

N-(Carboxymethyl) Trimellitimide-Based Polyesterimides as Film Formers for Air-Drying Protective Coatings*

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SYNOPSIS

N-(carboxymethyl) trimellitimide, the imidodicarboxylic acid, was prepared by the reaction between trimellitic anhydride and glycine. This was subsequently condensed in *N*-methyl-2-pyrrolidone with the alcoholysis products obtained from linseed oil and glycerine to get different oil length polyesterimide resins. The drying characteristics of the resins and the physicochemical properties of the clear and the iron oxide pigmented coatings were evaluated. The results indicate that these materials form a promising class of film—formers for coatings of good durability and protective properties.

INTRODUCTION

In the search for new air-drying binders for protective coatings, a few disclosures have been made mostly in the patent literature of oil-modified polyesterimide resins as potential film formers.¹⁻⁴ The ultimate performance of the coatings based on oil-modified resin binders depends on the balance between olefinic hydrocarbon units of the fatty acid of the oil, which are responsible for the film formation due to autooxidation, and the functional groups along the polymer chains, which are necessary for anchoring on substrates to be protected. It was therefore planned to synthesise air-drying polyesterimide resins by effecting variation in the polymer chains involving olefinic hydrocarbon units, ester-imide linkages, and other pendant polar groups. For this, the concept of oil length, which is generally used in formulating oil-modified polymeric materials, such as alkyd resins, was used in the synthesis of the polyesterimide resins from *N*-(carboxymethyl) trimellitimide, linseed oil, and glycerine. In order to retain air-drying properties, the synthesis was restricted to only 60, 65, and 70% oil length resins. The physicochemical properties of their

coatings, both clear and pigmented with iron oxide, were studied to evaluate them as binders for protective air-drying coatings.

EXPERIMENTAL

Materials

Trimellitic anhydride: practical grade, Fluka.

Glycine: chemically pure grade, LOBA-CHEMIE.

Linseed oil: alkali refined grade, acid value 0.5, specific gravity 0.931.

Glycerine: chemically pure grade, B.D.H., specific gravity 1.265, boiling point 290°C.

N-methyl-2-pyrrolidone: chemically pure grade, Sisco Laboratories, specific gravity 1.039, boiling point 202°C.

Xylene: commercial grade, boiling point 137–141°C.

White spirit: distilled, boiling point 150–200°C.

Iron oxide: natural, specific gravity 5.2.

Methods

Synthesis of Imido-dicarboxylic Acid: N-(carboxymethyl) Trimellitimide

Trimellitic anhydride [192 g (1 mol)] and glycine [75 g (1 mol)] were taken in a 500-mL round-bottom flask equipped with a mechanical stirrer, thermometer, and air condenser. To this, 75 mL of *N*-methyl-

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Schematic of monomer synthesis

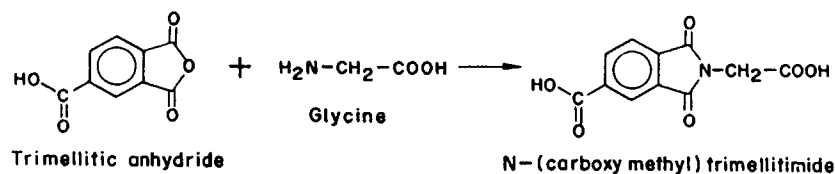


Figure 1 Schematic of monomer synthesis.

2-pyrrolidone was added and the mixture stirred for 3 h at room temperature. Thereafter, the temperature was slowly raised to 180°C and maintained there for 4 h. Then the reaction mixture was poured into 1000 mL of distilled water when *N*-(carboxymethyl) trimellitimide precipitated out. The acid was purified by repeated washing with distilled water, dried at 60°C under vacuum, and recovered. (Yield was 75%.) The schematic of monomer synthesis is given in Figure 1.

Synthesis of Polyesterimide Resins

A set of three oil-modified polyesterimide resins (60, 65, and 70% oil lengths) (Table I) was prepared by the reaction between *N*-(carboxymethyl) trimellitimide, glycerine, and linseed oil as described in what follows.

