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A Study on Synthesis of Polyesteramide and its Application to Coating Materials

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Abstract

In the present research work, thermosetting polyesteramide coatings were prepared to overcome the major drawback of conventional melamine cured coatings viz. high VOC emission, by reacting acrylic copolymer and hydroxy ethyl fatty amide (HEMA). Acrylic copolymer was synthesized using methyl methacrylate and maleic anhydride as monomers in xylene and benzoyl peroxide (BPO) as initiator. The copolymer and HEFA were characterized by Fourier Transform Infrared (FTIR). A series of compositions having varying amount of acrylic copolymer and hydroxyl ethyl fatty amide were prepared to form the polyesteramide coatings and their thermal properties were studied by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The coating films were baked at 155 °C for 30 minutes to effect film cure. Cured films were evaluated for their optical, mechanical and chemical resistance properties to ascertain the commercial utility in the field of surface coating.

Key-words : Coatings, Acrylic copolymers, Hydroxyl ethyl fatty amide, Blending, Film characteristics

1. Introduction

The use of petroleum based monomers in the manufacture of the polymers is expected to decline in coming years because of spiraling prices and the high rate of depletion of the stocks. This has inspired investigation of renewable natural materials as alternative resource of monomers for the polymer industry¹⁻⁴. The oil from various seeds specially waste fruit seeds can play an important role in the synthesis of different kinds of polymeric resins like alkyds, epoxies, polyurethanes, polyesteramides and other polymers⁵⁻⁷. The common seed oils used in paint and coating industries include safflower, soyabean, castor, linseed etc. These resins hold considerable scope of application in the paint and coating industries^{8,9}. Out of these, polyesteramide resins are of considerable interest¹⁰. The presence of repeating units of ester (-COOR) and amide (-NCOR) in the polymeric chain of polyesteramide (PEA),

improves the ease of application, thermal stability and resistance against chemicals. In the present study an acid functional acrylic copolymer has been synthesized using methyl methacrylate and maleic anhydride. In addition, hydroxyl ethyl fatty amide of dehydrated castor oil has also been synthesized which is used as a curing agent for this acid functional acrylic copolymer resin. The effect of cross-linking agent in films based on the acrylic copolymer was examined. A series of coating compositions having varying amount of acrylic copolymer and hydroxyl ethyl fatty amide were prepared, and their mechanical, optical & chemical resistance properties were studied.

2. Experimental Procedure

2.1 Reagents

Castor oil was procured from a commercial manufacturer. Maleic anhydride, methyl methacrylate (MMA), diethanolamine, zinc oxide, methanol, xylene, acetone, and potassium hydroxide were of laboratory reagent grade.

2.2 Synthesis of Acrylic Copolymer (Scheme 1)

The copolymer was synthesized by dissolving maleic anhydride (1 mol) in 100 ml of xylene in a 3 neck

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flask provided with inlet for N₂ gas, reflux condenser & mechanical stirrer. MMA (1 mol) containing 2 gm of benzoyl peroxide was added drop wise at a constant rate into the flask over the period of 2 hours keeping the temperature constant at 95 °C. The reaction mass was stirred for another 2 hours to complete the reaction. The resulting copolymer was diluted with acetone and precipitated with methanol with constant stirring. Likewise, polymers containing 0.3 ~ 0.7 mole maleic anhydride were also prepared. Table 1 shows the characteristics of acrylic copolymers.

2.3 Synthesis of Hydroxy ethyl fatty amide (HEFA) (Scheme 2)

Castor oil (0.1 mol) was taken in multinecked flask equipped with stirrer, thermometer & condenser. Oil

Synthesis of hydroxyl ethyl fatty amide

Scheme 1 Synthesis of acrylic copolymer and HEFA.

was heated to 150 °C and diethanolamine (0.34 mole) & zinc oxide (0.002 mole) were added. The temperature was raised up to 200 °C and maintained until it gave methanol solubility test. The formation of hydroxy ethyl fatty amide was further confirmed by TLC method⁷. After the completion of the reaction the product was dissolved in diethyl ether, washed with 15 % NaCl solution and dried over anhydrous sodium sulphate. The ethereal solution was filtered and evaporated in vacuum evaporator to obtain the light colored hydroxy ethyl fatty amide of dehydrated castor oil. Table 2 shows the physico-chemical properties of hydroxyl ethyl fatty amide of castor oil.

