Studies on Urethane-Modified Alumina-Filled Polyesteramide Anticorrosive Coatings Cured at Ambient Temperature

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ABSTRACT: Coatings prepared from polyesteramide resin synthesized from linseed oil, a renewable resource, have been found to show improved physicomechanical and anticorrosive characteristics. These properties are further improved when aluminum is incorporated in the polyesteramide resin. The coatings of this resin are generally obtained by baking at elevated temperatures. With a view toward the use of linseed oil, as a precursor for the synthesis of polyesteramide resins and to cure their coatings at ambient temperature, toluylene diisocyanate (TDI) was incorporated into polyesteramide and alumina-filled polyesteramide in varying proportions to obtain urethane-modified resins. The latter resins were found to cure at room temperature. The broad structural features of the urethane-modified polyesteramide and alumina-filled polyesteramide were confirmed by FTIR and ^{1}H–NMR spectroscopies. Scratch hardness; impact resistance; bending resistance; specular gloss; and resistance to acid, alkali, and organic solvents of the coatings of these resins were determined by standard methods. Physicomechanical and anticorrosive properties, specular gloss, and thermal stability of the urethane-modified alumina-filled polyesteramide coatings were found to be at higher levels among these resins. It was found that TDI could be incorporated in polyesteramide up to only 6 wt %, such that above this loading its properties started to deteriorate, whereas alumina-filled polyesteramide could take up to 10 wt % TDI. Explanation is provided for the increase in scratch hardness and impact resistance above 6 and 10 wt % addition of TDI in polyesteramide and alumina-filled polyesteramide, respectively, as well as for the decrease in flexibility and resistance to solvents, acid, and alkali of coatings of these resins above these limits of TDI addition. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1855–1865, 2001

Key words: coatings; polyesteramide; alumina; urethane; curing

INTRODUCTION

Polyesteramide resins are amide-modified alkyds that have improved characteristics over normal alkyds in terms of hardness, ease of drying, and water vapor resistance.[1–3] Generally, polyesteramide coatings are obtained by baking at and above 175°C.[4,5] To improve the physicomechanical and anticorrosive characteristics of baked coatings, we incorporated aluminum in the backbone of the polymer.[6] We found that the aforementioned properties of the coatings were enhanced appreciably in the case of alumina-filled polyesteramides.[6] Curing of the polyesteramide at elevated temperature is a multistep process and is also energy consuming. It is, therefore, desirable to develop a simple curing route operative at ambient temperature to produce

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Table I Characterization of Oil, HELA, PEA, and APEA

Characteristic	Linseed Oil	HELA	PEA	APEA
Acid value (mg KOH)	8.3	—	7.0	6.12
Hydroxyl value (%)	0.3	—	7.87	14.98
Saponification value	160	136	128	118
Iodine value	181	86	48	20
Specific gravity	0.896	0.926	0.938	0.976
Refractive index	1.478	1.497	1.507	1.543
Inherent viscosity (dL/g)	—	—	0.652	0.680
Linoleic acid (%)	14	—	—	—
Linolenic acid (%)	44	—	—	—
Oleic acid (%)	20	—	—	—

coatings of improved physicomechanical and anticorrosive properties compared to high-temperature baked coatings of polyesteramide and alumina-filled polyesteramide. It was previously reported that toluylene diisocyanate (TDI) can be used for curing aromatic polyesteramide at room temperature.[7,8]

The presence of a urethane linkage in the polyesteramide has been found to considerably enhance the performance of these coatings in terms of adhesion, toughness, weather resistance, and chemical/solvent resistance.[9] Polyurethane resins as a class are well recognized for their excellent adhesion, ambient-temperature curing, flexibility, weather resistance, and resistance to solvent and chemical attack.[10] In our earlier work we attempted to prepare alumina-filled polyesteramide from linseed oil, used as a precursor of renewable nature. In this work we have attempted to obtain urethane-modified polyesteramide using TDI with the double objective of using a precursor obtained from a renewable resource and of enhancing the physicomechanical and anticorrosive properties of the coatings of these resins through curing at room temperature. A survey of the literature reveals that modifications of polyesteramide by butylated melamine formaldehyde,[11] styrene,[12] and also by metals[6] have been attempted. However, no work has been reported on the modification of alumina-filled polyesteramide synthesized from a vegetable oil by urethane.[13–15] We report our findings on the above investigations in this communication.

EXPERIMENTAL

Materials

Oil was extracted from linseed (procured from a local market) through Soxhlet apparatus. Petroleum ether was used as a solvent. The fatty acid composition of the oil was determined by gas chromatography (GC; 111/8 s.s. column, FID detector) (Table I). Phthalic acid, sodium methoxide, aluminum hydroxide, xylene, toluylene-2,4 diisocyanate (Merck, India and Germany), and diethanolamine (S.D. Fine Chemicals, India) were of analytical grade.

