15 min. in an oven for curing of the films. The average dry film thicknesses (DFT) of all these coatings were 25-30 microns. The curing reaction is outlined in Scheme: 2

Coated film characterization:
IR-spectra of the films were recorded on Nicolet, Japan FTIR- spectrophotometer in the range of 4000-400 cm-l. The samples (1-2mg) were mixed well with dry potassium bromide (l gm) and the pellet prepared by compression. DSC thermograms were recorded on DSC (TA-instruments, USA, model: 5000/2920), at a heating rate 10 ^{0}C/min upto 500 ^{0}C under N_2 atmosphere. Thermogravimetric analysis (TGA) was performed on TA-Instruments, U.S.A. (Model 5000/2960), in the temperature ranged upto 600 ^{0}C with a heating rate 10 ^{0}C/min under N_2 atmosphere. A cross cut adhesion test [19] was used to test the adhesion of film with metal substrate. Flexibility [20] of the film was estimated by using conical mandrel bending tester. Impact resistance of films were determined according to IS: 101-1989 test method. Scratch hardness of the films was measured under specified load on a dried film of coating by a mechanized apparatus.

The chemical properties viz. alkali, acid, salt water and hot water resistance of all the films were studied by immersing the coated panels in 5% NaOH, 5% H_2SO_4, 5% NaCl and water at 50 ^{0}C for 96 hrs. and examined for any physical change on the films.

RESULTS AND DISCUSSION

IR- Spectral Studies:
The IR-Spectra of WACA, WACA cured with Water borne epoxy resin film and HMMM -resin, HMMM-resin cured with Water borne epoxy resin film are presented in fig.2 and fig.3 and the IR absorbance frequencies are listed in Table No.6. On comparing the IR spectra of water borne acrylamide based curing agents (WACA) with IR-Spectra of water borne epoxy resin cured with water borne acrylamide based curing agents (WACA), it is clearly seen that most of all the important bands are observed with almost same intensity, but the bands due to -OH group shows, lower intensity .This clearly can be attributed to the participation of -OH groups in curing process [16].

Thermo gravimetric Analysis:
The TGA thermograms (fig. 4) indicate that as percentage of acrylamide increases in the composition, initial decomposition temperature (IDT) decreases followed by almost identical rate of decomposition upto about 460^{0}C. It can also be seen that compositions are quite stable upto 300 ^{0}C. Comparing this TGA data with that of water borne resin cured with HMMM resin, it is observed that it has IDT of 245 ^{0}C. This is quite lower then those of WACA cured water borne epoxy resin, thus this indicates that WACA cured acrylic resins are quite stable compared to their equivalent HMMM counterparts.

Differential Scanning Calorimetric Analysis:
The DSC thermograms are shown in Fig.5. From the results, it is clear that the three water borne acrylamide based films do not show any transition upto 403 ^{0}C - 406 ^{0}C, Thus these are comparably stable as with conventional HMMM based films, which do not show transition upto 387 ^{0}C. Thus the DSC studies indicate that the acrylamide based films and conventional curing agents based films are having comparable stability.