The calculated amounts of linseed oil, glycerine, and litharge as catalyst were taken in a 2-L round-bottom flask equipped with a mechanical stirrer, a thermometer, a nitrogen inlet tube, and a Dean and Stark trap. The temperature of the reaction mixture was slowly raised to 240 ± 2°C and maintained there until the product was found to be soluble in four times its volume of methanol, which is an indication of completion of glycerolysis reaction. A small sam-

ple was withdrawn at this stage and its composition analyzed. The reaction mixture was then cooled to about 100°C and to this *N*-methyl-2-pyrrolidone and *N*-(carboxymethyl) trimellitimide were added. *N*-methyl-2-pyrrolidone was added in about 15% of the weight of the dicarboxylic acid. The temperature was again raised to about 135°C and xylene (5% of the total contents of the flask) was added. The esterification reaction was carried out at temperatures between 170 and 230°C at the rate of increase of 15 degrees per hour. After the theoretical amount of water was collected, the solvents were distilled off under vacuum and the temperature was further raised to 240°C to effect the bodying of the product until a cool bead of it on a glass plate gave a string of 16–18 in. The schematic of polymer synthesis is given in Figure 2.

Characterization of *N*-(carboxymethyl) Trimellitimide

The IR spectrum of the product was recorded as KBr pellets using Perkin-Elmer model 882 infrared spectrophotometer. The ¹H nuclear magnetic resonance (NMR) spectrum was obtained in DMSO-D₆ by using an 80-MHz NMR spectrophotometer. The mass spectrum was recorded in a VG Micromass 70-

Table I Compositions and Characteristics of Polyesterimide Resins

Oil Length of Polyesterimide Resins (%)	Composition of Polyesterimide Components			Characteristics of Polyesterimide Resins						Drying Time	
	Oil (g)	Glycerine (g) ^a	<i>N</i> -(Carboxymethyl)-trimellitimide (g)	Acid Value ^b	Hydroxyl Value ^c	Density 25°C (g/cm ³)	\bar{M}_n	\bar{M}_w	Dispersity (MWD)	Surface dry (h)	Through dry (h)
70	700	73.77	272	8.8	30.1	1.071	1540	3244	2.11	1	10
65	650	85.8	317	10.1	34.5	1.083	1668	3812	2.28	$\frac{3}{4}$	9
60	600	98.4	363	21.4	42.5	1.100	1944	4181	2.14	$\frac{3}{4}$	8

^a The weight includes 10% excess over theoretical amount.

^b Milligrams of KOH per gram of material.

^c Milligrams of KOH equivalent to the hydroxyl content.

Schematic of polyesterimide synthesis

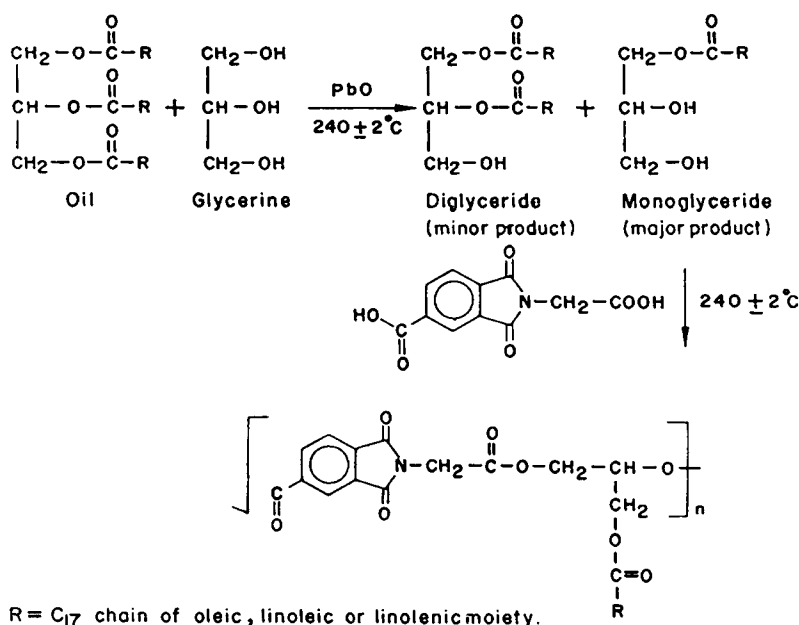


Figure 2 Schematic of polyesterimide synthesis.

70 H mass spectrophotometer at 70 eV and trap current of 200 μA with a source temperature of 180°C.

Characterization of Polyesterimide Resins

The acid and hydroxyl values of the resins were determined by the procedures described in the American Society for Testing and Materials ASTM-D-1639-61 and ASTM-D-1957-61-T, respectively. The molecular weights (\bar{M}_n and \bar{M}_w) were determined by gel permeation chromatography (GPC) using Water Associates model ALC/GPC 204 with μ -styragel columns 1000, 500, 200, 100 Å pore sizes connected in series. Tetrahydrofuran was used as eluant with a flow rate of 1.5 mL/min. The IR spectra were recorded in CHCl_3 solution in a Perkin-Elmer IR spectrophotometer and NMR spectra in CDCl_3 in a 300-MHz NMR spectrophotometer.

