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Synthesis, characterization and glass reinforced composites of low styrene emission unsaturated polyester resin having improved fire resistance and mechanical properties

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ABSTRACT

This work deals with synthetic modifications of unsaturated polyester resin (UPR) in order to achieve better fire resistance and mechanical properties, lower styrene emission, better styrene solubility and lower processing viscosity. These new ecological unsaturated polyester resins will be used for marine, automotive, electric and electronic, building construction, sport and leisure, domestic and sanitary appliances, furniture as well as military applications. Two concepts were used for development of these new ecological unsaturated polyester resins; Introduction of acrylic monomers viz; Methyl methacrylate (MMA), Butyl methacrylate (BMA) and Acrylonitrile (AN) into the unsaturated polyester resins to reduce styrene emission and use of halogen free fire resistance fillers (Zinc borate and antimony trioxide) in place of halogenated fillers. The main disadvantage of halogenated fillers is that a fire could create toxic and possibly corrosive smoke. Liquid crystalline unsaturated polyester resins were possible to synthesize and it was also possible to prepare solutions of unsaturated polyesters in styrene. By modification with acrylic monomers it is possible to prepare resins with a styrene content as low as 20 wt %. The mechanical and fire resistance properties of the cured samples depending on the type of acrylic monomer and amount and type of filler. Modification of unsaturated polyesters in this way is a possibility to get unsaturated polyester resins with low styrene emission, better fire resistance and mechanical properties, lower shrinkage, reduced brittleness and increased flexibility.

KEYWORDS

Low styrene emission;
Acrylic monomers;
Unsaturated polyester.
Resin;
Fire resistance.

INTRODUCTION

Unsaturated polyester resins are one of the most important matrix resins for commodity glass fiber reinforced composites[1]. They are obtained in a two step process; first unsaturated and saturated acids or anhydrides are reacted with diols in a polycondensation reaction, secondly the resulting linear polyester prepolymer is dissolved in styrene into syrup-like resin[2-3]. The resin is finally processed into a rigid thermoset in a free radical co-polymerisation between styrene and the double bonds in the polyester chain.

In the composite the unsaturated polyester holds the reinforcement in place, it transfers the external loads to the reinforcement and protects the reinforcement from the environment. If individual fiber are fractured, the matrix will redistribute the load to the surrounding fibers, thus preventing the complete failure of the material. The composite product will exhibit a broad range of mechanical, chemical, thermal and physical properties, depending on the composition of the unsaturated polyester[4]. Important product areas for unsaturated polyesters are marine, automotive, electric and electronic, building, construction, sport and leisure, domestic and sanitary appliances, furniture as well as military applications[5-10].

The unsaturated polyester blended with styrene to a reactive resin solution. The styrene acts both as a cross-linking agent and as a viscosity reducer so that the resin can be processed. In conventional unsaturated polyesters the styrene content varies between 35 - 45wt %.

The styrene monomer in the unsaturated polyester resin is an environmental and occupational health problem due to evaporation and emissions, which occur during the processing of the resin. In 1992 it was found that about 75% of the workers in the reinforced plastic industry in Finland are exposed to styrene concentrations exceeding the current occupational exposure limit of 20ppm[11]. Much improvement of the work environment has been made by using proper ventilation systems together with styrene absorbing collection systems, by improvement of the work practice and the housekeeping, by using personal respiratory protection and by using low styrene emission resins in the industry.

During the end of the 1980's the environmental problems caused by styrene emission from the processing of unsaturated polyesters were debated a lot in the society, especially in the Nordic countries. The producers of unsaturated polyesters started therefore to search actively for alternatives to styrene and started to develop additives inhibiting styrene emission. Today much of the styrene debate has silenced, instead the development of unsaturated polyesters is focused on resin formulations for resin transfer moulding and vacuum infusion processing, on resins with superior surface quality, on halogen-free flame retarded resin and on resins with improved mechanical properties.

This work deals with the development of low styrene emission unsaturated polyester resins with improved fire resistance and mechanical properties. These studies showed clearly that the styrene emission cannot be avoided as long as the basic chemical composition is kept unchanged. Structural modifications are therefore needed.

The fire behaviour of composites can also be improved by using a halogenated resin[12] in place of a traditional resin. The main disadvantage of this solution is that a fire could create toxic and possibly corrosive smoke[13]. Recently, environmental problems relating to brominated flame retardants (BFRs) have become a matter of greater concern than ever before, because of the recent marked increase in levels of polybrominated diphenyl ethers (PBDEs) found in human milk in Sweden and North America[14].