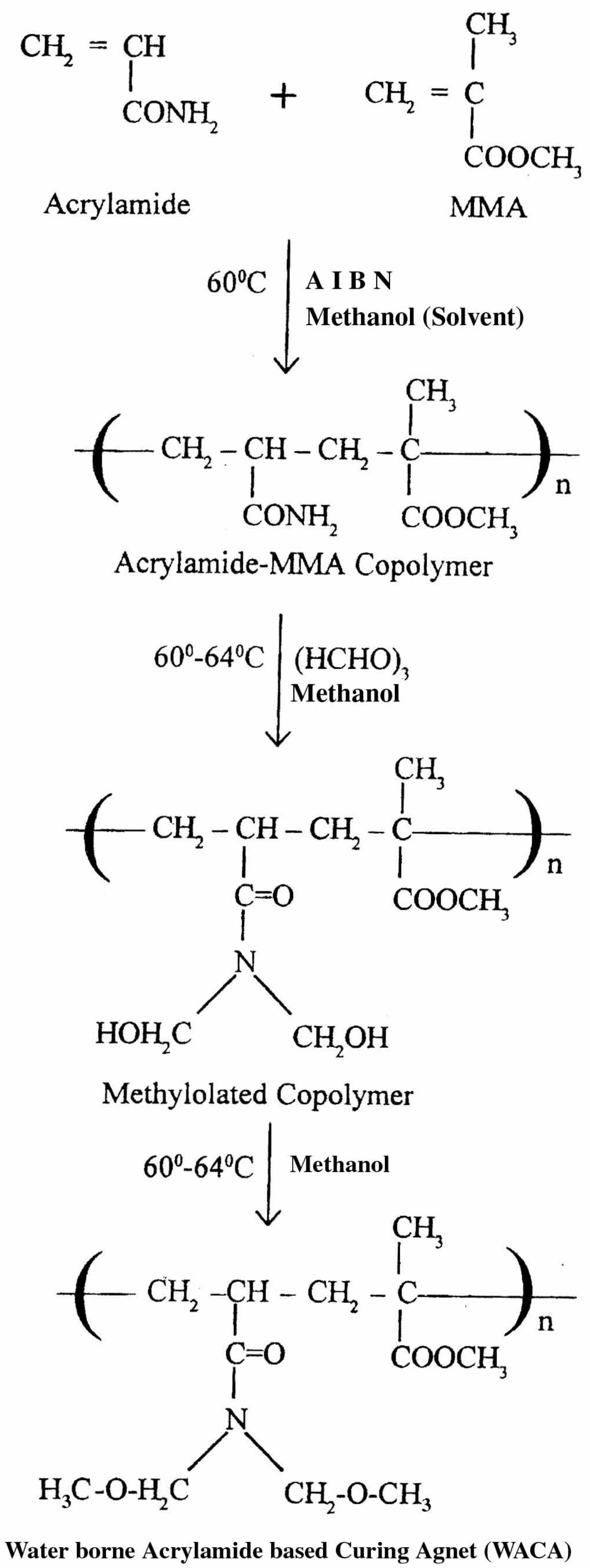
Adhesion & Flexibility:
The results for the adhesion and flexibility are reported in Table: 4. as apparent from the table, the films of compositions WEACA -13 to WEACA- 53, had poor flexibility and adhesion. The composition HMMM-3 also showed the same behaviours. The failure could be probably due to high proportion of the curing agents, which result into highly cross linked and brittle film. Compared to this, compositions with 80:20 and 70:30, water borne epoxy resin to acrylamide based curing agents ratio show better flexibility and adhesion.

Impact Resistance:
The results for the impact resistance of the cured films are shown in Table No 4. The compositions with low acrylamide curing agents pass the tests while the compositions with higher curing agent ratio results into less flexible films, resulting into failure in the test(9). It may be due to higher cross-link density (XLD) in the said sets of compositions. The remaining compositions gave satisfactory results.

