

## ENHANCING THE CHEMICAL AND MECHANICAL PROPERTIES OF UPR

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### ABSTRACT

*Recent research in medical field has revealed that phthalates are carcinogenic. The unsaturated polyester resins (UPRs) used in the manufacturing of products which come in contact with human foods or chewable (toys, buttons) should be phthalate free. In view of above we worked to develop phthalate free resins. We had to eliminate the sources of phthalates i.e. phthalic acid and its anhydrides also the solvents like Di butyl phthalate having phthalate molecules. This deteriorates the mechanical properties. To overcome this problem step by step reduction of phthalic anhydride was done through a series of recipes. The reaction time, temperature and raw materials were monitored to achieve the required branching of the molecular structure leading to improved mechanical properties of the product. The UPR developed through this experimentation was free of phthalates and exhibits tensile strength in the range of 34.79MPa or higher.*

**Keywords:** *Phthalates, Phthalic anhydride, Di butyl phthalate, Unsaturated polyester resin, Glass Reinforced Plastics (GRP), Fiber Reinforced Plastics (FRP).*

### 1) INTRODUCTION

Unsaturated Polyester Resins (UPR) were developed in USA, for the first time. They became basic raw material of glass reinforced plastics, GRP and FRP (BASF 1979). GRPs replaced conventional materials of construction and found multifarious applications in the fields of civil, mechanical, electrical and chemical engineering. With development of new applications of GRP, resins having corresponding novel properties were needed, hence were developed at same pace. Carlton Ellis found that unsaturated polyester pre polymers, could be diluted with styrene and copolymerized into rigid polymer (Osman 2012). These resins became commercially important, with the introduction of techniques of their reinforcement with glass fibers, resulting in composite materials, GRP

and FRP with good mechanical strengths comparable to metals with 50% weight and properties like corrosion and thermal resistance (Shahid et al., 2005) etc.

The GRP and FRP products because of their ease of fabrication, aesthetic look, durability, corrosion resistance, resistance to insecticides attacks, thermal resistance and above all economy have replaced conventional materials of construction in many areas and have found applications in almost all parts of life (Shimaa 2012) such as furniture, sanitary wears, pipes, automotives, boats, ships, aircrafts, buildings, electric meter boxes, electrical panels and polls, water tanks, chemical reactors, chemical storage vessels (BASF1979).

For these numerous applications listed above suitable techniques and raw materials are used to achieve the desired properties in the end product. Hand layup method, Chopper Gun, Centrifugal Casting, Pultrusion, Open Mould Castings, Resin Transfer Moulding, Compression Moulding, Vacuum Injection Mouldings, are some of the methods to produce GRPs which need particular type of UPR, glass reinforcements and machines. So for each new demand in the market, new unsaturated polyester resins, reinforcement materials and techniques are developed. (Johannes 2005).

## **2) EXPERIMENTAL WORK**

The experimental rig is shown in the figure 1. The system consists of, 5 liters glass reactor, an agitator having variable speed 10rpm-150rpm with stain less steel anchor shaped stirrer, covered with a glass lid having five holes, a condenser is provided to condense the water and glycols vapors escaping from the reactor, to monitor the reaction temperature a thermocouple and thermometer are provided, heating is done through an electrical heating device having range of 0-400°C, as shown in figure 1.



*Figure 1: UPR Glass Reactor*

## **2.1) Materials and Method**

The chemicals used are, Phthalic Anhydride, Maleic Anhydride, Adipic Acid, Di Ethylene Glycol, Propylene Glycol, Mono Ethylene Glycol, Neopentyl Glycol, Fumaric Acid, Styrene Monomer, Hydroquinones, Additives, Potassium Hydroxide, Methyl Ethyl Ketone Per oxide, Cobalt octate, Parafin wax.

Five batches were produced using different compositions and reaction conditions, with above dihydric alcohols and bivalent carboxylic acids both saturated and unsaturated. The quantities used depend on the stichometric requirements of the reactants and their contributing properties.