Synthesis

Synthesis of Polyesteramide (PEA) and Alumina-Filled Polyesteramide (APEA)

PEA and APEA were prepared according to a previously reported method.[6]

Synthesis of Urethane-Modified Polyesteramide (PEAU) and Alumina-Filled Polyesteramide (APEAU)

Polyesteramide and alumina-filled polyesteramide were dissolved in xylene and treated with varying amounts of toluylene-2,4 diisocyanate in a four-neck round-bottom flask fitted with a nitrogen inlet, a thermometer, and a stirrer. The extents of loading of TDI (in wt %) in PEA and APEA are provided in Table II. The reaction was carried out under stirring at 145 ± 5°C. The progress of the reaction was monitored by thin layer chromatography (TLC) as well as by hydroxyl value determination. The solvent was removed from PEAU and APEAU in a rotatory vacuum evaporator.

Characterization

PEAU and APEAU were characterized by FTIR and ^{1}H–NMR spectroscopies. FTIR spectra of these polymers were taken on Perkin–Elmer 1750 FTIR spectrophotometer (Perkin Elmer Cetus In-

Table II Characterization of Polyesteramide Urethane and Alumina Filled Polyesteramide Urethane

Resin Code[a]	Acid Value (mg KOH)	Hydroxyl Value (%)	Saponification Value	Iodine Value	Specific Gravity	Refractive Index	Viscosity[b] (dL/g)
PEAU-2	6.22	5.12	118	44	0.942	1.512	0.668
PEAU-4	6.08	4.98	110	42	0.948	1.515	0.678
PEAU-6	5.78	4.86	103	39	0.960	1.520	0.697
PEAU-8	5.62	4.42	101	36	0.968	1.522	0.730
APEAU-2	5.49	12.36	96	17	0.979	1.549	0.728
APEAU-4	5.38	11.95	92	14	0.980	1.568	0.732
APEAU-6	5.13	10.67	84	13	0.981	1.572	0.736
APEAU-8	5.10	10.21	83	12	0.983	1.574	0.742
APEAU-10	5.02	10.08	80	10	0.986	1.576	0.752

[a] Last digit of resin code indicates the wt % of TDI.
[b] Inherent viscosity.

struments, Norwalk, CT) using a NaCl cell. ^{1}H–NMR spectra were recorded on a JEOL 300 MHZ FX-1000 spectrometer (JEOL, Peabody, MA) using deuterated chloroform and tetramethyl silane (TMS) as an internal standard. The solubility of these polymers was tested in various organic solvents. The intrinsic viscosity of PEA, APEA, PEAU, and APEAU in *N,N*-dimethyl pyrollidone (stock solution: 5 g/100 mL solvent) at 25°C was determined with the help of a Ubbelhode viscometer. Iodine value and hydroxyl value were determined by ASTM method D555-6. Specific gravity and refractive index were determined by standard laboratory methods.

Preparation and Testing of Coatings

Coatings of PEAU and APEAU, cured at ambient temperature, were prepared by brush technique using a solution containing 40 wt % urethane-modified polymer in xylene on commercially available mild steel strips 30 × 10 × 1 mm, for chemical resistance test, and 70 × 25 × 1 mm strips for the determination of specular gloss at 60° [by gloss meter (model RSPT-20; Digital Instruments, Santa Barbara, CA)], scratch hardness (BS 3900), bending test (ASTMD 3281-84), and impact resistance (IS:101 part 5/sec. 3, 1988). Coating thickness was measured by Elcometer (model 345; Elcometer Instruments, Manchester, UK). The thickness of these coatings was found to be between 130 and 160 μm. Dry-to-touch and dry-to-hard times were also determined (Table III). Corrosion tests were performed in water, acids (5 wt % HCl, 5 wt % HNO_3), alkali (5 wt % NaOH), and xylene by placing them in 3″-diameter porcelain dishes and dipping the coated samples in the aforementioned media. Periodic examination was conducted until the coatings showed evidence of softening or deterioration (Table III). Salt-spray tests (ASTM B 117-94) were also carried out for a period of 10 days in a mist salt chamber.

RESULTS AND DISCUSSION

Figure 1 represents the FTIR spectra of PEA and APEA and Figure 2 represents the FTIR spectra of PEAU and APEAU. The ^{1}H–NMR spectra of PEAU and APEAU are presented in Figures 3 and 4, respectively. Figure 5(a) shows the reaction scheme of HELA [*N,N*-bis(2-hydroxy ethyl) linseed fatty amide] with phthalic acid to form polyesteramide; Figure 5(b) shows the formation of alumina-filled polyesteramide. Figure 5(c) and (d) represent the scheme of formation of urethane-modified PEAU and APEAU.

