Improvement in Properties of Poly(vinyl acetate): Emulsion with Dibasic Acids

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Synopsis

We report an attempt to graft *cis* (maleic and citraconic) and *trans* (e.g., fumaric and mesaconic) unsaturated dibasic acids onto poly(vinyl acetate) in emulsion systems, in the presence of an initiator and a small quantity of vinyl acetate. The resulting emulsions showed better adhesiveness, higher shear strength, and varied viscosity, and yielded relatively translucent films with faster drying properties. Grafting in the case of these acids was poor, but the *cis* acids were better grafted than the *trans* acids. Furthermore, saturated acids (e.g., oxalic and succinic acid) and an inorganic acid (boric acid) were only physically incorporated in the poly(vinyl acetate) emulsion (PVAc emulsion); the resulting product also showed similar improvement in the end properties.

INTRODUCTION

Interest in poly(vinyl acetate)-based adhesives having higher binding strength and better film properties has grown considerably in the past two decades because of their wide use in adhesives,[1] paints,[2] paper,[3] and in the textile[4] industries. Improvement in adhesiveness[5,6] by incorporation of maleic anhydride or maleic acid in 0.1% concentration in butadiene–acrylonitrile copolymer[7] (for metals), in poly(ethyl acrylates)[8] (for steel), in vinyl plastisols[9] (for nylon and polyester fabrics[10]), in vinyl chloride–vinyl acetate[11] (for cartons); and similarly of oxalic acid in 2–4% concentration in poly(vinyl butyral) (for glass),[12] has been well established.

In continuation of our studies[13,14] on poly(vinyl acetate) emulsions (PVAc emulsions) with an objective to obtain a better adhesive, a systematic attempt has been made to graft different classes of unsaturated dibasic acids and compare the resulting properties with those of emulsions in which saturated and inorganic acids were physically incorporated. Thus (1) Unsaturated *cis* acids, i.e., maleic acid (MA) and citraconic acid (CA); (2) *trans* acids, i.e., fumaric acid (FA) and mesaconic acid (MCA); (3) saturated acids, i.e., oxalic acid (OA) and succinic acid (SA); and (4) boric acid (BA) (in view of its special gelling effect[15] on poly(vinyl alcohol)) were chosen for the present study. The percent grafting, or chemical incorporation in the polymer chain, was determined by infrared (IR) spectroscopy and by quantitative estimation of acidity, (volumetrically). Grafting, in general, was poor, although *cis* dibasic acids, as expected due to the regioselectivity, were better grafted (0.09–0.1%, 2h) than *trans* acids (0.0–0.02%, 2h). Further, these emulsions showed better adhesiveness (as measured on an Instron) than

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the corresponding "unincorporated" emulsion (reference emulsion 1, ref-1). Films prepared from these emulsions were faster drying on nonporous surfaces and more translucent (light transmission was measured on a spectrophotometer, Toshniwal model).

EXPERIMENTAL

Material

1. Ref-1: PVAc emulsion was prepared[14] by radical emulsion polymerization of vinyl acetate. To a solution of protective colloid and emulsifier (46 g polyvinyl alcohol in 420 mL water) were added an initiator (30% hydrogen peroxide, 1.5 mL), acetic acid (0.2 mL to bring the pH to 4.5), a promotor (cobalt acetate, 2.25 mL of a 0.5% aq. solution), and a portion of vinyl acetate (50 g). After raising the reaction temperature to 80°C, remaining monomer (vinyl acetate, 366 g) was gradually added to this mixture, under stirring at 80°C over a period of 4 h. At the end of the polymerization reaction, the solution was cooled to 70°C and plasticizer (dibutyl phthalate, 18 mL) was added. This emulsion (ref-1), having a viscosity of 14,500 cps (at 20°C), a nonvolatile content of 49.4%, and a particle size of 3–4.5 μm, was used as the starting material for all the experiments reported here.