Maleic anhydride and adipic acid were in lumps form, we grinded them to fine powder state, developed a recipe of the reactants after calculation of their molecular weights, stichometric requirement, taking into account their properties as mentioned below in table: 1.(Hazizan Md Akil 2005).

Table 1: Properties of Raw Materials

Phtahlic Anhydride	Maleic Anhydride	Adipic Acid	Fumaric Acid	NeoPentyl Glycol	Di Ethylene Glycol	Ethylene Glycol
Improved hardness and stiffness in the product.	Branched polyesters.	Flexibility and increased toughness.	Higher reactivity, lesser gell time and curing time.	Good corrosion and chemical resistance.	Flexibility and toughness	Increased rigidity.

## 2.2) Reaction Methodology

The measured quantities were introduced into the glass reactor, first liquids and then solids. The heaters and stirrer were started, initially the RPM of stirrer was kept at 10 and temperature at 90<sup>0</sup> c, after half an hour the temp raised to 150<sup>0</sup> c and RPM to 20, after about 4 hrs laminar flow was established in the reactor at that time, temperature further raised to 190 c and RPM to 25. During this time water condensate coming from condenser was collected in the beaker to know that the reaction was going on smoothly, after 10 hrs, we took a sample from the reactor and titrated it against KOH and measured the acid number, samples were collected after regular intervals of one hour and titration with KOH was carried out till the acid number reached in the range of 45-50. After that reaction was stopped, by switching off the heaters and started cooling, the stabilizers were added and when the temperature reduced to 60<sup>0</sup> c styrene monomer was added, mixing was done again, till homogenization of the resin. After about 17 to 20 hours reaction was stopped and batches unloaded. Table 2, 3, 4, 5 and 6 represent the composition of different batches. (Johannes Karl Fink 2005).

Table 2: Composition of Batch # 1

Recipe No. 1	
Maliec Anhydride.	580 gms
Phthalic Anhydride.	680 gms
Adipic Acid.	120 gms
Propylene Glycol	380 ml
Ethylene Glycol	105 ml
Di Ethylene Glycol	580 ml
Water condensate	50 ml
Coloration	Dark yellow
Styrene	750 ml
Acid No.	40
Gel Time.	Batch gelled in the reactor. As there were no inhibitors to stop reaction
Curing Time	–
Reaction temperature 170° C, Reaction time 18 hrs.	

Table 3: Composition of Batch # 2

Recipe No. 2	
Maleic Anhydride.	500gms
Phthalic Anhydride.	270gms
Adipic Acid.	300gms
Propylene Glycol.	338ml
Di Ethylene Glycol.	850ml
Water condensate	50 ml
Acid No.	45
Styrene.	950ml
Coloration.	Pale yellow
Gel time.( Cobalt 0.25%, MEKP 1% )	12 mins
Curing time	50 mins
Hydroquinone	150 ppm.
Shelf life	More than one month.
Reaction temperature 190°C and reaction time 16 hrs.	

*Table 4: Composition of Batch # 3*

<b>Recipe No. 3</b>	
Maleic Anhydride.	550 gms
Phthalic Anhydride.	200 gms
Adipic Acid	320 gms
Propylene Glycol.	300 ml
Ethylene Glycol.	90 ml
Di Ethylene Glycol.	800 ml
Water Condensate.	75 ml
Acid No.	48
Styrene.	750 ml
Coloration.	Yellow
Gel Time.	15 mins
Curing Time.	65 mins
Inhibitors.	100 ppm
Shelf Life.	More than one month.
Reaction temperature 210° C and reaction time 18 hrs.	