Comparison of PEA and APEA Structures

On perusal of FTIR and ^{1}H–NMR peaks data (Table IV) we notice that the OH stretching peak in PEA appears as a shoulder at 3400 cm^{-1} in the IR spectra. In the case of APEA the peak is broad and is spread over 3120–3650 cm^{-1} because of the presence of the OH group attached to aluminum in APEA. The C=O peak in PEA appears at 1725 cm^{-1}, whereas in APEA it appears at 1760 cm^{-1}, attributed to the presence of aluminum in the chain. ^{1}H–NMR spectra of PEA show the peak of OH of carboxyl at δ 7.92 ppm. This peak is absent in APEA, thus verifying elimination of the

OH group of carboxyl on interaction with $Al(OH)_3$. The above observation confirms the incorporation of alumina in APEA. The ^1H–NMR peak of the CH_2 group adjacent to ester in PEA is sharp and pronounced (δ 2.0 ppm). This peak is suppressed and shifted slightly downfield (δ 2.29–2.30 ppm) in APEA because of the presence of aluminum in the chain. The peak for CH_2 attached to amide is observed at δ 1.58 ppm in PEA as well as in APEA. The peak for the aliphatic chain is observed at δ 1.29 ppm for PEA. In the case of APEA it is present at δ 1.25 ppm. These observations broadly confirm the structures of PEA and APEA, as shown in Figure 5(a) and (b).

Table III Film Properties of Ambient Cured Polyesteramide Urethane and Alumina-Filled Polyesteramide Urethane

Resin Code	Drying Time (min)		Scratch Hardness (kg)	Impact Resistance [lbs/in. (passes)]	Gloss at 60°C	Bending $\frac{1}{8}''$	Corrosion Resistance[a]				
	Dry to Touch	Dry to Hard					H_2O (10 days)	NaOH (5%) (3 h)	HCl (5%) (10 days)	NaCl (3.5%) (10 days)	Xylene (10 days)
PEAU-2	30	45	1.70	100	120	Passes[b]	d	a	b	a	c
PEAU-4	20	40	1.90	100	130	Passes	e	a	c	c	e
PEAU-6	20	40	2.10	100	130	Passes	e	a	c	c	e
PEAU-8	20	40	2.20	100	130	Fails	e	a	c	c	e
APEAU-2	25	40	1.85	150	135	Passes	e	a	c	c	e
APEAU-4	20	35	2.20	150	148	Passes	e	b	e	d	e
APEAU-6	15	30	2.60	150	160	Passes	e	c	e	d	e
APEAU-8	15	30	2.70	150	160	Passes	e	c	e	d	e
APEAU-10	15	30	2.75	150	170	Passes	e	c	e	d	e

[a] a = film completely removed; b = film cracked and partially removed; c = loss in gloss; d = slight loss in gloss; e = unaffected.

[b] Passes = coatings adhesion test shows on visible damage.

Comparison of PEA and PEAU Structures

Spectra for PEAU are more spread than those for PEA in the range of 3500–3150 cm^{-1}, showing the overlap of OH and NH groups. In the case of PEA the peak is suppressed and appears as a shoulder at 3460 cm^{-1}, indicating the presence of the OH group only. In PEAU, the NH deformation mode appears at 1557 cm^{-1}. In addition to the terminal methyl group peak of aliphatic chain at δ 0.9 ppm, ^1H–NMR spectra of PEAU show the presence of the methyl group of TDI at δ 2.1–2.24 ppm. The presence of C═O of ester, C—N, benzene ring, and aliphatic chain are confirmed by the appearance of their peaks in the spectra (Table IV). These observations broadly confirm the structures of PEA and PEAU, proposed in Figure 5(a) and (c), respectively. The peak of carboxyl OH at δ 7.9 ppm in PEA does not appear in PEAU. This also verifies the interaction of TDI with carboxyl-terminated PEA and disappearance of the carboxyl group.[16]

Comparison of APEA and APEAU Structures

Perusal of Table IV reveals that APEA shows a broad peak spread between 3650 and 3120 cm^{-1} (centered at 3455 cm^{-1}). APEAU shows well-resolved peaks in this range at 3600, 3460, 3300, and 3150 cm^{-1}. The broadness in the APEA peak may be attributed to the presence of alcoholic OH and OH attached to aluminum. NH stretching peak of the urethane group in APEAU appears at 3460 and 3300 cm^{-1}. The C═O peak in APEA appears at 1760 cm^{-1}, whereas in APEAU this peak shows at 1727 cm^{-1}. The C═O peaks in PEAU (1724 cm^{-1}) and in APEAU (1727 cm^{-1}) could be related to the presence of the urethane group in the chain. We also notice that the ^1H–NMR peak of C═O in APEAU is shifted upfield