Composition of the Glycerolysis Products

The compositions of the glycerolysis products, i.e., the partial glycerides used as polyols in the synthesis of polyesterimide resins (Table II), were determined by the thin-layer chromatography-flame ionization detection (TLC-FID) technique reported by the authors.⁵

Preparation of Polyesterimide Coatings and Their Evaluation

Preparation of Paints

A set of paints of different pigment volume concentrations (PVCs), ranging from 0 to 60% PVC of natural iron oxide pigment, was formulated using each polyesterimide resin as a binder. Paints were

Table II Compositions of the Glycerolysis Products of Different Oil Length Polyesterimides by TLC-FID

Oil Length of Polyesterimide (%)	Reaction Equilibrium Time (s)	Components of Glycerolysis Products (wt %)					Glycerine (Free)
		Triglycerides	1,3-Diglycerides	1,2-Diglycerides	1-Mono-glycerides		
70	75	8.4	31.1	8.2	50.2	2.1	
65	60	7.8	26.2	9.7	53.4	2.9	
60	45	6.6	20.7	11.2	55.6	5.9	

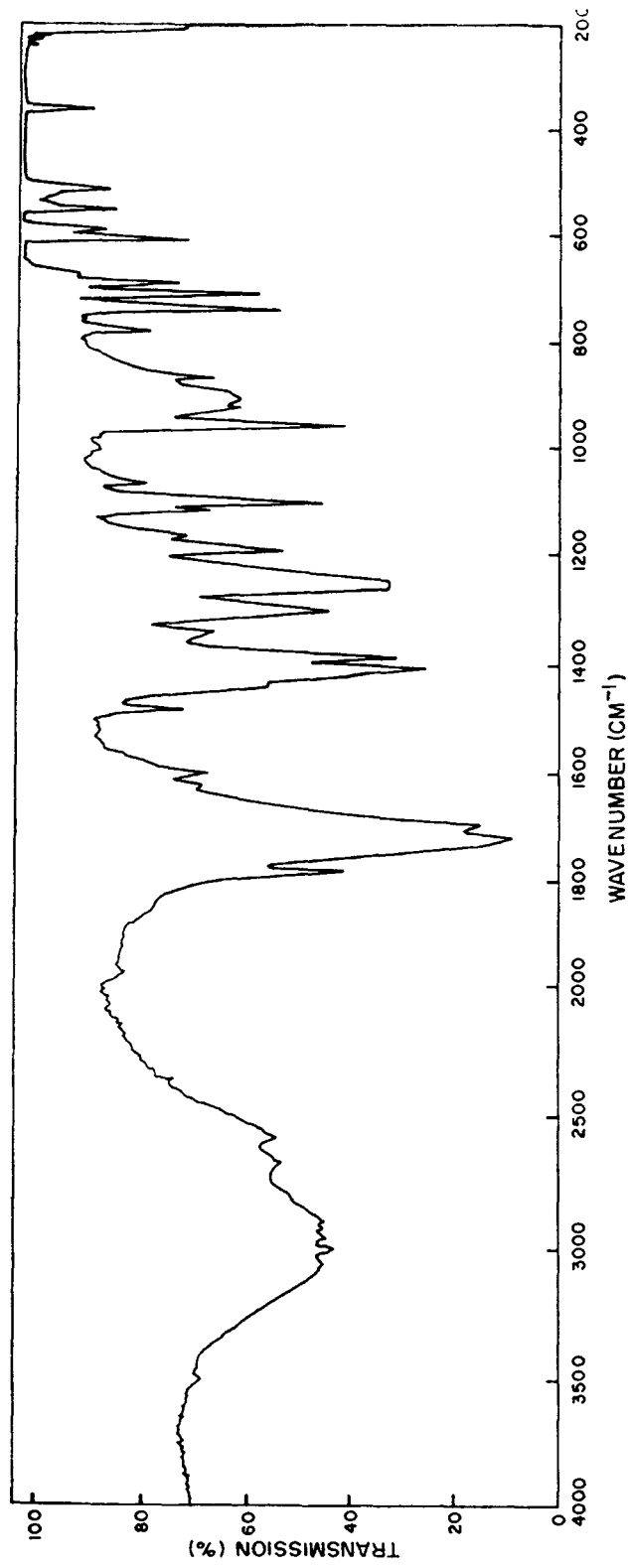


Figure 3 Infrared spectra of *N*-(carboxymethyl) trimellitimide.