*Table 5: Composition of Batch # 4*

<b>Recipe No. 4</b>	
Maleic Anhydride.	600 gms
Phthalic Anhydride.	50 gms
Adipic Acid.	320 gms
Fumaric Acid.	100 gms
Propylene Glycol.	600 ml
Ethylene Glycol.	100 ml
Di Ethylene Glycol.	500 ml
Water Condensate.	68 ml
Acid No.	50
Styrene.	650 ml
Coloration.	Yellow
Inhibitor	100 ppm
Gel time.	20 mins
Curing time.	70 mins
Shelf life.	More than one month
Reaction temp 8 hrs 200 C, 8-18 hrs 220 C	

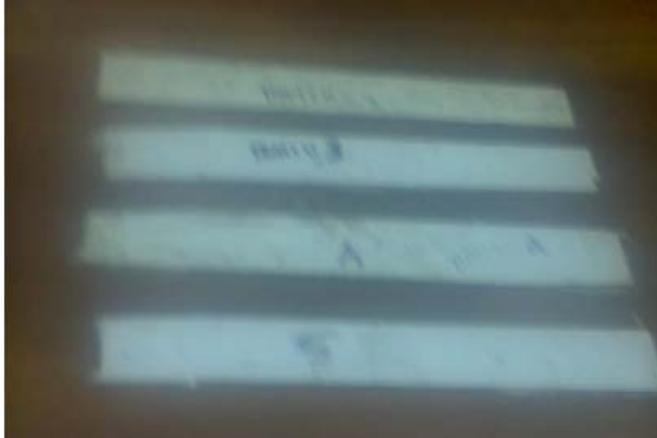
Table 6: Composition of Batch # 5

Recipe No. 5	
Maleic Anhydride.	635 gms
Adipic Acid.	350 gms
Fumaric Acid.	150 gms
Di Ethylene Glycol.	290 ml
Ethylene Glycol.	500 ml
Neo Pentyl Glycol.	150 ml
Water condensate.	75 ml
Acid No.	50
Styrene.	750 ml
Coloration.	Light yellow.
Inhibitor.	100 ppm.
Additives.	25 ppm
Gel time.	20 mins
Curing time.	90 mins
Shelf life.	More than one month.
Reaction temperature 8 hrs 190° C and 8-20 hrs 220° C.	