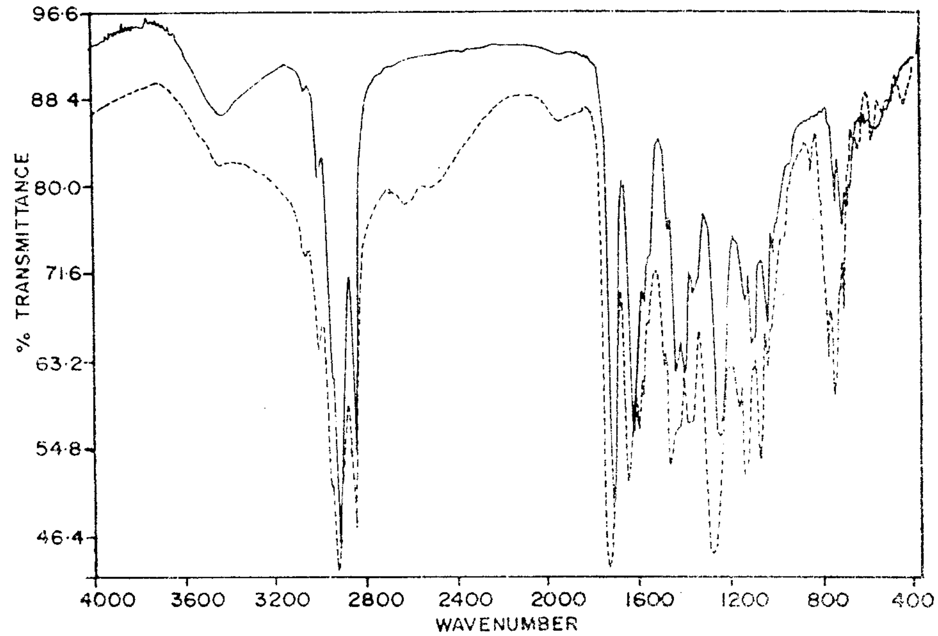


Figure 1 FT-IR of PEA (– – –) and APEA (——).

(from δ 2.3 to δ 2.28–2.31 ppm). This trend is similar to that for the C═O peak in IR spectra of the two polymers. We also find that this peak in APEA is suppressed, whereas in APEAU it is highly pronounced. The intensity of this peak in PEAU and APEAU is almost similar to, but much higher than, that in APEA. These features may be ascribed to the presence of the urethane C═O group. In ^{1}H–NMR spectra of APEAU we observe a peak at δ 2.61–2.65 ppm as in PEAU. This peak is not observed either in PEA or APEA. We attribute this peak to CH_2 adjacent to the urethane carbonyl group. We also observed the IR peaks for the benzene ring, C—N group, C—O—C group, and the ^{1}H–NMR peaks of the aliphatic chain, terminal methyl group of the aliphatic chain, and methyl group of TDI (Table IV). These observations broadly confirm the proposed structure of APEAU as given in Figure 5(d).

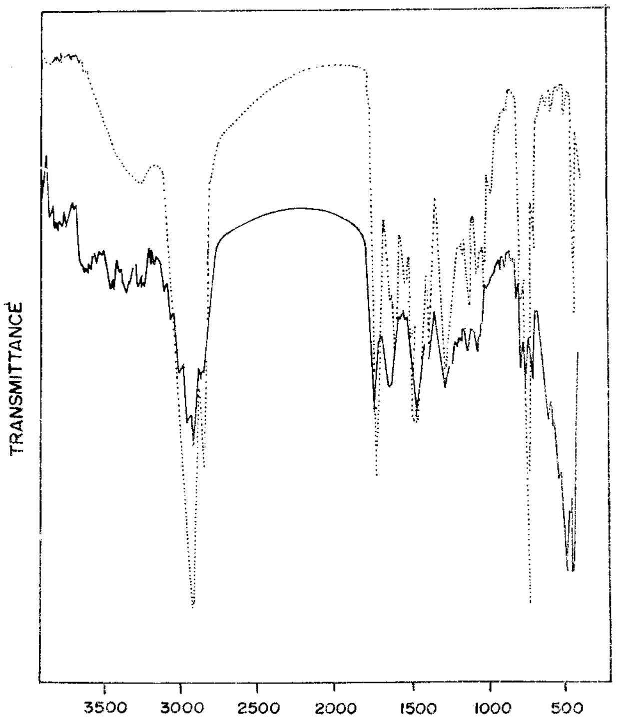


Figure 2 FT-IR of PEAU (– – –) and APEAU (——).

Physicochemical Characteristics of PEAU and APEAU

Tables I and II give the values of some physical and chemical characteristics of PEAU and APEAU along with those of PEA and APEA. We notice that on incorporation of TDI the acid value, hydroxyl value, saponification value, and iodine value all decrease from the respective values in PEA and APEA. This indicates the increase in molar mass on incorporation of TDI in PEA and APEA. The increase in molar mass is also observed from the increase in values of viscosity and specific gravity of PEAU and APEAU. Table II also shows the values of physical and chemical