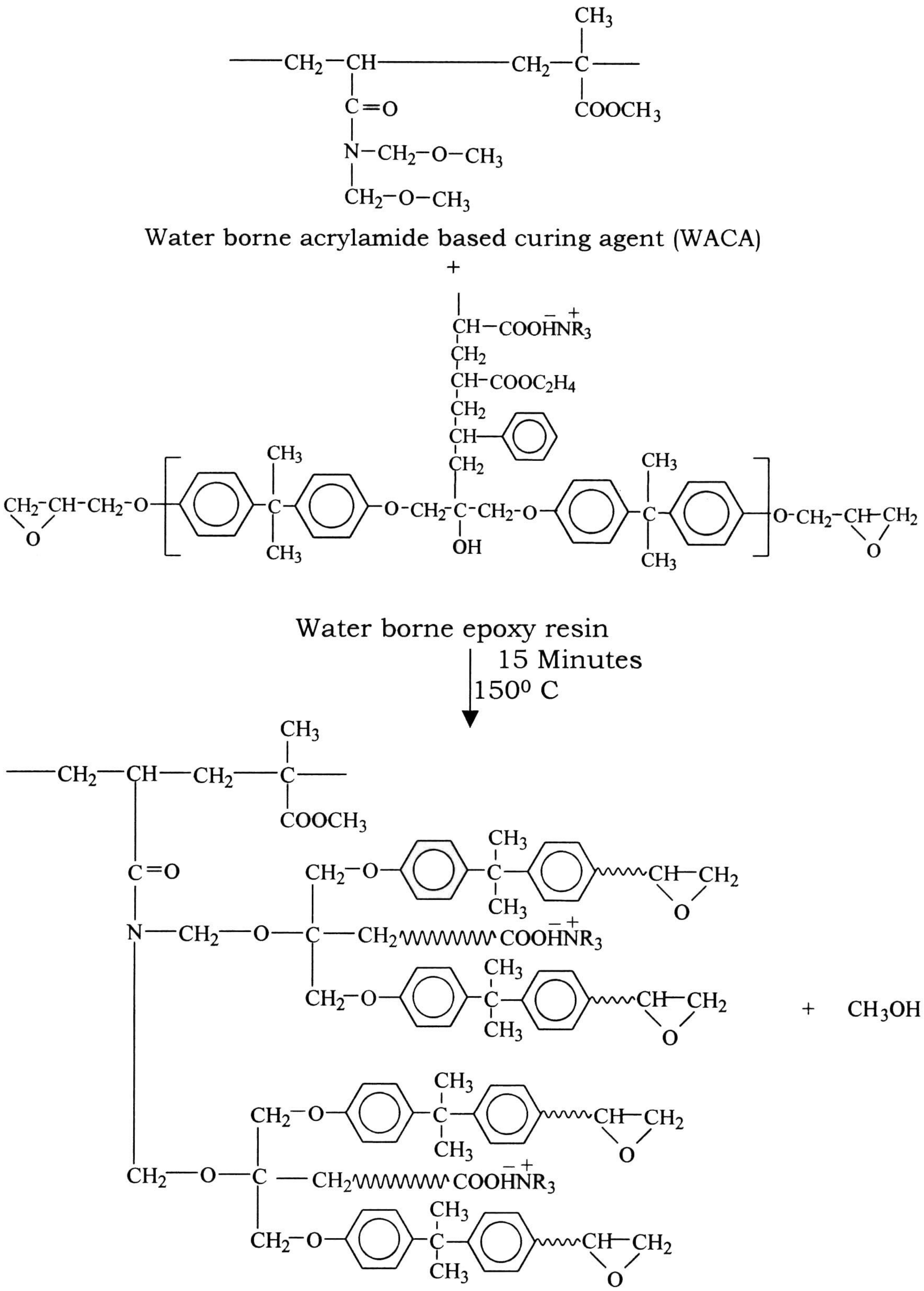
Scratch Hardness:
From the results given in Table No 4, it is proved that the compositions containing higher proportions of water borne acrylamide based curing agent gave good scratch hardness comparable to the HMMM resin compositions. The more crosslink density in these coatings made it very hard and scratches proof. The compositions with 70:30 and 60:40 ratio of water borne epoxy resin to water borne acrylamide based curing agent gave better performance.

Chemical resistance and solvent resistance:
The results for the chemical resistance & solvent resistance of the cured films have been given in Table No. 5. It is very clear from the results that the films with higher ratio of WACA showed better acid, alkali and solvent resistance. The results were almost identical with the HMMM resin compositions. The stable structure of the curing agent and higher cross-link density may be responsible for chemical resistance, and for solvent resistance the film becomes so hard and insoluble that there is hardly any effect on the film. The higher formaldehyde containing sets gave the better solvent resistance.

Hot water and salt water immersion resistance:
The hot water and salt-water immersions gave the better performance for certain sets as shown in Table No. 5. The compositions with 70:30 and 60:40 gave the balanced performance. This could be due to the formation of impervious film which does not allow water or salt water to pass through the film.


Acrylamide
MMA
60⁰C
A I B N
Methanol (Solvent)
Acrylamide-MMA Copolymer
60⁰-64⁰C
(HCHO)3
Methanol
Methylolated Copolymer
60⁰-64⁰C
Methanol
Water borne Acrylamide based Curing Agnet (WACA)

