



RESEARCH ARTICLE

Thermal and Mechanical Properties of Adipic Acid Modified Unsaturated Polyester Resin and Jute Composite

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ABSTRACT

Unsaturated polyester resin and adipic acid modify unsaturated polyester resin has been synthesized using phthalic anhydride, maleic anhydride, propylene glycol and adipic acid. Synthesized unsaturated polyester resin, styrene and jute fiber along with benzoyl peroxide as catalyst were used for the composite preparation. Mechanical and thermal properties of composites were evaluated. The results indicate the good thermal stability of some compounds. The obtained composites were characterized by TGA & DSC. The DSC scans of resins are analyzed by the method proposed by Borchardt and Daniels.

KEYWORDS

Adipic acid modify unsaturated polyester resin, Jute composite

INTRODUCTION

Since 1930, unsaturated polyester resins have been used remarkably for wide range of applications making them a thermosetting system of major importance¹⁻². These resins are compounded with varied fillers, reinforcements and cured by using free radical initiators to yield thermoset articles having a wide range of chemical and mechanical properties depending upon the choice of diacids, diols, cross-linking agents, initiators and other additives³. This versatility in the properties of the final thermoset product associated with comparatively low cost has renewed the interest in these resins as an important matrix material for wide range of applications.

Unsaturated polyester resins are the condensation products of unsaturated acids or anhydrides and diols with/without diacids. The unsaturation present in this type of polyesters provides a site for subsequent cross linking⁴.

Ford Motor Co. Ltd.⁵ synthesized unsaturated polyester resins by reacting maleic anhydride and phthalic anhydride with propylene glycol at 100⁰C and then at 250⁰C till the acid number diminished to the value less than 50 (mg of KOH per gm of sample). Corrado and his assistants⁶ synthesized low viscosity unsaturated polyester resins by reacting maleic anhydride, phthalic anhydride and dipropylene glycol at 200⁰C. Ochsenein and Olliver⁷ synthesized storage stable unsaturated polyester resin by reacting maleic anhydride, propylene glycol and dipropylene glycol at 185⁰C under inert atmosphere.

Polyesters are one of the most versatile synthetic copolymers. Polyesters are produced

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in high volume that exceeds 30 billion pounds a year worldwide. A large number of polyester structures have found use in industry today which displays a wide variety of properties and applications. More detailed discussion can be found in a number of excellent books and reviews. Carothers worked with aliphatic straight chain polyesters, which were soluble in organic liquids, low melting and had poor resistance to hydrolysis. These polyesters were not used as textile fibers. The extension of these concepts later led to the discovery of nylon-6,6 in 1935 and Whinfield and Dickson developed poly(ethylene terephthalate) (PET) in 1941⁸. A partially aromatic organic structure was necessary to increase melting temperature (T_m) above 250°C. Now a day's large numbers of polyesters are commercially available. These polyesters are mainly classified into four major categories, viz: Vinyl Ester Resin, Alkyd Resin, Saturated Polyester Resin and Unsaturated Polyester Resin.

Characterization of Resin & Composite

Reaction was monitored by continuous determination of the reaction mass. Completion of reaction was observed with FTIR and was compared data with a standard (Table-1 & Fig.1). The obtained composites were characterized by TGA & DSC (Fig. 2 & 3).

Table 1: Infrared spectra of UPR-S1

No.	Group	IR Characteristics (cm ⁻¹)	IR for UPR-S1
A	Esters α,β - unsaturated >C=O stretching	1730 – 1715	1729.00
B	C-H Stretching in aromatic	3030	2985.19
C	C-C multiple bend stretching in aromatic	1600	1600.16

D	Hydrocarbon Alkane –CH ₂ –	1445-1485	1454.35
E	Alcohols O-H bond stretching	1260-1350	1283.63
F	C-H stretching in aromatic ring (O- disubstituted)	735-770	743.78