2. Ref-2 was prepared by mixing 10.7 mL vinyl acetate, 250 mg initiator, and 2.5 g dibasic acid (dissolved in 7.5 mL hot water) in 250 g of ref-1 emulson.

3. Potassium peroxodisulfate was purchased from E. Merck, India.

4. Vinyl acetate manufactured at Vam Organic Chemicals Ltd., India, was used.

5. Dibasic acids, MA, FA, OA, SA, and BA were recrystalized as described in the literature.[16]

6. CA manufactured at Boehringer, Ingelheim, KG D 6567 Ingelheim, West Germany, and MCA from Fluka AG Chem Fabrik CH 9470 Buchs, West Germany were used.

Grafting Procedure

In a 500-mL three-necked RB flask, equipped with a thermometer, a mechanical stirrer, and a condenser, and provided with a heating arrangement (waterbath), were placed ref-1 (250 g), and the initiator, potassium peroxodisulfate (0.25 g). This mixture was heated to 60°C ($\pm$ 1°C). An aqueous solution of dibasic acid (2.5 g acid in 7.5 mL water) and vinyl acetate (10 g, 10.7 mL) was added to the reaction flask under stirring (500–600 rpm, measured by a tachometer). The reaction temperature was maintained throughout at 60°C ($\pm$ 1°C). Aliquots were withdrawn at 0-, 1-, and 2-h intervals from this and also from a parallel blank experiment (which was done in an identical fashion except that it did not contain initiator), and the acidity was determined as described below.

Twenty grams of aliquot was coagulated with aqueous 10% sodium sulfate solution (100 mL). After 15 h the solid polymer was filtered, washed with water (10 mL $\times$ 5), and the combined aqueous portion (filtrate and washings

collected in the same flask) was titrated against standard $0.01N$ NaOH solution to determine the total acidity in the aqueous part. From the following formula, the percent acid consumed in the grafting experiments was calculated.

$$\text{Dibasic acid consumed (DAC)} = (A_1 - A_2)$$

A_1 is the acidity in the parallel blank experiment at 0, 1, or 2 h, as the case may be; and A_2 is the acidity in the grafting experiment at 0, 1, or 2 h, as the case may be.

Characterization of Emulsions

The IR spectra of PVAc films were recorded on a Perkin-Elmer IR spectrophotometer 267 (Gratings). The PVAc film was prepared by coagulating the emulsion and dissolving the dried, coagulated PVAc in methanol (4% solution). This solution was spread on a Teflon sheet and dried at room temperature (25–30°C). After the film was dried, its thickness was measured with a micrometer. Nonvolatile contents were determined gravimetrically, by heating the emulsion in an oven at 120°C for 2 h.

The viscosity of the emulsions was measured at 20°C with the Brookfield Viscometer and use of spindle no. 3.

Particle sizes were measured with a scanning electron microscope (model Philips SEM 501, made in Holland) at magnification 2000× as discussed.[14]

Shear strength of the emulsions was determined according to ASTM D1002[17] with an Instron Tensile Tester, model Instron 1121, made in the UK. A gauge length of 83 mm, crosshead speed of 5 mm/min, and chart speed of 50 mm/min were employed.

Film transparency was measured at 624 nm, using a spectrophotometer from Toshniwal, India.

Film drying behavior of the emulsion (percent water loss vs time) was determined by spreading the emulsion quantitatively on a porous surface (plywood) and on a comparatively nonporous surface (laminate). These samples were dried at 25°C at 40% humidity, and the water loss was determined after every 5- or 10-min interval.

RESULTS AND DISCUSSION

Because unsaturated dibasic acids like maleic acid do not polymerize alone,[18] the grafting of dibasic acid onto ref-1 was carried out in the presence of an initiator (peroxodisulfate) and a small quantity of vinyl acetate at 60°C (± 1°C). It was observed that when initial dibasic acid concentrations of 1% were used, grafting onto ref-1 ceased after 2 h, as determined acidometrically.