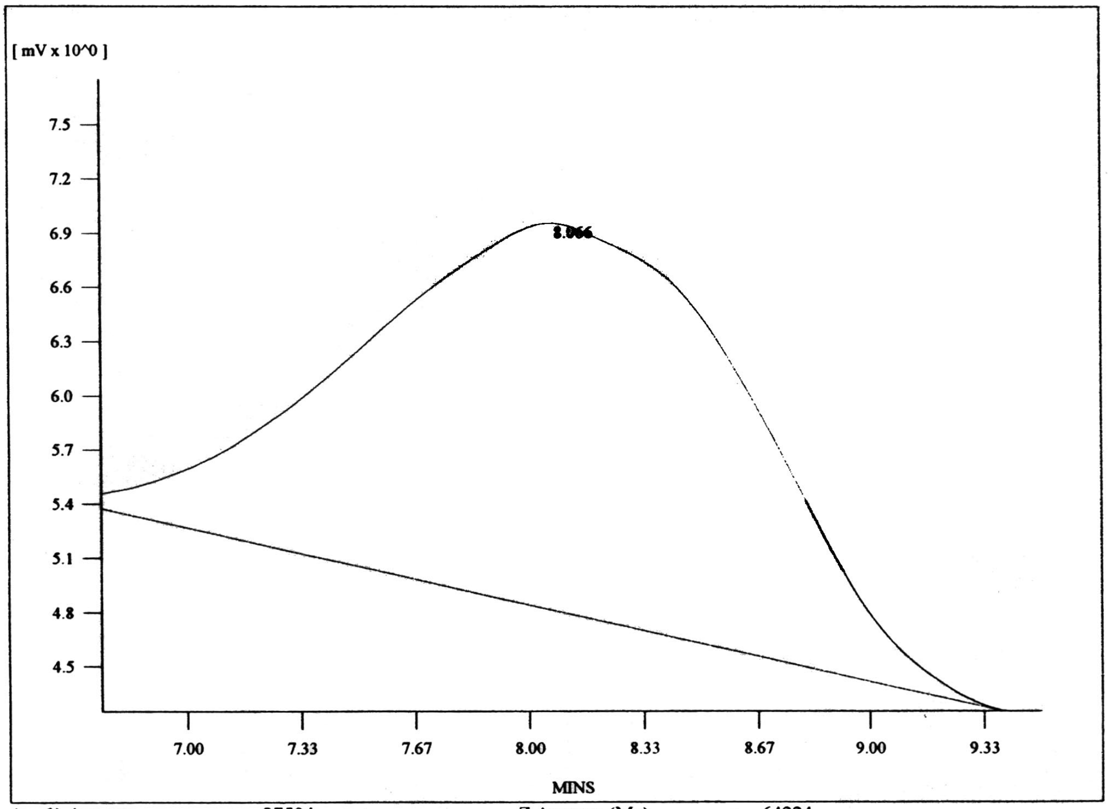
SCHEME ~ 1



Structure of cured film of water borne epoxy with WACA

Scheme 2

Fig.1



(n - 1) Average	:	27504	Z Average (Mz)	:	64224
Number Average (Mn)	:	35289	(Z + 1) Average	:	83409
Weight Average (Mw)	:	47442	PolyDispersity (Mw/Mn)	:	1.344
Total Area	:	1.7290200e+005 (microvolt seconds)			

Peak Molecular Weight Report

Peak	Component	RT	Area	%Area	PMwt	Mw	Mn	Mw/Mn	StartMw	EndMw
1		8.066	172902.0	100.000	40591.3	47441.6	35288.9	1.3444	197807.5	9541.5

Figure- 1: GPC of water borne acrylarnide based curing agent (WACA)