prepared by grinding in Red Devil dispersing unit to Hegman gauge 7-8 the calculated amounts of pigment and resin in solvent system consisting of xylene and white spirit (1 : 1, v/v). The driers (zirconium octate, calcium octate, and cobalt naphthenate) were added in requisite quantities, and the paints were thinned with sufficient amount of the solvents to get the consistencies suitable for application with different coating techniques.

Physicochemical Properties of Coatings. In order to evaluate the film-forming characteristics and protective performance of the polyesterimide coatings, the following properties were studied. For the evaluation of the unpigmented resin coatings, 50% solutions of the resins in xylene-white spirit (1 : 1, v/v) were used.

Drying Time. The drying characteristics of the coatings were studied on glass panels using a B.K. drying time recorder at ambient conditions.

Scratch Hardness. The scratch hardness of the coatings (40-50 μm) on mild steel panels (150 \times 100 \times 0.9 mm) obtained by brushing and air drying for a week at ambient conditions was determined using the Erichsen model 601 scratch hardness tester.

Adhesion. Adhesion of the coatings of 40-50 μm thick obtained by the spin coating technique on mild steel discs (32 mm diameter, 0.9 mm thick) and air drying for a week was determined using a Hounsfield tensometer.⁶

Tensile Strength and Percentage of Elongation. The tensile strength and percentage of elongation of the free films obtained by the amalgamation technique⁷ were determined by the procedure described in ASTM-D-2370-73 using an Instron tensile tester.

Toughness. The toughness, which is a measure of the energy required to deform the film up to the point of rupture during a tensile measurement and is equal to the area under the stress-strain curve,⁸ was calculated using the following relationship:

$$\text{Toughness} = \frac{1}{2} \times \text{tensile strength (kg/cm}^2\text{)} \\ \times \text{elongation (cm)}$$

Impact Resistance. The impact resistance of the films on mild steel panels (150 \times 100 \times 0.9 mm) obtained by brush coating and drying for a week was measured by a falling-weight-type impact tester using 10.5 lb weight fixed at a height of 23 in.

The results of the preceding tests are summarised in Table II.

RESULTS AND DISCUSSION

Characterization of Imidodicarboxylic Acid

N-(carboxymethyl) trimellitimide, the imido dicarboxylic acid, is a white crystalline powder with a melting point of 249°C. The IR spectrum of the product (Fig. 3) shows the bands at 1785 and 1700 cm^{-1} , which are characteristic of the cyclic five-membered imide ring. The bands at 1650 and 3000 cm^{-1} account for C=O and OH stretching of the carboxyl groups. Thus the IR spectral analysis of the product satisfies the structure assigned to *N*-(carboxymethyl) trimellitimide. The data of ^1H NMR and mass spectra that follow also support this structure: the ^1H NMR spectrum (ppm), 8.40 (t, 2H), 8.14 (d, 1H), 4.26 (s, 2H); the mass spectrum EI (M/Z), 249 (M^+ , 2%), 204, 177, 148, 120, 103.

Characterization of Polyesterimides

The polyesterimide resins of 60, 65, and 70% oil lengths were pale-colored viscous liquids. Densities

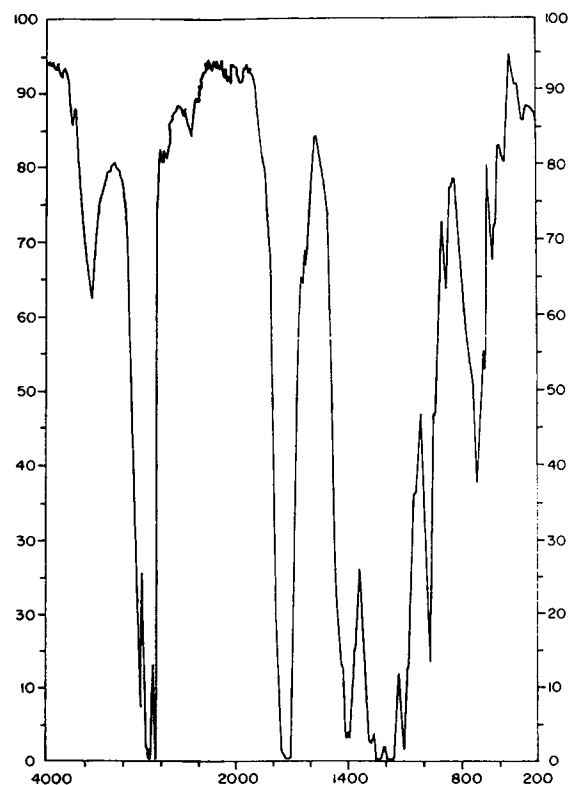


Figure 4 Infrared spectrum of 65% oil length polyesterimide.