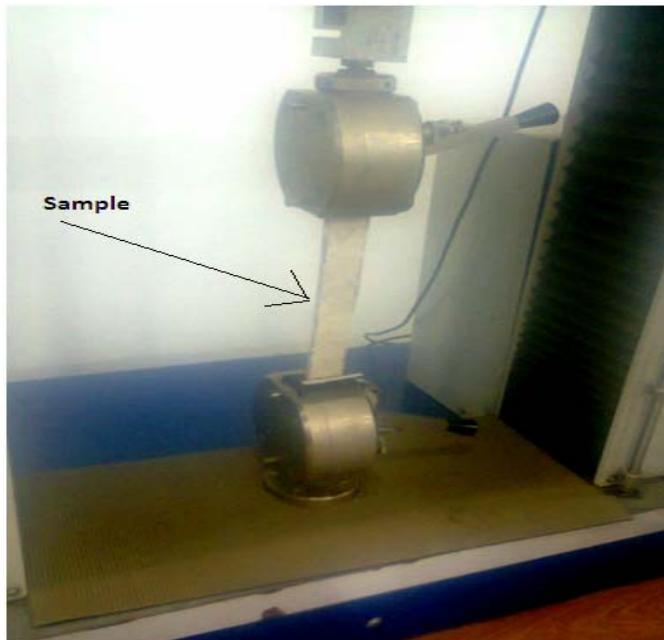
### 3) TESTS AND RESULTS

Four sheets of GRP with hand layup method (shahid, et al 2005), dimensions 1 ft<sup>2</sup> area and 3mm thickness were produced using above **resins** as matrix and 450 gms/m<sup>2</sup> chopped strand mat as reinforcement material, for surface reinforcement tissue mat of 50 gms/m<sup>2</sup> was used, sheets were laminated in a glass mould. To determine their tensile strength and flexural strength, according to ASTM, D3039 and D 3479 respectively on UTM, samples strips of 127 mm length and 25.4 mm width and thickness 2.54mm(for tensile strength measurement) and strips of 101.6mm length, 13mm width and 2.5mm thickness(for flexural strength measurement) were developed, as shown in the figure 2. The strips were, gripped in Universal Testing Machine one by one as shown in the figure 3, tensile strengths and flexural strengths were assessed. Results of the UTM for tensile strength and flexural strength from four strips corresponding to the four batches are shown below in the figures 4 to 9, against the corresponding recipes. Recipe No. 5, showed the maximum

strength 34.79 N/mm<sup>2</sup>, no phthalic anhydride was used in this batch as shown in the recipe No. 5, the strength reduced because of phthalic anhydride was adjusted with the careful selection of proper acids and glycols. (Schulze, U. et al, 1997). (Ying peng, jian Hua Liu, 2010).



*Figure 2: ASTM D3039 Specimen Strips (2.5mm x 25.4mm x 127mm) prepared from Recipes 2 to 4*



*Figure 3: Tensile Strength Measurement, UTM TIRA Test 2810*

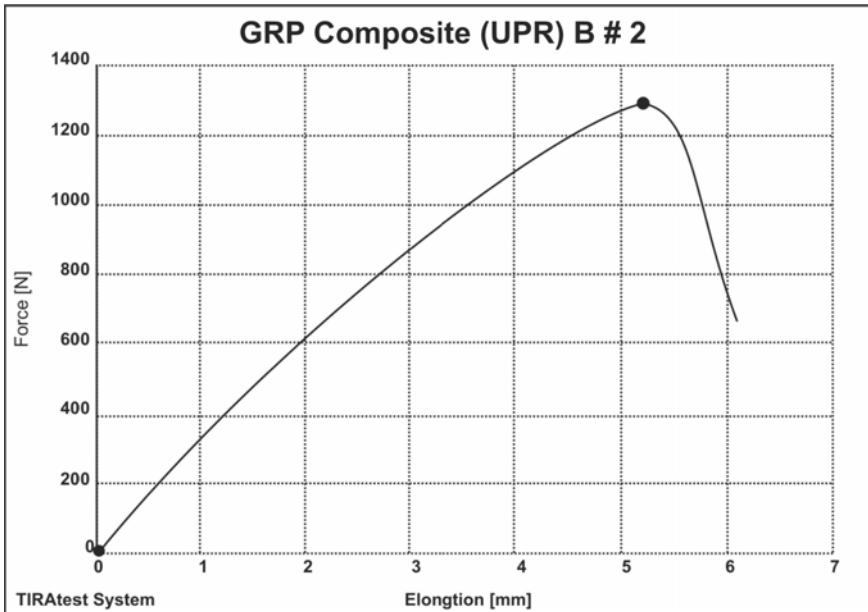
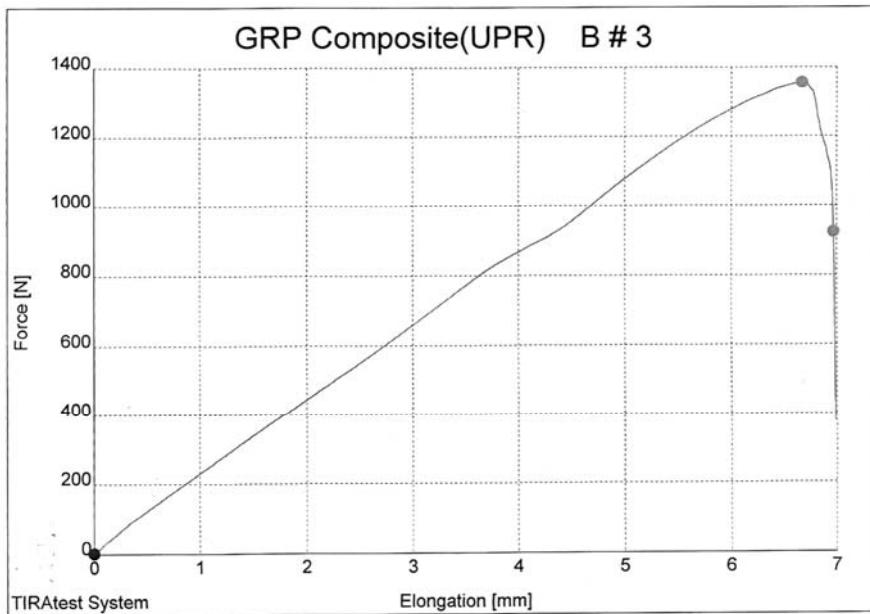