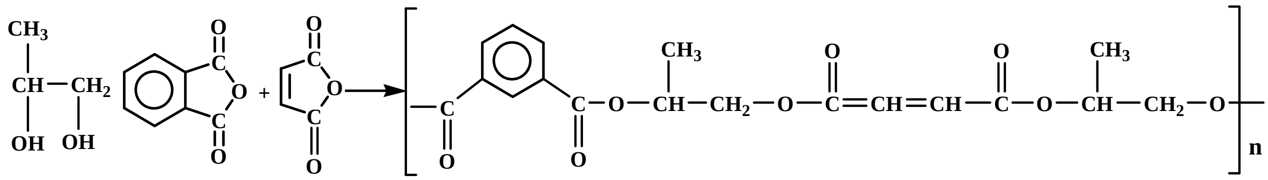
It is shown in this work that non-halogen flame retardants are very effective and does not create any toxic and corrosive smoke in unsaturated polyester resins. Their advantages lie in their high effectiveness, which enables very low concentrations to be used, while at the same time meeting the most stringent requirements.

The experimental work in this article deals with two important topics: development of low styrene emission unsaturated polyester resin by introduction of acrylic monomers and improvement of fire performance by use of halogen-free fillers. The aim of the synthetic work was to tailor the chemical structure of the unsaturated polyester in order to achieve lower styrene emission and improved mechanical properties and enhance fire performance.

EXPERIMENTAL

Materials

Phthalic anhydride, Maleic anhydride, Propylene glycol, Styrene, Methyl methacrylate(MMA), Butyl methacrylate(BMA), Acrylonitrile(AN) Hydro-quinone and p-Toluene sulfonic acid have been purchased from S.D.Fine Chem.Ltd. Vadodra, Gujarat, India. Zinc borate and antimony trioxide were obtained from Chiti-Chem Ltd. Vadodara, Gujarat, India.



SCHEME 1 : Unsaturated polyester resin (UPR)

Synthesis of the unsaturated polyester

Unsaturated polyester resin(UPR)(SCHEME 1) was prepared in the present work by the technique reported by B.Parkyn[15]. A mixture of 1.25mol Propylene glycol (PG), 0.5mol Phthalic anhydride, 0.2% p-Toluene sulfonic acid (PTSA) and Xylene as distilling solvent was charged in a three-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 120^{0}C under nitrogen gas stream, and esterification was carried out while removing water formed by the reaction from the reaction system. When reaction mass becomes clear, it was allowed to cool. When the temperature was dropped to 80^{0}C, 0.5mol Maleic anhydride (MA) was added and continues heating at 150-200^{0}C until an acid number of 20 were reached. The Xylene was completely distilled out and reaction product was allowed to cool. When the temperature was dropped to 160^{0}C, 20mg of hydroquinone was added. When the temperature was dropped to below 100^{0}C, an amount of styrene was added to a styrene content of 20%.

Low styrene emission unsaturated polyester resin (LSEUPR)

Unsaturated polyester resin(UPR) was modified by replacing 15% styrene(TABLE 1) by acrylic monomers viz. Methyl methacrylate(MMA), Butyl methacrylate (BMA) and Acrylonitrile(AN) and resultant resin was named as low styrene emission unsaturated polyester resin(LSEUPR).

Modification of unsaturated polyester resin was carried out in three neck flask equipped with stirrer. Firstly required quantity of styrene diluted unsaturated polyester resin (20% styrene) was added and than 15% of acrylic monomers were added with constant stirring at room temperature. The resultant modified unsaturated polyester resin was named as low styrene emission unsaturated polyester resin (LSEUPR).