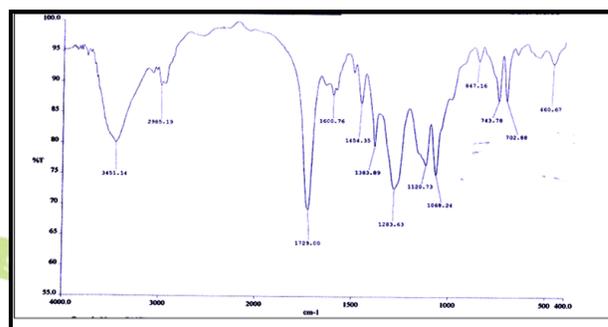


Figure 1: Infrared spectra of UPR-S1

MATERIALS AND METHODS

Materials

Phthalic anhydride, maleic anhydride, propylene glycol and adipic acid were obtained from Chiti –Chem Corp. Ltd, Vadodara. All the chemicals used were of analytical grade.

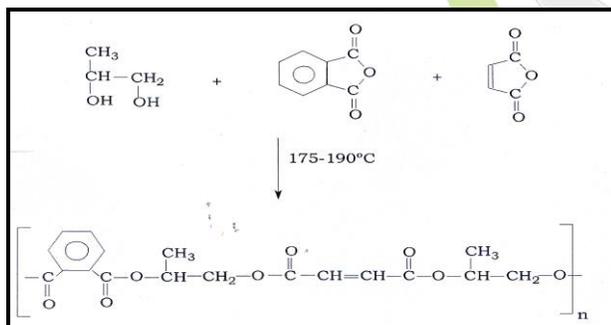
Synthesis of Unsaturated Polyester Resin

Almost all commercial production of unsaturated polyesters is done by the melt polycondensation of unsaturated and saturated acids or anhydrides with glycols. No solvents are used and the formed water is continuously removed, in order to force the esterification reaction towards completion. The condensation temperature is typically between 170-230°C. At the end of the condensation, vacuum is often applied in order to remove remaining water from the viscous melt. The total reaction time can be from 8 to 25 hrs, and the reaction is followed by acid number titrations and viscosity measurements.

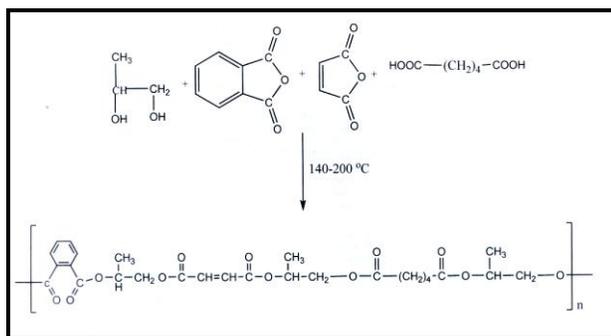
Azeotropic polycondensation in the presence of organic solvents such as xylene or toluene can

also be used. The reaction takes place at lower temperatures and it is possible to avoid losses of volatile reactants. The drawbacks are longer reaction times and environmental problems with solvent removing and recycling. Polyester resins were prepared in the present work by the technique reported by B.Parkyn⁹. A mixture of Propylene glycol (PG), Phthalic anhydride, maleic anhydride, p- Toluene sulfonic acid (PTSA) and Xylene as distilling solvent was charged in a four - neck reaction kettle equipped with stirrer, thermometer, nitrogen-gas introducing tube, Dean & Stark apparatus and water condenser. The mixture was mechanically stirred and heated at 140-200°C under nitrogen gas stream and esterification was carried out while removing water formed by the reaction from the reaction system, continues heating at 140-200°C until an acid number of 25-30 were reached. The Xylene was completely distilled out and reaction product was allowed to cool.

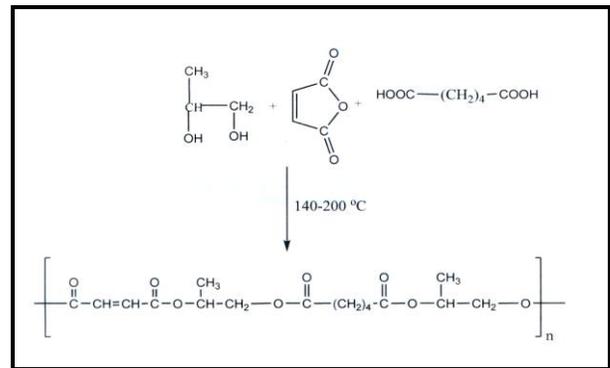
The details about the molar ratio of acids/anhydrides to glycols, styrene monomer and reaction temperature for the synthesis of the unsaturated polyester resins (UPR) are as shown in the Table 2.