Fig. 2

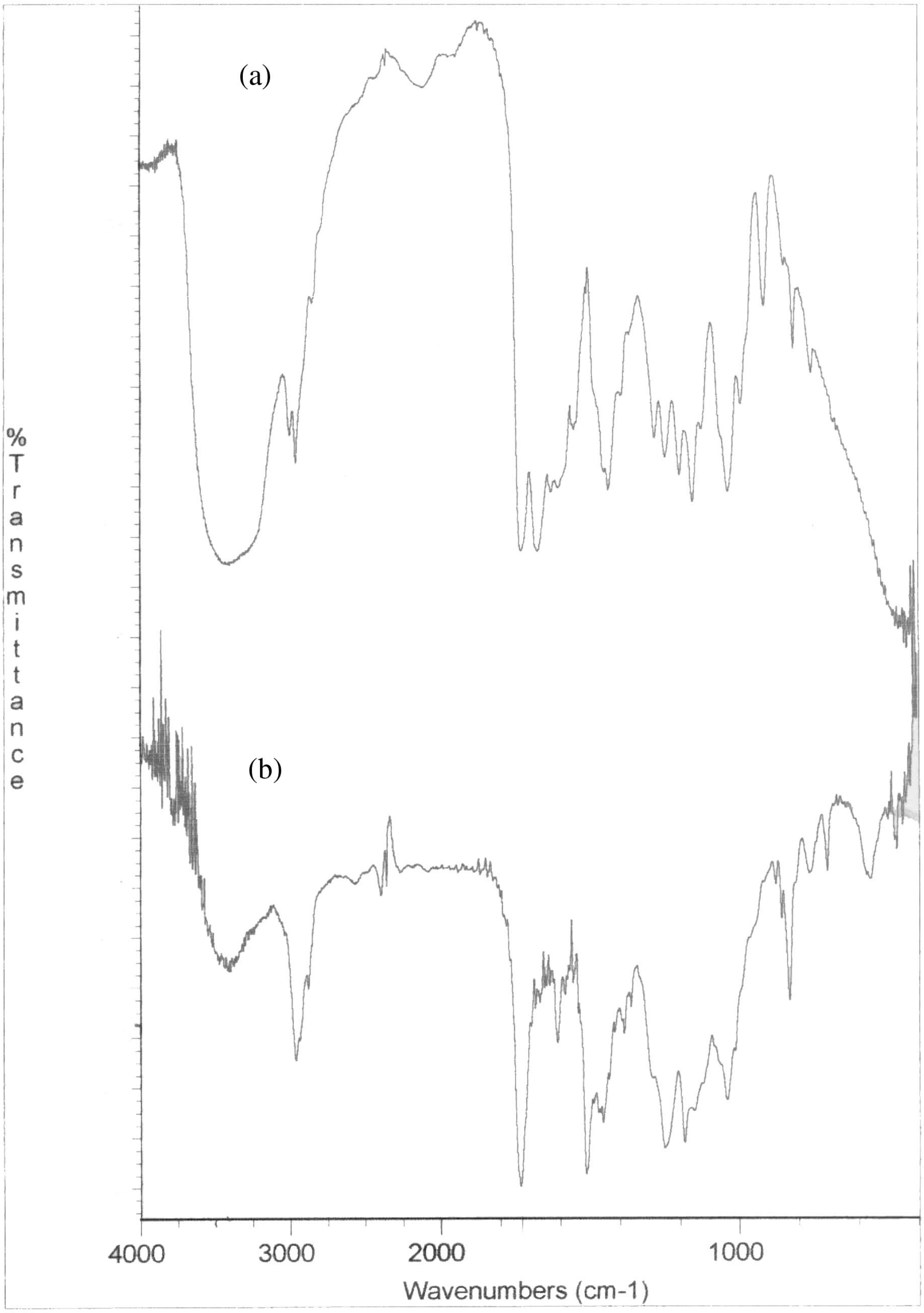


Figure -2: IR- Spectra of (a) 30:70 water borne WACA, (b) 30:70 WACA + water borne epoxy resin film

Fig. 3

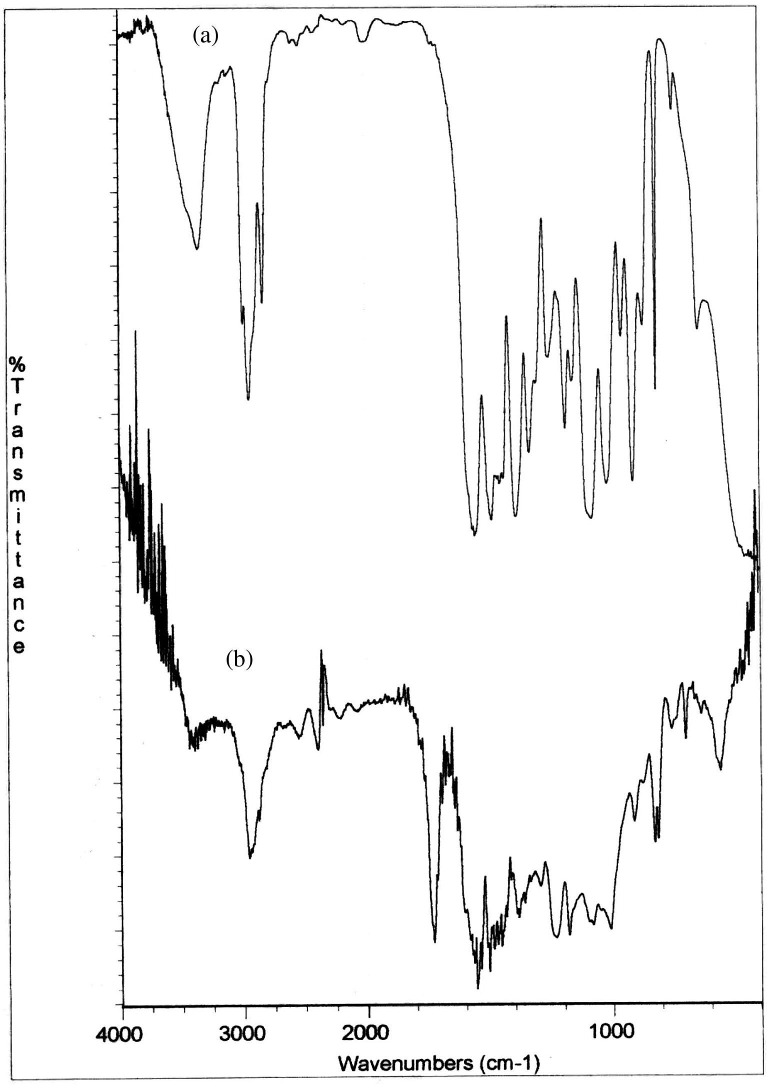


Figure -3: IR-Spectra of (a) HMMM-Resin, (b) HMMM-Resin + water borne epoxy resin film