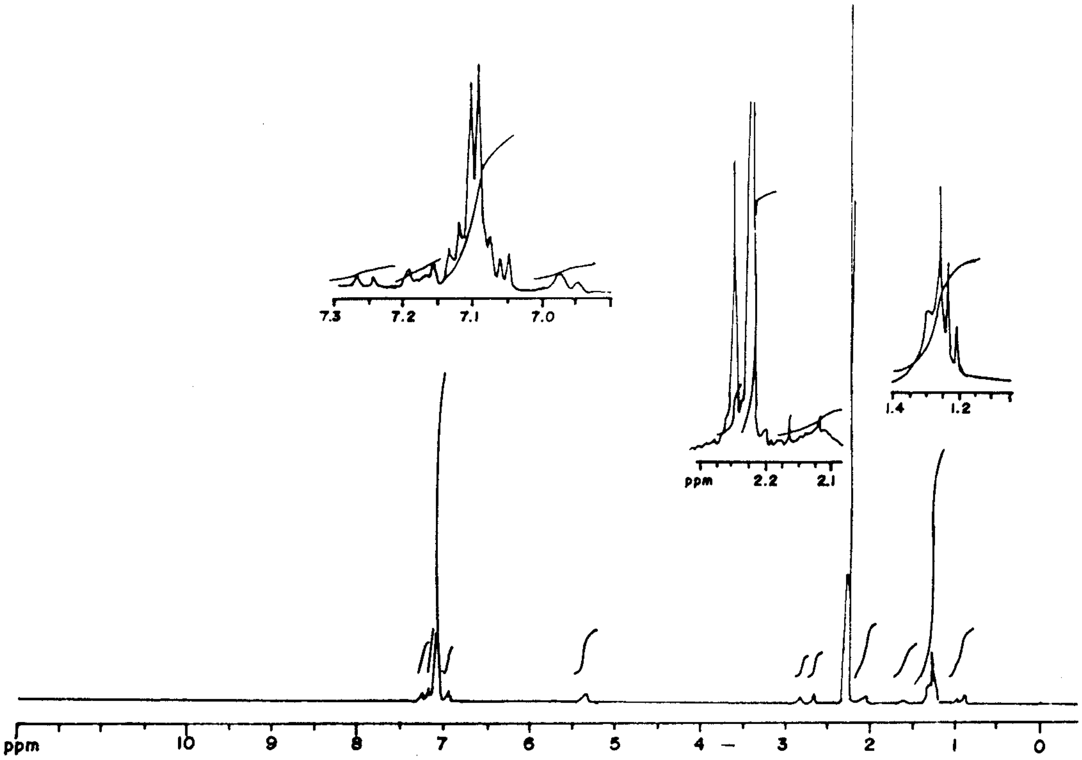


Figure 3 ^{1}H-NMR spectra of PEAU.

characteristics of the resins on incorporation of varying amounts of TDI (2–10 wt %) in PEAU and APEAU. The solubility test below the limit of brushability for these resins shows that PEAU and APEAU are soluble in both polar and nonpolar solvents, unlike PEA, which shows solubility mainly in nonpolar solvents such as toluene, xylene, diethyl ether, carbon tetrachloride, and other such solvents. We presume that the enhanced numbers of polar groups in PEAU and APEAU cause the increase in their solubility.

Coatings of PEAU and APEAU: Mechanical and Chemical Characteristics

On perusal of Table III we observe that PEAU coatings begin to show brittleness above 6 wt % incorporation of TDI in PEA. The films of APEAU remain intact and plastic in nature even up to 10 wt % loading of TDI. We have noticed that in the case of PEAU the resin becomes unbrushable above 6 wt % incorporation of TDI. In the case of APEAU the condensate turns extremely viscous at 10 wt % loading of TDI and above this loading become unbrushable.

The structure of PEA [Fig. 5(a)] shows that PEA has a hydroxyl group at one terminal of the chain and a carboxyl group at the other. TDI reacts with the hydroxyl group to form a urethane group, whereas it reacts with the carboxyl group to establish amide linkage.[17] In PEAU polymer chains, therefore, both the urethane and amide linkages will be present. Our results show that beyond 6 wt % loading of TDI PEAU forms lumpy aggregates, indicating network formation that makes it unbrushable. This may be explained by considering that above this loading percentage, a secondary reaction of TDI with amide groups ensues.[17] The secondary reaction with TDI with urethane groups present in PEAU is almost negligible.[17] In the secondary reaction of TDI with PEAU one of the –NCO group reacts with the labile hydrogen of the amide group present on the polymer chain, whereas the other –NCO group is linked to another amide group present on a neighboring polymer chain. In this manner crosslinking of PEAU chains occurs, which may cause its gelation.

In the case of APEA [Fig. 5(b)] we have already noted that no terminal carboxyl group is present and only the OH group is present at either terminal of the polymer chain. TDI on reaction with APEA, therefore, forms only urethane linkage. Thus on progressive loading of TDI, we may expect that the polymer chain will increase linearly in size with