Grafting

The grafting efficiencies of the dibasic acids onto ref-1 were calculated[19] according to (1) and are given in Table I.

TABLE I
Properties of Ref-1 and Ref-2 Modified Emulsions

Sample No.	Sample	Dibasic acid	Reaction time (h)	Grafting of acid onto PVAc emulsion	Nonvolatile content (% ± 0.2%)	Viscosity (cps. ± 100)	Particle size (μm ± 0.5)
1	Ref-1	—	0	0	49.4	14,500	3.0–4.5
2	Ref-2	—	0	0	46.7	6,000	3.0–4.5
3	CPVA-189	MA	1.0	0.02	48.8	18,000	4.0–6.0
4	CPVA-190	MA	2.0	0.09	50.3	100,000	6.0–9.0
5	CPVA-193	CA	1.0	0.03	47.0	8,000	3.0–4.5
6	CPVA-194	CA	2.0	0.10	48.3	16,000	3.0–4.5
7	CPVA-215	FA	1.0	0.00	46.8	6,000	3.0–4.5
8	CPVA-216	FA	2.0	0.01	46.7	6,200	3.0–4.5
9	CPVA-191	MCA	1.0	0.01	46.9	6,200	3.0–4.5
10	CPVA-192	MCA	2.0	0.02	47.5	9,200	—
11	CPVA-229	OA	1.0	0.01	50.2	25,000	4.0–6.0
12	CPVA-227	SA	2.0	0.0	46.8	6,000	3.0–4.5
13	CPVA-226	BA	1.0	0.0	Caused coagulation of the emulsion		3.0–4.5

$$G(E) = \frac{\text{Wt. of dibasic acid in grafted copolymer}}{\text{Initial wt. of dibasic acid in the reaction}} \times 100 \qquad (1)$$

From Table I, it is obvious that grafting is generally poor; however, *cis* acids, as would be expected from the stereo-indisposition of the carboxylic group, are better grafted than the *trans* acids (FA and MCA). Furthermore, in both the *cis* and the *trans* series, the presence of a methyl group in the dibasic acid, irrespective of its stereochemistry, seemed to increase the grafting slightly, as is demonstrated by results with CA and MCA (Table I).

Incorporation of dibasic acids in the polymer chain could conceivably arise by (a) grafting, (b) an esterification reaction between the acid and hydroxyl groups, the latter being present in small proportions due to poly(vinyl alcohol), present in the ref-1; and (c) intermolecular hydrogen bonding. The possibilities (b) and (c) are clearly ruled out because more than at least 99% free acid (of that originally taken) was present in the filtrate obtained during filtration and water washing of the solid polymer, resulting from coagulation of these emulsions; esterification, or even hydrogen bonding, would result in consumption of substantial quantity of acids and hence would give much lower values of acidities than actually obtained in the aqueous portion. This is further confirmed by the presence of a free carboxylic group (wave number ν^{OH} 3760, 3550, and 3460 cm^{-1} in conjunction with $\nu^{C=O}$ 1720 cm^{-1}) in the IR spectra (Fig. 1) of the film made from the solid copolymer derived from the emulsions. In the case of MA, CA, FA, and MCA, where grafting occurred in the polymer chain, it should have followed a mechanism involving the interaction of low-molecular-weight dibasic acid–vinyl acetate copolymer radical (I) with a radical (II) derived from PVAc due to facile abstraction of H from the methyl group by the initiator radical.[20]
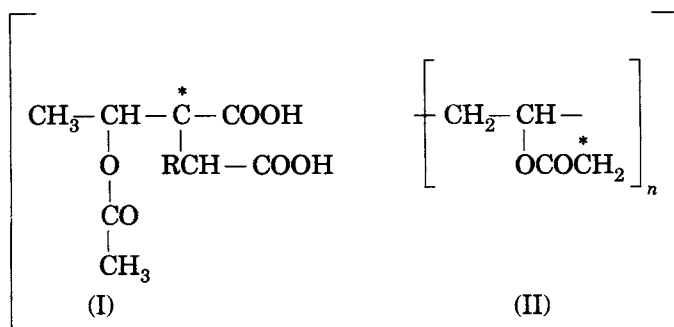
where R = H or CH$_3$.