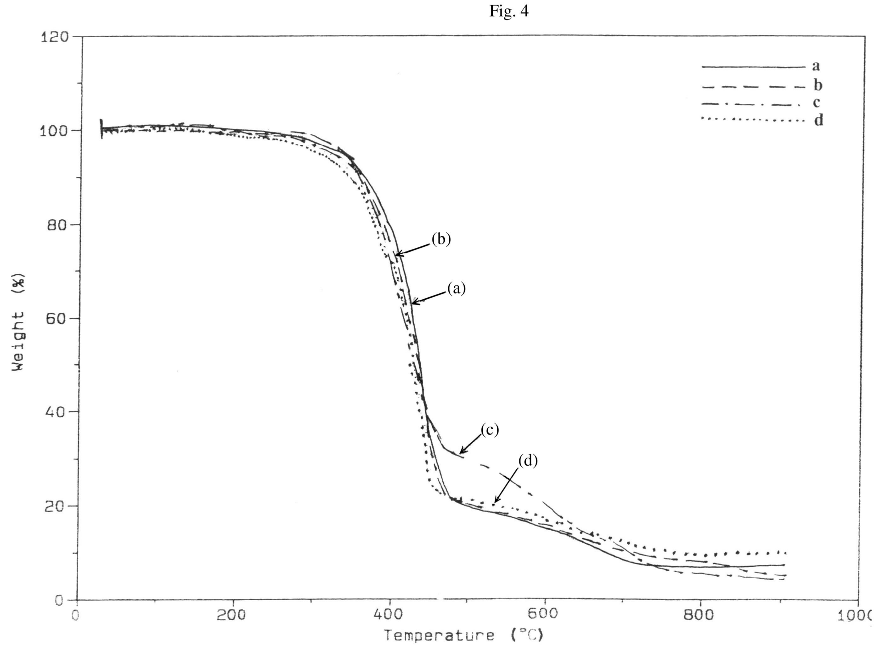


Figure -4: TGA- Thermogram
(a) 30: 70 WACA + water borne epoxy resin film, (b) 50: 50 WACA+ water borne epoxy resin film, (c) 70: 30 WACA + water borne epoxy resin film, (d) HMMM -Resin + water borne epoxy resin film

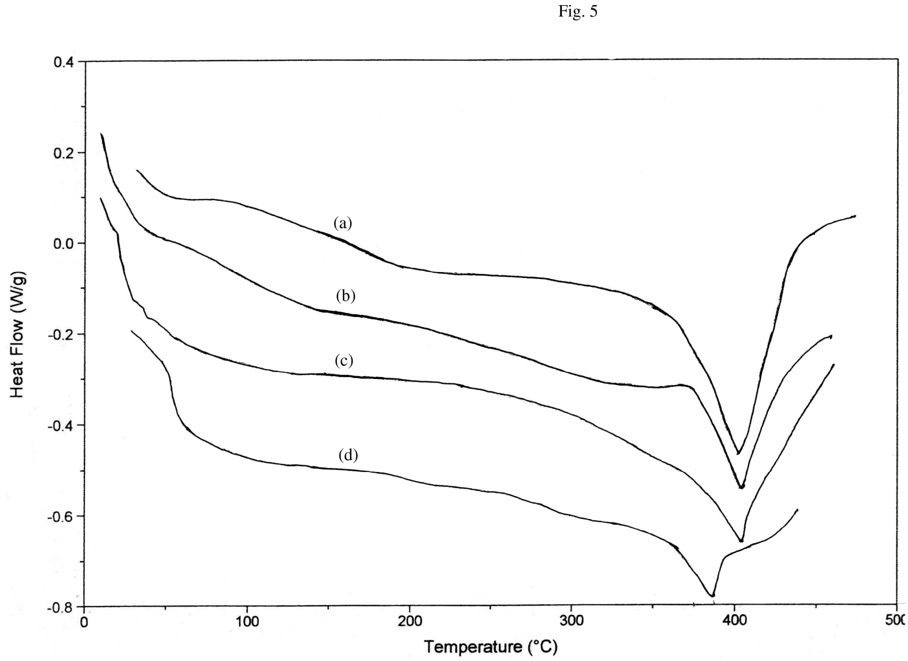


Figure- 5: DSC -Thermogram
(a) 30: 70 WACA + water borne epoxy resin film, (b) 50: 50 WACA + water borne epoxy resin film, (c) 70: 30 WACA + water borne epoxy resin film, (d) HMMM -Resin + water borne epoxy resin film