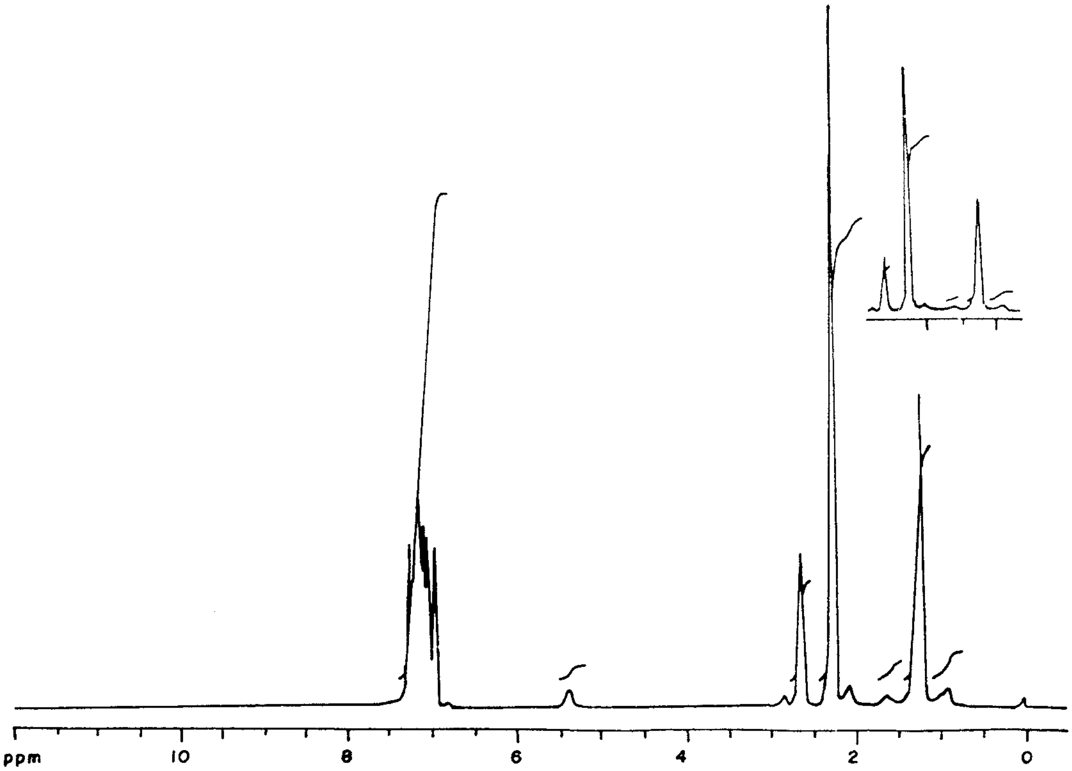


Figure 4 ^{1}H-NMR spectra of APEAU.

little secondary reaction of TDI with urethane groups present on polymer chains. It is worth mentioning that the APEAU does not form lumpy aggregates, indicating that network formation and gelation do not occur in this case, even above 10 wt % addition of TDI, although only its viscosity increases to the extent of loss of flow property.

When left at room temperature PEAU coatings will be cured through the secondary reaction of the moisture with the terminal NCO groups on PEAU polymeric chains[18,19] (ASTM type 2).

It has been observed that scratch hardness of PEAU coatings increases even above 6 wt % loading of TDI. However, above this loading the coatings fail the bending test; even chemical properties of the coatings improve only up to 6 wt % loading of TDI, beyond which concentration deterioration is noticed, such that the coatings are increasingly subject to chemical attack.

The scratch hardness depends on the cohesive force between the polymer chains and, hence, as the size of the PEAU chains increases, the cohesive force between the PEAU polymeric chains also increases, thus enhancing the scratch hardness of the coatings with the increased loading of TDI. Beyond 6 wt % addition of TDI, although the size of the polymer chain still increases, thus generating an increase in scratch hardness, because of the secondary reaction of TDI with the amide groups present on PEAU chains additional crosslinks start to form between the neighboring polymeric chain apart from terminal crosslinks formed between the neighboring chains through moisture curing.[18] The additional crosslinks formed through amide groups produce stiffening in the chains, which not only causes the coatings to fail the bending test but also lowers the chemical resistance of these coatings, as has been observed (Table III).

In the case of APEAU we notice the same effect, that viscosity, scratch hardness, impact resistant, and flexibility all increase with the increased loading of TDI. In this case we found that these properties were higher than those in PEAU. This may essentially be ascribed to the higher molar mass and higher chain length of APEAU, as exhibited by higher viscosity and specific gravity of APEAU condensates.

We have observed that immobility of APEAU condensate above 10 wt % loading of TDI makes it unbrushable. It is interesting to note in this case that, although the viscosity of APEAU condensate at this loading of TDI is extremely high, no lumpy