Atacticity

The atacticity, which is directly linked with 1125 cm^{-1} absorption in the IR spectrum,[21] was found to be greater for *trans* unsaturated dibasic acids. Taking a peak at 610 cm^{-1} as reference, we have calculated the relative intensity ratios of several related absorption bands; the results are summarized in Table II.
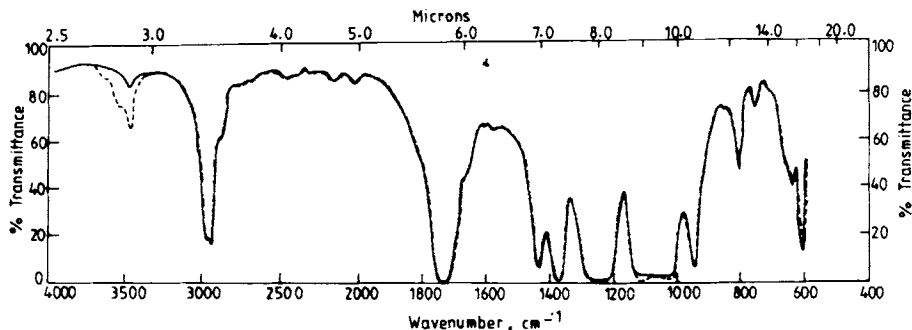
Fig. 1.   IR spectra of reference emulsion (- -) and emulsion grafted with CA(——).

Nonvolatile Content

In ref-1, nonvolatiles are 49.4%. Due to initial dilution of ref-1 with (a) vinyl acetate and (b) aqueous solution and dibasic acids, theoretically the nonvolatiles (as in ref-2) should be 46.7%; however, depending upon the extent of polymerization of added vinyl acetate, the nonvolatile content could vary from 46.7% to 50.4%. The percentage of nonvolatiles was determined for various emulsions and these are given in Table I; they are well within the expected range.

Viscosity

It is interesting to note that incorporation of MA and OA resulted in a substantial increase in viscosity (Table I). In the case of FA, MCA (1 h), and SA, the viscosity drop (to 6000) is essentially due to a dilution effect. This was clearly confirmed by the viscosity measurement (6000 cps) of ref-2 emulsion prepared by diluting ref-1 with vinyl acetate, under the conditions of grafting. A trend of increasing viscosity in the case of CA (from 6000 to 8000 in the first hour and 16,000 cps in the second hour) and MCA (from 6000 and 9200 cps in 2 h) can be rationalized in terms of the slow polymerization causing an increase in the viscosity.

In view of the established[15] gelling effect of boric acid through a monodiol type of bond, at least in poly(vinyl alcohol), it was of interest to see its effect

TABLE II
Relative Intensity Ratios of Important IR Absorption Bands in PVAc and Grafted PVAc

Sample No.	Sample	Peak ratios[a] at wave numbers (ν in cm^{-1}):				
		3650	3540	3465	1125	610
1	Ref-1	0.05	0.05	0.24	.007	1.0
2	CPVA-189	0.04	0.04	0.18	0.004	1.0
3	CPVA-190	0.06	0.226	0.37	0.009	1.0
4	CPVA-193	0.03	0.04	0.18	0.052	1.0
5	CPVA-194	0.02	0.04	0.09	0.156	1.0
6	CPVA-191	0.04	0.085	0.259	0.037	1.0
7	CPVA-192	0.02	0.032	0.172	0.052	1.0

[a] Absorption band intensity ratios have been calculated, taking 610 cm^{-1} as the reference.

in PVAc emulsions, but in our hands only a coagulated emulsion was obtained under these conditions.