Scheme 1: Reaction mechanism for UPR-S1



Scheme 2: Reaction mechanism for AAMUPR-S12



Scheme 3: Reaction mechanism for AAMUPR-S15

Composite Fabrication

Two basic methods are generally used for the fabrication of composites, which are known as wet and dry lay-up lamination. Wet lay-up method implies the use of liquid resins to impregnate the matrix material either before or after it has been laid in place. In case of conventional dry-up method the reinforcement is impregnated with a solution of the resin in appropriate solvent and the solvent evaporated or flushed off and the result is dry resin impregnated sheet known as a prepreg which is used to prepare composites [10]. Laminating is normally carried out manually by brush, roller or squeezer application to glass fiber [11]. The composites were made by using glass fiber and various resin systems. In present study the compositions used for the composites preparation are shown in Table 3

The resin composition containing styrene as cross linking agent and benzoyl peroxide as a catalyst and applied to 6 × 6 inch square pieces of jute with brush. The solvent allowed evaporating at 50°C. The dried eight prepreps prepared in this way were stacked one over another and pressed between two plates using Teflon sheets as mould releasing agent. The plates were compressed under 95-100 psi at specified temperature (110-110°C) and then kept in an oven maintained at required temperature for two hours. The composites so obtained were cooled to room temperature before releasing the pressure. All the composites were prepared by the same procedure.

Table 2: Composition and reaction temperature for unsaturated polyester resin (UPR-S1)

SAMPLE: S1				
Monomers	Molecular Wt. Gm/Mole	Moles Gm	Weight Gm	Wt. of 100% Basis in Gm
P.A	148.12	0.5	74.06	33.36
M.A	98.06	0.5	49.03	22.08
P.G	76.10	1.3	98.93	44.56(43.01 ml)
TOTAL Wt.	-	-	222.02	99.99
* PTSA = 2%/100gm = 2 .0 gm				
* Weigh = Molecular Wt. x Moles * ρ = m/v				

Table 3: Composition for adipic acid modified unsaturated polyester resin (AAMUPR-S12)

SAMPLE: S12				
Monomers	Molecular Wt. Gm/Mole	Moles Gm	Weight Gm	Wt. of 100% Basis in Gm
P.A	148.12	0.3	44.44	20.05
A.A	146.12	0.2	29.23	13.19
M.A	98.06	0.5	49.03	22.12
P.G	76.10	1.3	98.93	44.64(43.09ml)
TOTAL Wt.	-	-	221.63	99.99
* PTSA = 2%/100gm = 2 .0 gm				
* Weigh = Molecular Wt. x Moles * ρ = m/v				

Table 4: Composition for adipic acid modified unsaturated polyester resin (AMMUPR-S15)

SAMPLE: S15				
Monomers	Molecular Wt. Gm/Mole	Moles Gm	Weight Gm	Wt. of 100% Basis in Gm
P.A	148.12	0.0	-	-
A.A	146.12	0.5	73.07	33.06
M.A	98.06	0.5	49.3	22.18
P.G	76.10	1.3	98.93	44.76(43.21ml)
TOTAL Wt.	-	-	221.3	99.99
* PTSA = 2%/100gm = 2 .0 gm				
* Weight = Molecular Wt. x Moles * ρ = m/v				

Table 5: Composition of composites

Sample UPR	Jute (40%) in gms	SDUPR (60%) in gms	Total Weight in gms	BPO (2% of total Wt) in gms	Cureing Temp. in °C	Cureing time in hrs.
S1	36.20	54.30	90.50	1.81	100-110	2
S12	35.15	52.73	87.88	1.76	100-110	2
S15	31.92	47.88	79.80	1.60	100-110	2

S1: unsaturated polyester resin (UPR-S1),

S12 & S15: Adipic acid modify unsaturated polyester resin (AAMUPR-S12-S15)

The specimens for testing were made by cutting the composites and matching them to required final dimensions. All the tests were conducted according to ASTM methods.