Table: 1 Composition of water borne Acryl amide based curing agents and water borne epoxy resin - Acrylamide curing agent based coating

Ratio Acrylamide MMA (Wt/Wt)	**70:30**						**50:50**						**30:70**						**Coventional Hexamethoxymethyl melamine Curing Agent (HMMM)**		
Mole Ratio of Acrylamide : **Formaldehyde**	**1:2**			**1:1.5**			**1:2**			**1:1.5**			**1:2**			**1:1.5**					
Designation of Curing Agents	**WACA-1**			**WACA-2**			**WACA-3**			**WACA-4**			**WACA-5**			**WACA-6**			**Ratio Water borne epoxy** Resin : HMMM **(Wt/Wt)**		
Coating Composition water borne epoxy resin : WACAs Ratio (Wt/Wt)	80:20	70:30	60:40	80:20	70:30	60:40	80:20	70:30	60:40	80:20	70:30	60:40	80:20	70:30	60:40	80:20	70:30	60:40	80:20	70:30	60:40
Coating Designation	WEACA-11	WEACA-12	WEACA-13	WEACA-21	WEACA-22	WEACA-23	WEACA-31	WEACA-32	WEACA-33	WEACA-41	WEACA-42	WEACA-43	WEACA-51	WEACA-52	WEACA-53	WEACA-61	WEACA-62	WEACA-63	EHMMM-1	EHMMM-2	EHMMM-3

Table: 2 Physical properties of the Water borne Acrylamide based curing agents (WACAs) and conventional Hexamethoxymethyl melamine based curing agents (HMMM)

Sr. No.	**Designation**	% Solids	**Wt./Lt. 30°C (Kg/Lt)**	**Viscosity 25°C FC-B IV in Butyl cellosolve (40%)**	**Color (Gardner)**	**Clarity**	**Free Formaldehyde (%)**	**Water Solubility**
1	WACA-1	50.10	0.989	75	**3**	Clear	**0.71**	S
2	WACA-2	49.20	0.984	71	**2**	Clear	**0.65**	S
3	WACA-3	48.90	0.990	65	**2**	Clear	**0.42**	S
4	WACA-4	50.30	0.987	78	**2**	Clear	**0.67**	S
5	WACA-5	50.70	0.987	69	**1**	Clear	**0.50**	DS
6	WACA-6	49.50	0.989	60	**1**	Clear	**0.42**	DS
7	HMMM	99.59	1.18	20	**Water white**	Clear	**0.12**	S

S = Soluble; DS = Difficulty Soluble

Table: 3 Physical properties of Water borne epoxy resin

Physical Properties	Results
Percentage Solids (%)	60
Viscosity 30°C FC-B IV (40 % in Butyl cellosolve)	155
Density Wt/ Lt 30°C (Kg/Lt.)	0.975
Hydroxyl Value (mg of KOH/gm of resin)	98
Solubility in Water (Neutralized resin)	Soluble

Table: 4 Mechanical Properties of WEACA and HMMM based coating films

Sr. No.	**Coating (Compositions)**	Adhesion (Cross-hatch)	**Flexibility 1/8" mendral**	**Impact Resistance (2 lbs from 25" height)**	**Scratch Hardness (gms)**	**Dry film Thickness (Microns)**
1	WEACA-11	P	P	P	**2100**	27
2	WEACA-12	P	P	P	**2600**	26
3	WEACA-13	F	F	F	**3500**	25
4	WEACA-21	P	P	F	**2300**	24
5	WEACA-22	P	P	P	**3000**	22
6	WEACA-23	F	F	F	**3700**	21
7	WEACA-31	P	P	P	**1700**	25
8	WEACA-32	P	P	P	**2700**	24
9	WEACA-33	P	P	P	**3100**	25
10	WEACA-41	P	P	P	**2000**	23
11	WEACA-42	P	P	P	**3200**	26
12	WEACA-43	F	F	F	**3500**	24
13	WEACA-51	P	P	P	**1500**	22
14	WEACA-52	P	P	P	**1800**	21
15	WEACA-53	P	F	F	**2000**	25
16	WEACA-61	P	P	P	**1200**	24
17	WEACA-62	P	P	P	**2100**	22
18	WEACA-63	P	P	P	**2400**	21
19	EHMMM-1	P	P	P	**2000**	26
20	EHMMM-2	P	P	P	**2700**	27
21	EHMMM-3	F	F	F	**3200**	25