TABLE 1 : Composition for low styrene emission unsaturated polyester resin (LSEUPR)

Low styrene emission unsaturated polyester resin code	Styrene(20%) diluted unsaturated polyester resin	Acrylic monomer (15%)
LSEUPR-1	UPR	MMA
LSEUPR-2	UPR	BMA
LSEUPR-3	UPR	AN

TABLE 2 : Compositions of FRC

Composite code	Styrene diluted unsaturated polyester resin	Resin composition in Wt %	Reinforcement in wt %	Fillers in wt %		Catalyst in wt %
				Sb_2O_3	Zinc borate	
FRC-1	LSEUPR-1	100	100	-	-	2
FRC-2	LSEUPR-1	100	70	30	-	2
FRC-3	LSEUPR-1	100	70	20	10	2
FRC-4	LSEUPR-1	100	70	10	20	2
FRC-5	LSEUPR-1	100	70	-	30	2
FRC-6	LSEUPR-2	100	100	-	-	2
FRC-7	LSEUPR-2	100	70	30	-	2
FRC-8	LSEUPR-2	100	70	20	10	2
FRC-9	LSEUPR-2	100	70	10	20	2
FRC-10	LSEUPR-2	100	70	-	30	2
FRC-11	LSEUPR-3	100	100	-	-	2
FRC-12	LSEUPR-3	100	70	30	-	2
FRC-13	LSEUPR-3	100	70	20	10	2
FRC-14	LSEUPR-3	100	70	10	20	2
FRC-15	LSEUPR-3	100	70	-	30	2

FRC=Fire resistance composites of LSEUPR

Fire resistance formulations

In present study low styrene emission unsaturated polyester resins were used with antimony trioxide and zinc borate(TABLE 2). Several combinations were tested to determine effects of additives in the polymer formulations. Fire resistance formulations were prepared by adding these additives in different amounts (10 to 30wt%) in low styrene emission unsaturated polyester resin.

Additives in different amount were mixed with low styrene emission unsaturated polyester resin in a round bottom flask equipped with high speed agitator by means of agitation. The resultant formulations were compounded with glass fiber as reinforcing materials and

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benzoyl peroxide as curing catalyst for composite preparation.

Composites were prepared by hand lay-up technique using about 50 weight percent of glass fiber and filler. After application of resin on glass fiber, the composites were cured by compression moulding technique at 100 *psi* pressure and 120°C temperature for 30minutes. 1% Benzoyl peroxide(BPO) was used as an initiator.

The composites obtained from fire resistance formulations were characterized by Limiting oxygen index according to ASTM D-2863[16].

Fire resistance properties of composites

Many procedures exist to evaluate fire behaviour of the composite materials[17-20]. The key fire resistance properties of interest for plastics to be used in fire resistance applications are ease of ignition, flame spread, ease of extinction, smoke obscuration, smoke toxicity, heat release rate and limiting oxygen index. In the present study limiting oxygen index (ASTM D-2863) was determined to characterize the composites.

Limiting oxygen index (LOI) ASTM D-2863

Fennimore and Martin developed this method. This is very simple and advantageous method for assessing fire resistance of polymers. LOI is defined as measure of minimum amount of oxygen in an environment (O_2+N_2) necessary to initiate and support the burning (flame) under specified conditions.

In this test a mixture of O_2 and N_2 was burned. The flow of the gases was adjusted in such a way that minimum amount of oxygen was required for combustion. Any further decrease in the oxygen amount extinguished the burning material. The critical amount of oxygen was measured. LOI is expressed in percentage as:

$LOI=[O_2]/[O_2]+[N_2]\times100$

The results of the Limiting Oxygen Index of all composites under study has been obtained and reported in TABLE 3

TABLE 3 : Fire resistance properties of FRC

Composite code	Limiting oxygen index (LOI) in %
FRC-1	21
FRC-2	25
FRC-3	28
FRC-4	30
FRC-5	32
FRC-6	22
FRC-7	26
FRC-8	29
FRC-9	31
FRC-10	34
FRC-11	21
FRC-12	25
FRC-13	27
FRC-14	29
FRC-15	31

Mechanical properties of composites

Mechanical properties measured in this study include Izod impact, Rockwell Hardness and Flexural strength. A study of Izod impact strength was carried out in terms of resistance to breakage under high velocity impact conditions, according to ASTM D-256[21]. Zwick model no. 8900 impact machine was used for present study. Rockwell hardness study was carried out at room temperature according to standard method of testing ASTM D-785[22]. In the present study rockwell hardness Tester Model RAS/Saroj Engg. Udyog, Pvt. Jaysingpur was used. A study of Flexural properties was carried out in terms of stress-strain relationship according to standard method of testing ASTM D-790[23]. A Dutron's Tensile Tester, Model-130 was used in present study.