RESULTS AND DISCUSSION

The IR spectra of cured unsaturated polyester resins are as shown in Fig. 1. The data regarding the IR spectral characteristics presented in Table 1 reveals that small variations in the location of the peaks due to absorptions by functional groups like $-CH_2$ and $C=O$ are observed depending upon the structure of the diols/anhydrides/acids.

For UPR-S1, a strong absorption band at 743.78 cm^{-1} can be attributed to $-C-H$ stretching in aromatic ring (O-disubstituted). Spectrum absorption band at 1729.00 cm^{-1} & 2985.19 cm^{-1} confirms the presence of α,β -unsaturated $>C=O$ bond in ester linkage & $C-H$ stretching in aromatic respectively. Absorption peak does not appearing at 1652 cm^{-1} for $C-C$ multiple bond stretching in alkene after curing of UPR-S1, so it was missing in Table 1. Spectrum absorption band at 1600.16 cm^{-1} was $C-C$ multiple bond stretching in aromatic. Alkane $-CH_2-$ & $O-H$ bond stretching was confirmed by the presence of band at 1454.35 cm^{-1} and 1283.63 cm^{-1} respectively.

For AAMUPR-S12, a strong absorption band at 748.70 cm^{-1} can be attributed to $-C-H$ stretching in aromatic ring (O-disubstituted). Spectrum absorption band at 1728.00 cm^{-1} & 3025.10 cm^{-1} confirms the presence of α,β -unsaturated $>C=O$ bond in ester linkage & $C-H$ stretching in

aromatic respectively. Absorption peak appearing at 1605.60 cm^{-1} was $C-C$ multiple bond stretching in aromatic. Alkane $-CH_2-$ & $O-H$ bond stretching was confirmed by the presence of band at 1456.30 cm^{-1} and 1285.66 cm^{-1} respectively.

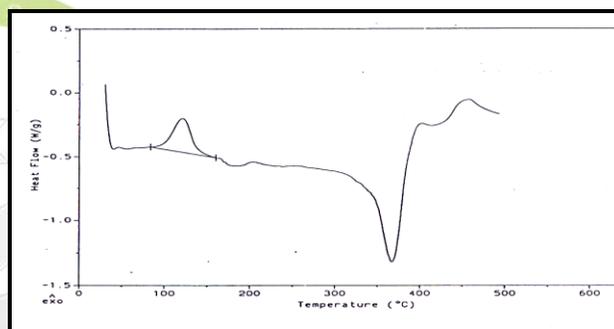


Figure 2: DSC Scan of UPR-S1

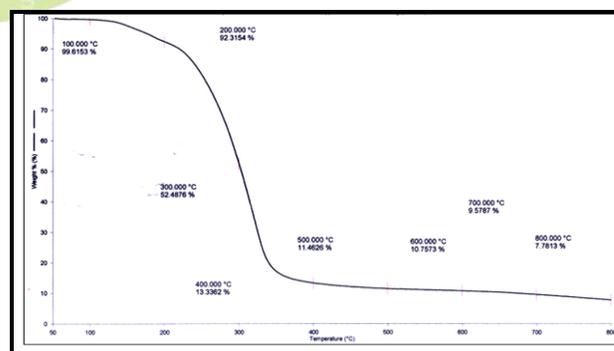


Figure 3: TGA Scan of UPR-S1

The synthesized polyester resins were cured by DSC technique using benzoyl peroxide as catalyst.

The TA Instruments, USA model 5000/2920 differential scanning calorimetry was used to obtain the data on the exothermic curing reactions.

Table 6: TGA of UPR-S1, AAMUPRS-12 (S12), AAMUPRS-15 (S15)

Sample	% Weight loss at various Temperature (°C) from TGA							
	100	200	300	400	500	600	700	800
S1	0.38	7.68	47.51	86.66	88.54	89.24	90.42	92.22
S12	0.59	4.53	24.04	89.05	90.70	91.39	92.71	94.36
S15	0.88	2.75	13.50	90.63	92.59	93.41	94.51	96.54

The sample weights used for the investigation were in the range of 8 - 10mg.