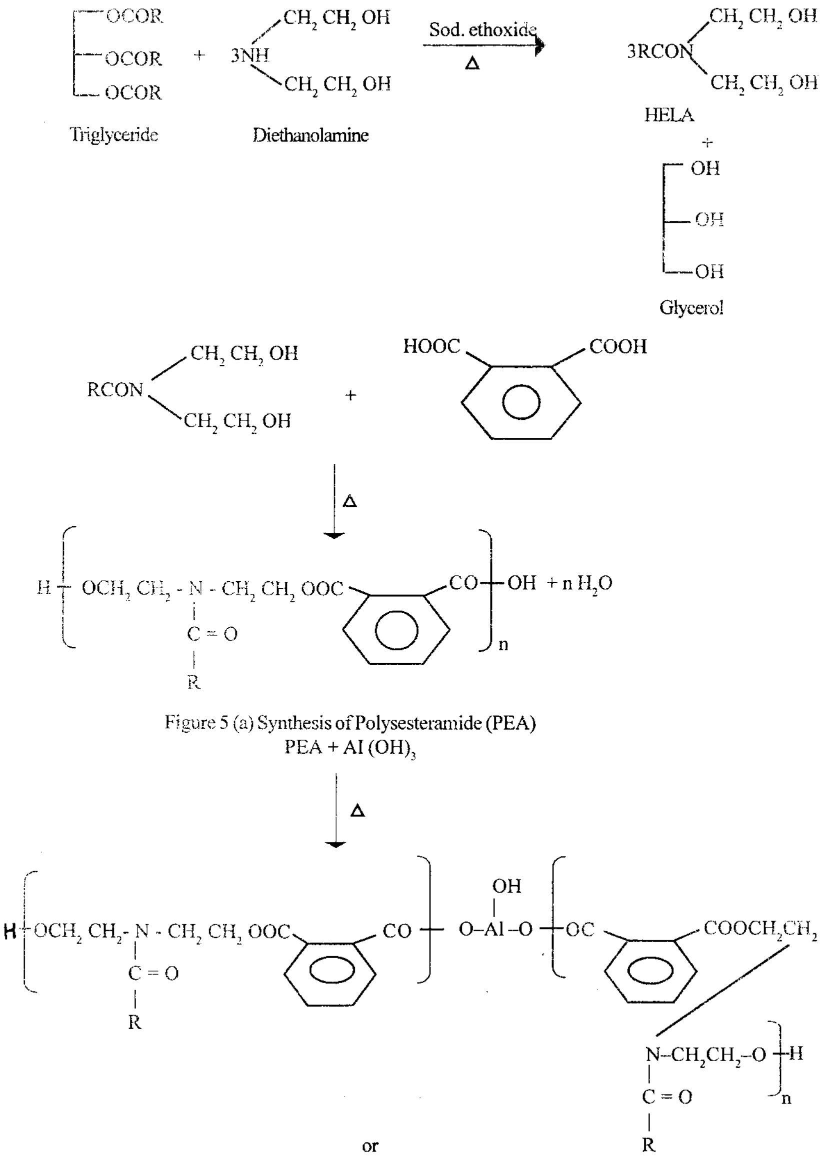
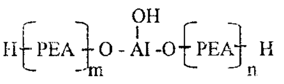


Figure 5 (a) Synthesis of polyesteramide (PEA); (b) synthesis of alumina filled polyesteramide (PEA); (c) synthesis of polyesteramide urethane (PEAU); (d) synthesis of alumina filled polyesteramide urethane (APEAU).

aggregate formation (gelation) occurs, unlike in the case of PEAU. We presume that because of the presence of only the urethane group in the polymer chains, the secondary reaction of TDI with this group is negligible,[17] resulting in nonformation of crosslinks with the urethane groups present on the polymeric chains; thus gelation of the condensate does not occur as in the case of PEAU. On curing of APEAU resins the crosslinks between the polymer chain will be found only at the terminal isocyanate groups of the polymeric chains initiated by reaction with moisture.[18] Because of this behavior coatings of APEAU resin will be more flexible. We have actually observed that APEAU coatings pass the bending test up to 10 wt % loading of TDI. The improved resistivity of these coating to chemical attack can also be attributed to lesser stiffness or stresses in these films because of higher flexibility.

Specular Gloss of PEAU and APEAU Coatings

Table V shows the values of gloss of PEAU and APEAU coatings with 6 wt % loading of TDI at various temperatures. We notice that at ambient



$$H\!\left[PEA\right]_m O-\overset{OH}{\overset{|}{Al}}-O\left[PEA\right]_n H$$

Figure 5 (b) Synthesis of alumina filled Polyesteramide (APEA)

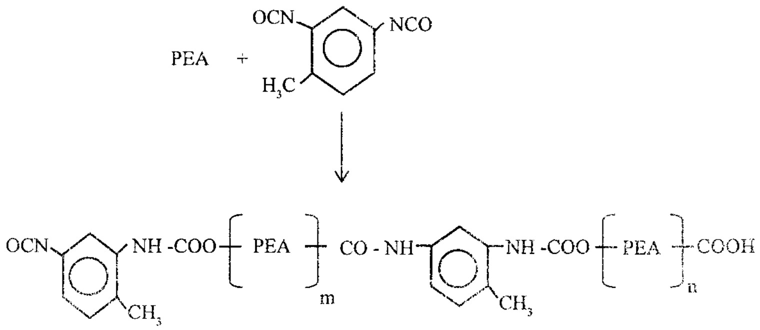


Figure 5 (c) Synthesis of polyesteramide urethane (PEAU)