2.4 Measurements

Infrared spectra of the synthesized co-polymers (before neutralization) were recorded by using NaCl discs on a Perkin-Elmer 1750 FT-IR spectrophotometer. Molecular weight was determined by GPC (model HPLC 600, RI detector with two ultra styragel columns) polystyrene was used as a standard & THF was eluent. For DSC analysis, a universal V4.2E TA instruments Q20 differential scanning calorimeter was

Scheme 2 Cross-linking reaction between acrylic copolymer and HEFA.

Table 1 Characteristics of acrylic copolymer.

Sr. No.	Copolymer Code	Monomers (mol)		Number average molecular wt. (Mn)	Weight average molecular weight (Mw)	Poly dispersity index (PDI)	Acid Value
		MMA	MA				
1.	A	1	0.3	3,020	11,200	2.24	140
2.	B	1	0.5	6,000	16,020	2.67	232
3.	C	1	0.7	10,350	22,980	3.70	275
4.	D	1	1	12,240	24,985	2.04	350

Table 2 Physical properties of Hydroxy Ethyl Fatty Amide (HEFA).

Sr. No.	Properties	Hydroxy Ethyl Fatty Amide (HEFA)
1.	Hydroxyl Value	8.9
2.	Iodine Value	86
3.	Viscosity at 25°C (poise)	20
4.	Specific Gravity	0.926
5.	Refractive Index at 25°C	1.4870

Table 3 Formulation of coating samples.

Sr. No.	Coating Code	Copolymer	Curing Agent	Molar Ratio Copolymer : HEFA
1.	PE-1	A	HEFA	1 : 1
2.	PE-2	B	HEFA	1 : 1
3.	PE-3	C	HEFA	1 : 1
4.	PE-4	D	HEFA	1 : 1

used. The temperature range was kept as 20 ~ 200 °C ; at the rate of 20 °C/min. The analysis was carried out in nitrogen atmosphere at the rate of 40 ml/min. The thermal stability of the resin was measured by using a universal V4.2E TA instruments Q50 thermogravimetric analyzer under dynamic scans from 0 ~ 600 °C at the rate of 20 °C/min under the dry flow of nitrogen at the rate of 30 ml/min. Viscosity of the fatty amide was determined by Brookfield cone and plate 2000 + viscometer, at 25 °C.

2.5 Preparation of Coating Samples

Coating compositions having varying ratio of acrylic copolymers/HEFA have been prepared using xylene/acetone (95/5 % v/v) as a solvent. All the compositions were thinned by above mixture to 50 % weight of non volatile matter. The sample designations are given in Table 3.

2.6 Preparation of Coating Films

The coating films were prepared by applying the various coating formulations on the mild steel panels using bar applicator. The dry film thickness of the coating films was tried to maintain at 30 ~ 35 microns for the evaluation of various mechanical and chemical resistance properties. The films of various compositions were subjected to baking at 155 °C for 30 min. The curing reaction is shown in Scheme 2.

3. Result and Discussion

3.1 Spectral Analysis of MMA-MA Copolymer

IR spectrum of MMA-MA copolymer is shown in Fig. 1. The IR spectrum shows the presence of absorption

Fig. 1 IR spectrum of acrylic copolymer. **Fig. 2** IR spectrum of hydroxyl ethyl fatty amide.

band at 2925 cm^{-1} due to carboxylic acid of the saturated anhydride. This confirms the inclusion of maleic anhydride in the copolymer. A strong band at 1738 cm^{-1} may be due to the ester group of the methyl methacrylate.