TABLE 4 : Mechanical properties of FRC

Composite code	Izod impact in J/cm	Flexural strength in MPa	Hardness (M scale)
FRC-1	5.09	238.85	59
FRC-2	4.15	230.85	57
FRC-3	7.25	242.00	61
FRC-4	10.10	246.15	63
FRC-5	11.80	247.90	66
FRC-6	4.90	240.00	58
FRC-7	4.00	231.85	56
FRC-8	7.15	242.25	60
FRC-9	10.00	246.55	62
FRC-10	11.55	248.10	65
FRC-11	5.65	235.90	60
FRC-12	4.85	228.15	58
FRC-13	7.65	240.00	63
FRC-14	10.20	244.35	66
FRC-15	11.85	246.15	68

TABLE 4 represents Izod impact strength, Rockwell hardness and flexural strength. Mechanical properties of laminates improve remarkably with introduction of acrylic monomers and fillers. Increase in strength with increase in filler content is due to the reinforcement action provided by the filler particles to the polymer matrix. Laminates prepared using LSEUPR and fillers give better mechanical performance than traditional unfilled laminates and also there is increase in mechanical properties with increase in amount of filler.

Also acrylic modification by using various acrylic monomers viz; methyl methacrylate, butyl methacrylate and acrylonitrile of unsaturated polyester resins greatly influences mechanical properties and also reduced styrene emission. Butyl methacrylate modified LSEUPR gives better flexural strength than methyl methacrylate and Acrylonitrile modified LSEUPR. Methyl methacrylate modified LSEUPR gives better flexural strength than acrylonitrile modified LSEUPR but lower than butyl methacrylate modified unsaturated polyester resin. Acrylonitrile modified LSEUPR shows better Izod impact strength and Rockwell hardness than methyl methacrylate and butyl methacrylate modified LSEUPR.

Characterization of unsaturated polyester resin

Spectral analysis of unsaturated polyester resin

An IR spectrum of unsaturated polyester resin is shown in figure 2. A Nicolet Impact 400D FT-IR Spectrophotometer was employed for the measurements. The spectrum was run by applying resin sample on KBr cell covering the range of frequencies from 4000-400cm^{-1}. A strong absorption band at 755.97cm^{-1} and a weak band at 1004.48cm^{-1} can be arributed to –C-H bending arising from 1 and 3 position in benzene ring and –C=CH bending arising from isomerization of maleic anhydride to fumarate during polymerization. A broad spectrum absorption bend at 1145.52cm^{-1} confirms the presence of –C-O-C- of ester linkage. A strong absorption peak appearing at 1306.72cm^{-1} was assigned to –C=C– group of polyester. A medium absorption band at 1461.19cm^{-1} can be attributed to –C-H bending. The presence of –C=O and symmetric –CH stretching was confirmed by the presence of strong bend at 1736.57cm^{-1} and 2985.82cm^{-1} respectively.

Gel permeation chromatography (GPC) of polyester resin

Gel permeation chromatography of unsaturated polyester resin is shown in figure 3. Gel permeation chromatography of polyester resin was done by using Perkin Elmer 200 GPC instrument. PL GEL mixed B type of column, Tetrahydrofuran as solvent and refractive index detector was used in this analysis. Volume of sample injected was 20µl/min. with retention time 9.309 minutes. The number average(M_n) of polyester resin sample is 1554, weight average(M_w) is 3576 and polydispersity(M_w/M_n) is 2.301.