and molecular weights (both \bar{M}_n and \bar{M}_w) are found to be in increasing order with decreasing oil length of the resins (Table I). However, there is very little difference in the molecular weight distribution of different oil length resins. The increasing molecular weight with decreasing oil length of the resin can be attributed to the higher content of monoglycerides in the glycerolysis products, the intermediates in the polyesterimide synthesis (Table II).

The IR spectra of all the resins were found to be qualitatively identical. In the IR spectrum (Fig. 4) of 65% oil length polyesterimide, the imide band is found to be merged with the strong band of ester groups in the region of about 1730 cm^{-1} . The presence of a C—O—C bond of the ester group is confirmed by the peak appearing in the region $1172\text{--}1240\text{ cm}^{-1}$.

The chemical shifts tabulated in Table III for various types of protons of the polyesterimide resin

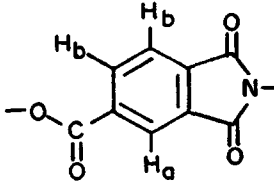
of 65% oil length also account for the general structure assigned to polyesterimide (Fig. 2).

Physicochemical Properties of Polyesterimide Coatings

The results given in Table IV and Figure 5 show that all the resins synthesised possessed excellent drying properties, the lower oil length resin being slightly faster drying than that of the corresponding longer oil length. It can be noticed in Figure 5 that the drying time of each resin does not change much when they are pigmented up to the levels of pigmentation of 20% PVC. However, drastic reduction in drying time can be observed when level of pigmentation of the resins is above 20% PVC.

Adhesion of the polyesterimide coating varies with the composition of the resin binder: the lower the oil length of polyesterimide, the higher the

Table III Chemical Shifts δ of Various Protons in the Structure of 65% Oil Length Polyesterimide

Group	δ (ppm)	Proton Type	Origin
—CH ₃	0.96	Terminal methyl	Fatty acid
—CH ₂ —	1.25	Methylene	Fatty acid
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—CH}_2\text{—CH}_2\text{—C—O} \end{array}$	1.6	β -Methylene to carbonyl	Fatty acid
—CH ₂ —C=C—	2.02	Monoallylic	Fatty acid
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—CH}_2\text{—C} \end{array}$	2.33	α -Methylene to carbonyl	Fatty acids
$\begin{array}{c} \text{O} \\ \parallel \\ \text{N—CH}_2\text{—C—} \end{array}$	4.26	α -methylene to imide	<i>N</i> -(carboxymethyl) trimellitimide
—CH=CH—CH ₂ —CH=CH—	2.81	Diallylic	Fatty acids
$\begin{array}{c} \text{CH}_2\text{—O—} \\ \\ \text{CH—O—} \\ \\ \text{CH}_2\text{—O—} \end{array}$	3.5–4.5	—	Glycerol
—CH=CH—	5.35	Olefinic	Fatty acids
	7.45	Aromatic	<i>N</i> -(carboxymethyl) trimellitimide
	—8.02 ^a		
	8.20 ^b	Aromatic	<i>N</i> -(carboxymethyl) trimellitimide