3.2 Spectral Analysis of Hydroxy ethyl fatty amide (HEFA)

The FT-IR spectrum of HEFA is shown in Fig. 2. The characteristic band absorption band at 3391 cm^{-1} is for alcoholic -OH. Asymmetric and symmetric stretching bands appear at 2923 and 2853 cm^{-1} , respectively. The stretching vibration band of C=O NCOR appears at 1739 cm^{-1} , the band at 1052 cm^{-1} is due to C-N stretching vibrations and the band at 1621 cm^{-1} is due to double bond of fatty acid constituents in HEFA. Strong absorption band at 1455 cm^{-1} can be attributed to (-C-H-) bending and to the presence of tertiary amide

3.3 Thermal Analysis

Fig. 4 shows the TGA thermogram of the Polyesteramide. It is quite obvious that the thermal stability is quite high as only 10 % weight loss is observed upto a temperature of 250 °C. Beyond this temperature a sluggish decomposition takes place as a

Fig. 3 DSC thermogram of polyesteramide.

Fig. 4 TGA of polyesteramide.

result about 50 % weight loss occurs upto 370 °C and 80 % weight loss occurs upto 405 °C.

In the Fig. 3 an endothermic peak is observed at 160 °C in the DSC thermogram. The DSC thermogram does not show any significant weight loss at this temperature. The endothermic peak can be attributed to the melting of the material.

3.4 Physical properties of Coating Films

The panels of various coating formulations were cured and were tested for different mechanical and chemical resistance properties, as per test methods viz. gloss at 60° (ASTM : D-523-99), scratch hardness (ASTM : D-5178), pencil hardness (ASTM : D-3363-00), chemical resistance (EN : 438-2 : 1991). The results are given below in the Table 4.

3.4.1 Scratch Hardness

Results of scratch hardness are shown in Table 4. The comparison of mechanical properties of the films of various compositions reveals that, in general scratch

Table 4 Physical properties of coating films.

Sr. No.	Property	Results			
		PE-1	PE-2	PE-3	PE-4
1.	Scratch Hardness (grams)	2100	2300	2750	2900
2.	Pencil Hardness	2H	3H	3H	4H
3.	X-Hatch Adhesion (%)	100%	100%	100%	100%
4.	Flexibility (1/4" mandrel)	Pass	Pass	Pass	Pass
5.	Impact Resistance (lbs.inch)	162	150	135	130
6.	Gloss (60°)	83.1	86.4	89.5	90.4

hardness increases as the amount of curing agent (HEFA) decreases.

The scratch hardness property of the film in general improves with an increase in the film complexity resulting from higher degree of crosslink density, but in the present case it decreases as the HEFA content increases. This might be due the presence of nonpolar fatty acid moiety in HEFA which brings the plasticizing effect in the films.

3.4.2 Pencil Hardness

In this test, a strip of the cured film was drawn under a pencil until a hardness grade of pencil was reached to scratch the surface. The coating film was then assigned a hardness value such as H, 2H, 3H etc signifying the hardness grade using Pencil Hardness Tester (Sheen, UK). Results of pencil hardness test are also shown in Table 4.

Coating films of PE-4 has shown high pencil hardness due to higher maleic anhydride content which lead to high degree of crosslinking.

3.4.3 X- Hatch Hardness

It was measured by using cross cut adhesion tester. The tester consists of die made up of 9 parallel blades, 1/16 inches apart & 1 mm long. The die is pressed into the panel in two directions right angles to each other. A strip of self adhesive was staked over the pattern, left in contact for 10 seconds and stripped rapidly by pulling the tape back on itself at an angle of approx. 120°. The test was rated good if less than 5 % of squares were removed.

All the coating films had shown good X-hatch hardness property.

3.4.4 Gloss

It was measured using Triglossometer (Sheen). After watching the films from 60° angle. It had been observed that all the coating films had good gloss. All the coating films had shown good gloss.

3.4.5 Flexibility

Flexibility was carried out on 1/4 inch mandrel bend

Table 5 Chemical resistance properties of the coating films.