Figure 1 : Limiting oxygen index apparatus

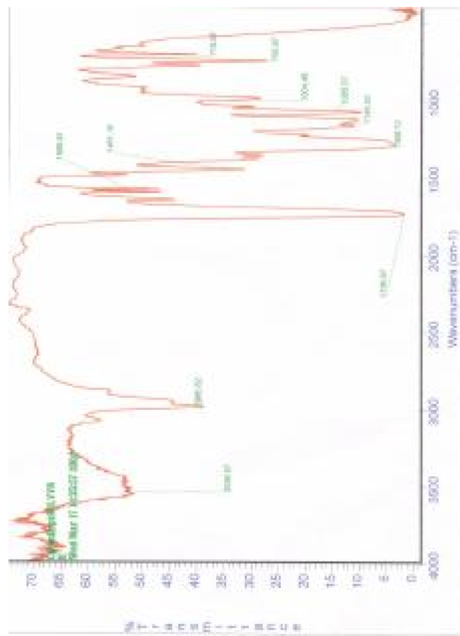

Figure 2 : Infrared spectra of unsaturated polyester resin

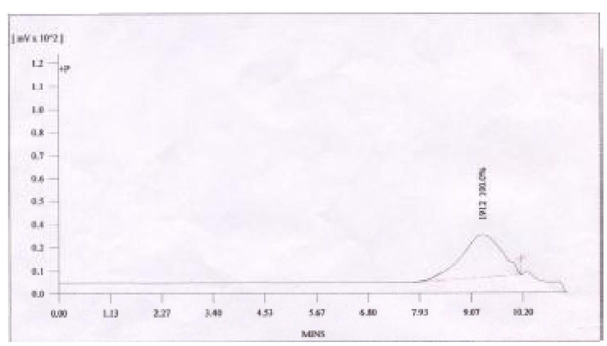

Figure 3 : Gel permeation chromatography (GPC) of polyester resin

RESULT AND DISCUSSION

In this work, fire behaviour of unsaturated polyester resin was carried out. Limiting oxygen index was evaluated for all the composites filled with different weight percentage of fillers. TABLE 3 represents limiting oxygen index of filled and unfilled composites.

In the present study values of limiting oxygen index of filled composites are in the range of 25-34. Material is normally considered as flame resistance if LOI is greater than 26[24-25]. Thus the results of present study are in good agreement with the reported values. The results clearly indicate that the composites of present study can be used in all fire resistance applications.

Composites prepared using fillers give better fire resistance than unfilled composites and also there is increase in fire resistance with increase in amount of filler. The fire behaviour of polymeric matrices can be improved by adding mineral fillers such as antimony trioxide and fly ash. Tests show that the fire results are good with a decrease in heat and smoke production during combustion and also decomposition does not release additional toxic gases.

Mechanical properties of composites improve remarkably with increase in the filler content except in antimony trioxide. Increase in mechanical properties with increase in filler content is due to the reinforcement action provided by the filler particles to the polymer matrix.

Composites prepared using fillers antimony trioxide and zinc borate gives better performance than unfilled composites and also there is increase in mechanical properties with increase in amount of fillers. Antimony trioxide gives poor results compared to zinc borate and also mechanical performance decreases with increase in amount as antimony trioxide is poor in mechanical performance.

The results revealed that concentration and type of filler remarkably influences the mechanical and fire behaviour of composites. Also cost effective fire resistance composites can be formulated with competitive performance by using cheaper and widely available fillers. Also halogen free composites with good mechanical performance were prepared by acrylic modification with various acrylic monomers. The composites can be used for facade elements, dome light crowns, in the transportation sector, in the electrical industry, e.g. for cable distribution cupboards, for boats and shipbuilding, tanks, tubes, vessels and others electrical, electronic and electro technical applications like circuit breakers, switch board cabinets, automotive distributor caps, printed circuit board etc.

Also acrylic modification greatly influences mechanical properties and also reduced styrene emission. Butyl methacrylate modified LSEUPR gives better flexural strength than methyl methacrylate and Acrylonitrile modified LSEUPR. Methyl methacrylate modified LSEUPR gives better flexural strength than acrylonitrile modified LSEUPR but lower than butyl methacrylate modified unsaturated polyester resin. Acrylonitrile modified LSEUPR shows better Izod impact strength and Rockwell hardness than methyl methacrylate and butyl methacrylate modified LSEUPR.

CONCLUSION

The study reveals that acrylic modification of unsaturated polyester resin by partially replacing styrene monomer drastically reduces styrene emission and greatly influences mechanical properties.

Acrylic modification by using various acrylic monomers viz; methyl methacrylate, butyl methacrylate and acrylonitrile of unsaturated polyester resins greatly influences mechanical properties and also reduced styrene emission.

Mechanical properties of filled composites improve remarkably with increase in the filler content. Composites prepared using fillers antimony trioxide and zinc borate gives better performance than unfilled composites and also there is increase in mechanical properties with increase in amount of fillers. Antimony trioxide gives poor results compared to zinc borate and also mechanical performance decreases with increase in amount as antimony trioxide has poor binding property. So, cost effective composites can be prepared by using both these fillers.

Composites prepared using fillers give better fire resistance than unfilled composites and also there is increase in fire resistance with increase in amount of filler. Methyl methacrylate, butyl methacrylate and acrylonitrile show almost same results in fire resistancy but there is significant difference in mechanical performance.

Zinc borate gives good results as compared antimony trioxide. Tests show that the fire results are good with a decrease in heat and smoke production during combustion and also decomposition does not release additional toxic gases.

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