The DSC scans of resins are analyzed by the method proposed by Borchardt and Daniels¹².

The results of DSC study (Table 2.) shows that the curing reaction starts at or above 100°C and gets completed almost around 142°C. This clearly indicates that the unsaturated polyester resins have good induction period under this condition and therefore it can be expected that at room temperature the unsaturated polyester resins would have a very long induction period which is needed for better safe storage stability.

The curing range is of 43°C to 44°C which indicates that after initiation of curing actual curing gets completed within 4.4 min which is also very good indication of processing time for which unsaturated polyester resins are to be kept under compression during compression moulding process. The kinetic parameters indicate the heat of reaction of UPR-S1 (40.7 J/gms).

The TGA data in table 6 indicates that the thermal stability increases when phthalic anhydride is replaced by adipic acid up to 300°C temperature. AAMUPR-S15 (without phthalic anhydride) is thermally more stable than UPR-S1 (without adipic acid). After 300°C temperature, thermal stability is approximately similar for UPR & AAMUPR.

Mechanical Property

Flexural Properties

Flexural properties were carried out in terms of stress-strain relationship using standard method of testing ASTM D-790[13]. A Dutron's Tensile Tester Mode I No. 130 was used for the study.

A strip of the dimensions 8.0 x 1.25 cm² 131 was cut from the laminate for measurement. It suited the gauge length of 7.5 cm i.e. the experiment was carried out a distance between two jaws to be 7.5 cm apart. The results were recorded with the chart speed of 2 mm/min at room temperature. The test was initiated by applying the load to the specimen at the specified crosshead rate. The deflection was measured by gauge under the specimen in contact with it in the center of the support span. The calculation of flexural strength was carried out and the results are included in Table 5.

Izod Impact Strength

A study on Izod impact strength was carried out in terms of resistance to breakage under high velocity impact conditions, according to ASTM D-256 [14]. The impact test indicates the energy to break standard test specimen of specified size under the stipulated conditions of specimen mounting and pendulum velocity at impact. Zwick mode I No. 8900 Impact Machine was used for the study. All the measurements were carried out at room temperature. For the measurement, a specimen was cut from the fabricated composite (6.4 x 1.27 cm 2146) and V notched (2.5 mm) at the middle. The test specimen was clamped into position so that notched end of the specimen remained facing the striking edge of pendulum. All the Izod impact strength data of synthesized composites were given in Table 5.

Rockwell Hardness Study

The Rockwell hardness study was carried out at room temperature according to standard method of testing ASTM D – 785. In the present study, Rockwell hardness tester model RAS/Saroj

Table 7: Flexural Strength & Flexural Modulus (kg/cm²)

Sample	Flexural Strength	Flexural Modulus	Izod impact Strength J/Cm ²	Rockwell Hardness "M" SCALE
S1	425.44	6412.58	1.60	69
S12	330.50	5019.25	1.75	72
S15	198.06	2816.68	1.63	80

Engg. Udyog Pvt. Ltd., Jaysingpur was used. Load of 100kgf was applied for each measurement. The specimen with parallel flat surfaces was placed on the avail of the apparatus and minor load (10kgf) was applied by lowering the steel ball onto the surface of the specimen. The dial was adjusted to zero on the scale under minor load and the major load (100kgf) was immediately applied by releasing the trip lever. After few second the major load was removed and the specimen was allowed to recover for 15 second. Rockwell hardness was read directly on the dial with the minor load still applied. All the mechanical data of synthesized composites were given in Table 5

CONCLUSION

Unsaturated polyester resin (UPR-S1) compared with modified unsaturated polyester resin. Flexural Strength & Flexural Modulus of AAMUPR-S12 and AAMUPRS-15 (adipic acid modified unsaturated resin are lower than UPR-S1.

The Impact Strength of both modified unsaturated polyester resin are incresis, if moles of Adipic acid incresis, so Impact Strength of all modified unsaturated polyester resin are higher than the unsaturated polyester resin(UPR-S1). The Rockwell Hardness of AAMUPRS-12 and AAMUPRS-15 are higher than UPR-S1.

Composites of unsaturated polyester resin were synthesized using different monomers having various concentrations. All the composites show good thermal stability.

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