P = Passes F = Fails

Table: 5 Chemical resistances, Solvent resistant. Salt water and Hot Water Resistance of the Films of WEACAs and HMMM based coating compositions

Sr. No.	**Coating (Composition)**	**Alkali Resistance 5 % NaOH (96 hrs Immersion)**	**Acid Resistance 5 % H_2SO_4 (96 hrs Immersion)**	**MEK Double rubs**	**Water resistance (50°C) (120 hrs Immersion)**	**5 % NaCl salt water Sol. (96 hrs Immersion)**
1	WEACA-11	2	1	70	**2**	3
2	WEACA-12	2	2	80	**2**	3
3	WEACA-13	3	2	110	**3**	4
4	WEACA-21	2	1	65	**2**	3
5	WEACA-22	3	3	85	**1**	2
6	WEACA-23	4	3	100	**3**	3
7	WEACA-31	2	2	70	**2**	3
8	WEACA-32	3	3	85	**2**	2
9	WEACA-33	4	3	105	**2**	3
10	WEACA-41	1	1	65	**1**	3
11	WEACA-42	2	3	75	**2**	3
12	WEACA-43	3	3	95	**3**	4
13	WEACA-51	1	1	60	**1**	3
14	WEACA-52	3	2	75	**2**	3
15	WEACA-53	3	3	85	**2**	4
16	WEACA-61	1	1	40	**1**	2
17	WEACA-62	1	1	65	**2**	3
18	WEACA-63	3	2	75	**3**	4
19	EHMMM-1	1	1	80	**1**	3
20	EHMMM-2	3	2	95	**3**	3
21	EHMMM-3	4	3	115	**4**	4

1: Complete Film Lift – Off; 2: Partial Film Lift – Off; 3: Severe Blistering; 4: Slight Blistering; 5: No Effect

Table: 6 IR-Spectral Characteristic of Water borne acrylamide based curing agents (WACAs) and its film with water borne epoxy Resin

30:70 WACA	**50 : 50 WACA**	**70 : 30 WACA**	**30 : 70 WACA + water borne epoxy resin Film**	**50: 50 WACA + water borne epoxy resin Film**	**70 : 30 WACA + water borne epoxy resin Film**	**HMMM + water borne epoxy resin Film**	**Probable band Assignment**
3400 (b)	3200-3500 (b)	3200-3600 (b)	----	3400 (m)	3430 (m)	---	υ O-H stretching υ NH Stretching of υ $CONH_2$ υ OH Stretching of CH_2OH Group
2920 (s)	2920 (s)	2940 (s)	2900 (s)	2900 (s)	2930 (s)	2950 (s)	-CH Stretching of $-CH_2$
1730 (s)	1725 (s)	1720 (w)	1725 (s)	1720 (s)	1725 (s)	1725 (s)	υ >C=O Group of ester
1640 (s)	1650 (s)	1630 (s)	1640 (w)	1650 (w)	1630 (w)	1620 (w)	>C=O Group of amide
1550 (m)	1560 (m)	1550 (s)	1550 (w)	1560 (w)	1550 (w)	1560 (s)	N-H Bending Vibrating
1420 (s)	1440 (s)	1440 (s)	1450 (s)	1430 (s)	1460 (s)	1450 (s)	**υ C-H Deformation of CH_3 and C-N of amide linkage**
1030-1130 (s)	1035-1120 (s)	1120-1040 (s)	1130 (s)	1120 (s)	1170 (s)	1110 (s)	Ether Linkage

CONCLUSION

The water borne acrylamide based curing agents with 50: 50 acrylamide: MMA ratio and 1:2 acrylamide to formaldehyde ratio and 70:30 water borne epoxy resin: WACA gave the optimum balanced film performance. The results of mechanical properties, chemical resistance, solvent and water resistance for these compositions were quite comparable to the conventional HMMM resin. Compositions with an added advantage of easiness of preparing WACA and also in single step process are the main features of the system. Such coatings can be used in place of conventional curing agents without affecting the film performance, in general purpose industrial coatings as well as in Original Equipment Manufacture (OEM) coating applications. Thus above results reveal their eco-friendly high performance surface coating application potentials.

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