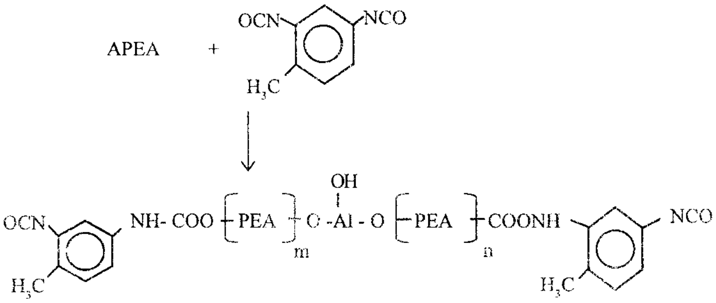


Figure 5 (d) Synthesis of alumina filled polyesteramide urethane (APEAU)
R= Alkyl chain of fatty acid of oil

Figure 5 (*Continued*)

temperature PEAU coatings show a specular gloss of 130 at 60° angle of reflection, whereas APEAU coatings show a far-enhanced specular gloss of 160 at 60° angle of reflection. The gloss decreases with increase in temperature for both PEAU and APEAU coatings. It has been observed that PEAU coatings become brownish at 150°C, whereas APEAU coatings remain stable up to 175°C; only at 200°C does the latter turn brownish. We may infer from the above observation that structural deformation in PEAU starts from 150°C, whereas in APEAU deformation starts from 175°C. The complete charring of PEAU coatings has been found to occur at 250°C, whereas the coatings of APEAU char at 300°C. The above result shows that incorporation of aluminum in polyesteramide significantly enhances gloss along with thermal stability.

CONCLUSIONS

1. Polyesteramide and alumina-filled polyesteramide resins synthesized from linseed oil can be cured at ambient temperature by the incorporation of toluylene diisocyanate.
2. The coatings obtained from PEAU, having up to 6 wt % loading of TDI, exhibit a progressive increase in physicomechanical and anticorrosive properties. However, above 6 wt % loading of TDI, PEAU coatings start to become brittle and their anticorrosive properties also decrease. PEAU resin also becomes unbrushable above 6 wt % loading of TDI.
3. In APEA, TDI can safely be incorporated up to 10 wt % of the resin. APEAU coatings also show progressive increases in physicomechanical and anticorrosive properties up

Table IV FTIR and ^{1}H–NMR Values for Polymeric Resins

	PEA		PEAU		APEA		APEAU	
Functional Group	IR (cm^{-1})	^{1}H–NMR (PPM)	IR (cm^{-1})	^{1}H–NMR (PPM)	IR (cm^{-1})	^{1}H–NMR (PPM)	IR (cm^{-1})	^{1}H–NMR (PPM)
OH (alcoholic)	3460 (shoulder)	δ 5.3	3500–3150 centered at 3285	δ 5.3	3455 (3650–3120)	δ 5.3 (higher intensity)	3600–3150	δ 5.37
OH (carboxyl)	—	δ 7.92	—	—	—	—	—	—
N—H (deformation)	—	—	1557	—	—	—	—	—
C═O (ester)	1725	δ 2.3 (CH$_2$ adjacent to ester)	1724	δ 2.29–2.37 (CH$_2$ adjacent to ester)	1760	δ 2.23 (CH$_2$ adjacent to ester)	1727	δ 2.28–3.31
C═O (amide)	1636	1.58 (CH$_2$ prominent peak attached to amide)	1651	δ 1.58 (CH$_2$ attached to amide)	1660	δ 1.58 (CH$_2$ attached to amide group)	1631	δ 1.58 (CH$_2$ attached to amide)
C═C	1560	δ 2.0 (CH$_2$ attached to C═C)	—	2.03–2.07 (CH$_2$ attached to C═C)	—	δ 2.0 (CH$_2$ attached to C═C) pronounced	—	δ 2.02 (CH$_2$ attached to C═C)
C—N	1130	δ 3.43	1140–1168	—	1120	δ 3.43 (broad and suppressed peak)	1134	—
C—O—C	1305 and 1280	—	1277–1383	—	—	—	1273	—
Benzene ring	1615, 1585, 750	δ 6.92–7.3	780, 750	δ 6.9–7.3	780, 750	δ 7.0–7.5	1525, 1529, 1545 (attributed to benzene ring 702, 750)	δ 6.96–7.28
Aliphatic chain	—	δ 1.29	—	δ 1.2–1.3	—	δ 1.25	—	δ 1.20–1.28
Terminal methyl	—	δ 0.9	—	δ 0.82–0.96	—	δ 0.92	—	δ 0.9
Methyl group of TDI	—	—	—	δ 2.1–2.24	—	—	1522, 1529, 1545	δ 2.2–2.26 (closely spaced peaks)

Table V Performance of Polyesteramide Urethane and Alumina-Filled Polyesteramide Urethane at Different Temperatures

Temperature (°C)	PEAU (Gloss at 60°)	APEAU (Gloss at 60°)
50	130	160
75	130	160
100	130	160
125	130	160
150	100 (turns brownish)	160
175	70	175
200	70	110 (turns brownish)
225	65	110
250	Turns black	103
275	—	97
300	—	Turns black

to the above limit. The physicomechanical and chemical characteristics of APEAU coatings are much better than those of PEAU or APEA coatings. The specular gloss of APEAU coatings is the highest among the resin studies.

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