S.No.	Chemical	Results			
		PE-1	PE-2	PE-3	PE-4
1.	1.0 N H ₂ SO ₄	C	C	B	A
2.	1.0 N NaOH	A	A	A	A
3.	Distilled water	B	B	B	A
4.	Mineral turpentine oil	A	A	A	A
5.	Methyl ethyl ketone	B	B	B	A
6.	Xylene	A	A	A	A
7.	Ethyl alcohol	B	B	B	B

A-Not affected, B-Loss in gloss, C-Slight softening

tester. Films of all the coatings compositions were flexible enough to pass through the mandrel. (See Table 4)

3.4.6 Impact Resistance

It was measured using Impact Tester. In the measurement, an indenter of low mass is dropped from greater and greater height until the coating on the panel cracks.

The comparison of impact resistance of the films of various compositions reveals that, in general coating films having lower HEFA content have poorer impact resistance, indicating the plasticizing effect of the crosslinking agent in the coating films. The presence of nonpolar fatty acid moiety of the HEFA is thought to improve the film toughness resulting in the high impact resistance.

3.5 Chemical Resistance Properties

3.5.1 Acid resistance

The coating films were immersed in 1.0 N aqueous solution of sulfuric acid upto a period of 2 weeks. The films of PE-1 and PE-2 were highly affected by acid solution due to their alkaline nature, while the films of PE-3, due to their slight alkaline nature had shown only slight loss in gloss. This behaviour of the films can be attributed to the fact that after crosslinking some unreacted hydroxyl groups are present in the coating films. Whereas the films of PE-4 showed high degree of acid resistance indicating the presence of a significant number of free carboxylic acid groups.

3.5.2 Alkali resistance

All the coating films were unaffected by alkali solution when the coating films were immersed in 1.0 N aqueous solution of sodium hydroxide for 2 week.

3.5.3 Water resistance

Resistance to distilled water was found to be greatest at the highest HEFA content. Coating films of PE-1, PE-2 and PE-3 were slightly affected due to moderate polarity because of presence of free hydroxyl groups when they were immersed in distilled water upto a

period of 2 weeks.

3.5.4 Solvents resistance

All the coating films exhibited good solvent resistance when they were immersed in non-polar solvent like xylene and mineral turpentine oil. But when, the coating films were exposed to high polar MEK, slight loss in gloss was observed in PE-1, PE-2, and PE-3. This behaviour of the films might be due to the fact that even after crosslinking, presence of some unreacted functional groups (OH) which lead to develop moderate polarity in coated films. On immersion into ethanol almost all the coating films showed slight loss in gloss due to attack of moderate polar ethanol on moderate polar films. In the coating films of PE-1 loss in gloss alongwith slight softening was observed due to the high polarity in the coating films.

4. Conclusion

Acrylic copolymer was synthesized successfully using methyl methacrylate & maleic anhydride. Hydroxy ethyl fatty amide derived from dehydrated castor oil was also synthesized and was used successfully as cross-linking agent for these acrylic copolymer/resins to get the polyesteramide coatings. The results shows that the mechanical and chemical resistance properties of the films are dependant on the HEFA content of the compositions and an optimum acrylic copolymer/HEFA ratio i.e. PE-4 can be selected to obtain the balanced film properties.

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ポリエステルアミドの合成とコーティング材料への応用に関する研究

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要 旨

本研究では、従来のメラミン硬化樹脂の欠点である高VOC排出の課題を解決するため、熱硬化ポリエステル樹脂をアクリル共重合体とヒドロキシエチル脂肪酸アミド (HEFA) を反応させて調製した。メタクリル酸メチルとマレイン酸無水物をキシレン中で過酸化ベンゾイル (BPO) を開始剤として重合しアクリル共重合体を合成した。この共重合体と HEFA の構造をフーリエ変換赤外分光分析 (FT-IR) により同定した。アクリル共重合体と HEFA の配合量を変化させたポリエステルアミドを調製し、熱重量分析 (TGA) と示差熱量分析 (DSC) によりその熱特性を評価した。その際、155℃で30分焼き付けて硬化塗膜を作製した。その硬化塗膜の光学的、機械的そして化学的耐性を評価し、コーティング材料としての実用性を調査した。