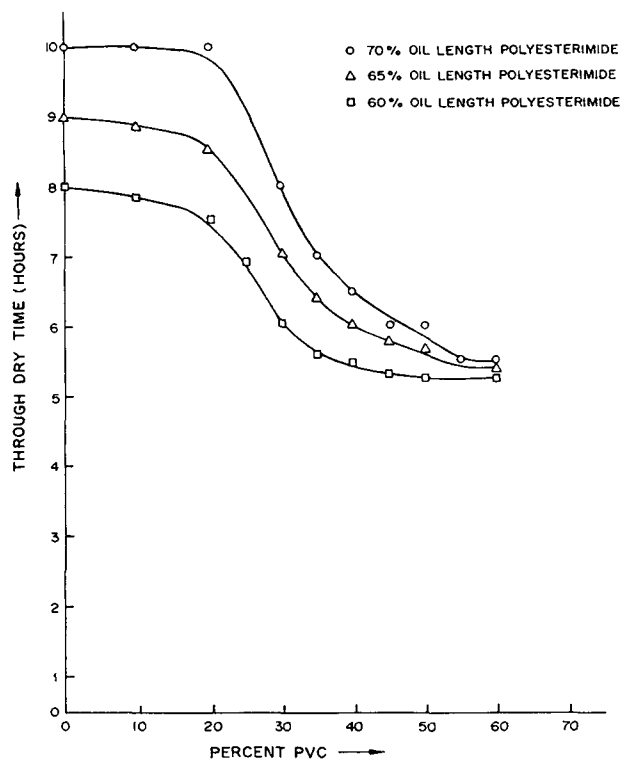


Figure 5 Drying time of polyesterimide-iron oxide coatings of different PVCs.

adhesion of its coating (Table IV). The higher bond strength of the lower oil length resin coating could be attributed to the longer polymer chains with higher proportion of adhesion promoting polar functional groups like carboxyl, hydroxyl, imide, and

esters in lower oil length resin when compared with the corresponding higher oil length polyesterimide resin binders. The bond failure of the unpigmented polyesterimide coatings were found to be mostly cohesive type, indicating that the adhesive strength of the coating is much higher than the fracture value recorded (Table IV). It can also be seen in Table IV that for each polyesterimide resin binder there is a critical level of pigmentation of the paint formulation at which the highest value for bond strength was obtained. Such levels of pigmentation, called critical pigment volume concentration (CPVC), are found to be around 30, 35, and 40% PVC of iron oxide for 60, 65, and 70% oil length polyesterimide resin binders, respectively, and the fracture values of these systems are approximately 364, 336, and 315 kg/cm² respectively. The bond failure of the critically pigmented systems was mostly adhesive type.

The values of scratch hardness and tensile strength of iron oxide-polyesterimide coating systems recorded in Table IV are also found to be in the same order as that of adhesion values of both the unpigmented and pigmented coating systems. The CPVCs determined from the measurement of these properties are found to be similar to those determined from adhesion property.

The values recorded in Table IV show that the coatings obtained from 60% oil length resin binder were far superior in toughness to those derived from 65 and 70% oil length polyesterimide resins. Also the lower level of pigmentation of each binder was found to enhance the toughness of coatings, but with

Table IV Physicochemical Properties of Polyesterimide-Iron Oxide Coatings for Oil Lengths of 60, 65, and 70%^a

PVC (%)	Practical Adhesion ^b (kg/cm ²)			Tensile Strength ^b (kg/cm ²)			Scratch Hardness ^c (g)			Toughness ^b (kg/cm ¹)		
	60%	65%	70%	60%	65%	70%	60%	65%	70%	60%	65%	70%
0	284	275	251	94 (95)	38 (61)	28 (50)	1300	1150	900	223	58	35
10	290	287	262	140 (84)	123 (55)	68 (48)	1300	1125	925	294	170	82
20	326	297	271	164 (59)	152 (41)	100 (30)	1350	1175	950	242	155	75
30	364	309	276	189 (30)	164 (20)	114 (20)	1375	1200	1000	142	82	57
35	347	336	294	177 (21)	173 (12)	117 (14)	1350	1225	1000	93	52	40
40	315	282	315	160 (11)	150 (10)	120 (8)	1350	1200	1025	44	37	24
45	215	222	200	100 (9)	114 (8)	81 (6)	950	1050	1000	22	20	12
50	180	165	160	80 (6)	54 (6)	44 (5)	800	875	950	12	8	5
60	122	120	86	50 (6)	44 (4)	13 (5)	750	700	650	8	4	3

^a Values in parentheses indicate percentage of elongation.

^b Average value of 10 test samples.

^c Average value of 5 test samples.

higher pigmentation level, particularly above 10% PVC, the toughness of the coating decreases rapidly. However, it can be seen that elongation drops rapidly as the pigmentation level increases. All the polyesterimide coatings exhibited good impact resistance.

CONCLUSIONS

1. *N*-(carboxymethyl) trimellitimide is a novel functional monomer for the synthesis of air-drying polyesterimides.
2. By using the concept of oil length, the polyesterimide resins with a wide range of film-forming properties can be synthesised as binders for air-drying protective coatings from *N*-(carboxymethyl) trimellitimide.

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