Particle Size

Emulsions incorporated with MA and OA were found to contain larger particles (size, 4–6μm) than those of ref-1, when emulsions were examined at 2000 × magnification in the electron microscopy (Table I). In these instances, a tendency of the particles to agglomerate was also observed. In all other remaining cases, particle sizes were more or less the same as in ref-1 (Table I).

Adhesiveness or Shear Strength

One of the most important properties of adhesives, shear strength (τ), was measured according to ASTM-1002[17] on an Instron under the conditions described in the Experimental section. Shear strength was calculated by dividing the maximum load by the total area of the specimen (for a particular thickness). Based on the measurement of five strips (from same emulsion), the average τ was calculated for that emulsion and is reported in Table III.

It is obvious from the τ data that the reaction of the reference emulsion with MA, CA, or MCA for 1 and 2 h resulted in an enhancement of τ values to > 1.5 and 2 times, respectively, the original τ value (26.2 kg/cm^2); OA doubled the τ value after it was reacted with ref-1 for 1 h only.

Film Properties

The drying behavior of emulsion films was studied by determining the percent water loss at 10-min intervals, at 25°C and 40% relative humidity, both on nonporous (SUNMICA laminates) and porous (plywood) surfaces. The results are given in Table IV. On a nonporous surface, the emulsion films containing a dibasic acid having a methyl group (CA and MCA) were faster-drying; in the pair (CA) where the methyl group has a *cis* configuration with respect to hydrogen, drying was found to be the fastest (Fig. 2).

TABLE III
Shear Strength of Ref-1 and Modified PVAc Emulsions

Sample No.	Sample	Dibasic acid used	Emulsion film thickness (μm, ± 2.5)	Average shear Strength, τ (kg/cm^2, ± 1.5)
1	Ref-1	—	40	26.2
2	CPVA-189	MA	40	38.3
3	CPVA-190	MA	40	58.6
4	CPVA-193	CA	40	36.7
5	CPVA-194	CA	40	62.4
6	CPVA-216	FA	40	59.0
7	CPVA-191	MCA	40	36.4
8	CPVA-192	MCA	40	58.6
9	CPVA-229	OA	40	56.6
10	CPVA-227	SA	40	58.9
11	CPVA-226	BA	40	46.9

TABLE IV
Film Properties of Ref-1 and Modified Emulsions

| Sample No.	Sample	Dibasic acid used	Film thickness (μm ± 2.5)	Film drying (%) on polywood in 260 min	Film drying (%) on laminates in 200 min
1	Ref-1	—	40	45.0	45.0
2	CPVA-189	MA	40	35.0	45.5
3	CPVA-190	MA	40	46.0	44.0
4	CPVA-193	CA	40	49.0	48.5
5	CPVA-194	CA	40	42.0	53.5
6	CPVA-216	FA	40	39.0	50.0
7	CPVA-191	MCA	40	36.3	48.3
8	CPVA-192	MCA	40	40.0	53.5
9	CPVA-229	OA	40	39.8	46.5
10	CPVA-227	SA	40	39.8	42.0
11	CPVA-226	BA	Emulsion gets coagulated with BA reaction.		
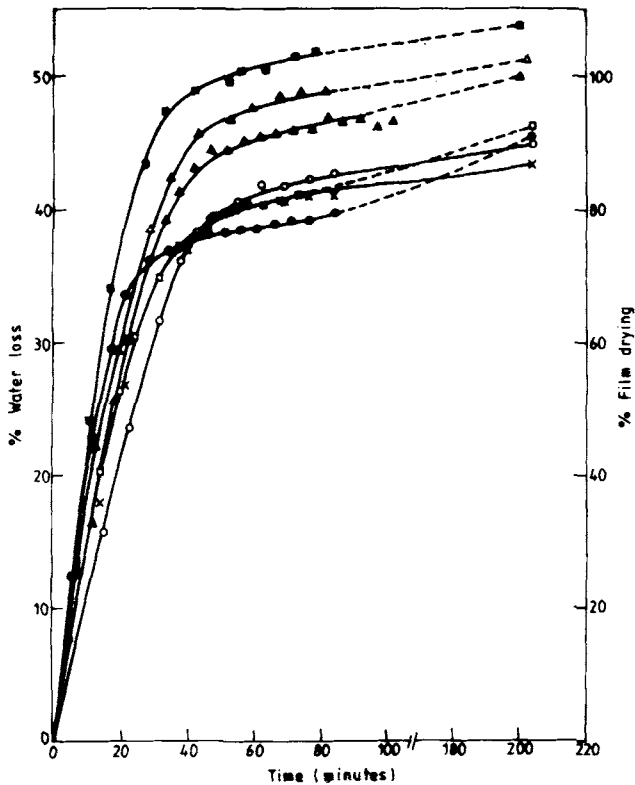
Fig. 2.   Percent water loss (percent film drying) versus time on nonporous surface (SUN-MICA), of the reference emulsion and after reacting the emulsion with dibasic acids for 2h. (○) Reference emulsion, (×) with MA, (△) with MCA, (□) with OA, (■) with CA, (▲) with FA, and (●) with SA.
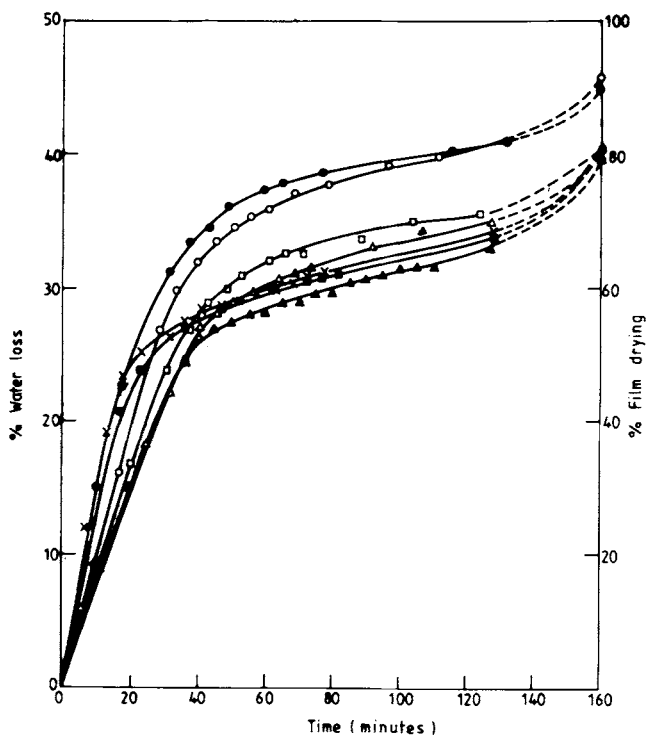
Fig. 3. Percent water loss (percent film drying) versus time on porous surface (plywood) of the reference emulsion and after reacting the emulsion with dibasic acids for 2 h. (●) Reference emulsion, (▲) with FA, (■) with OA, (×) with SA, (○) with MA, (△) with MCA, and (□) with CA.

On a porous surface, ref-1 had the shortest drying time. Next in the series were MA and CA grafted copolymers, both having a *cis* stereochemistry for their carboxylic functions (Fig. 3). The total drying time of the same emulsion on a porous surface, as compared to that on a nonporous surface, is higher, as would be expected; in the former case, the emulsion fills up the pores, and water evaporation is highly limited to the low surface area exposed to the atmosphere.

Films of 40-μm thickness were prepared from a 4% methanolic solution of the dried polymer obtained after coagulation of the emulsion. A comparison revealed that in all cases, these were more transluscent (percent transmission, 62–68%) than those from ref-1 (percent transmission, 72–74%) at 624 nm.

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