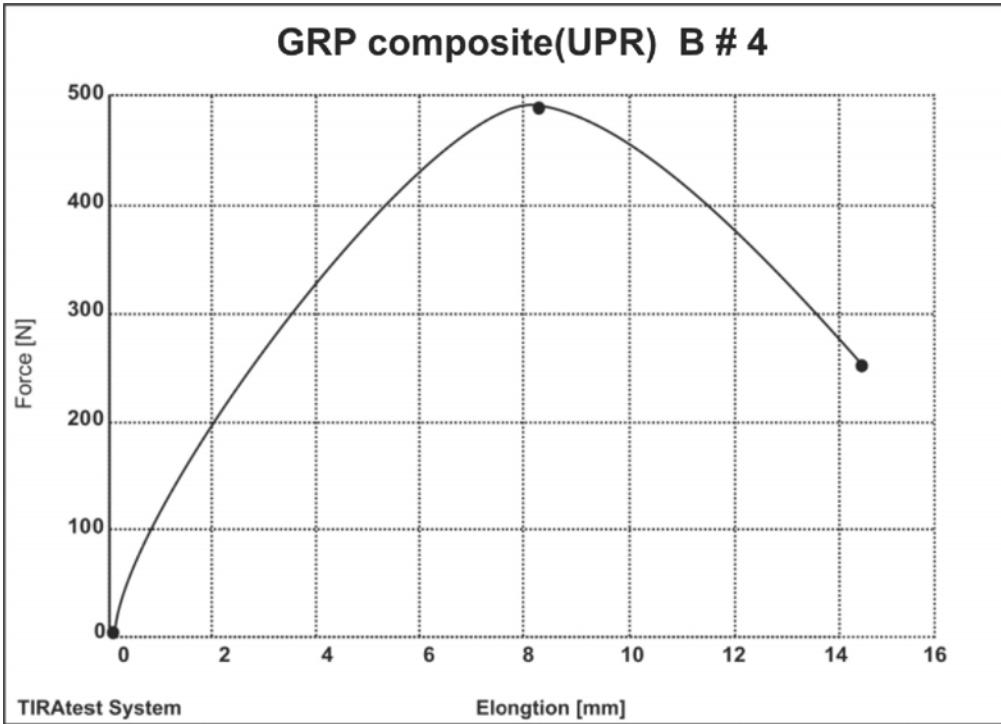
Figure 4: UTM Result from Specimen of Recipe # 2

GRP strip prepared from UPR of recipe No. 2, according to ASTM 3039 beared a load of 1285 N, the corresponding tensile strength was 20.25N/mm<sup>2</sup>, elongation was 4.10%, extension was 5.22mm, before breakage.



*Figure 5: UTM Result from Specimen of Recipe # 3*

The GRP strip prepared from UPR of recipe No. 3, according to ASTM 3039 beared a load of 1354N, the corresponding tensile strength was 21.34N/mm<sup>2</sup>, elongation was 5.25%, extension was 6.67mm, before breakage.



*Figure 6: UTM result from specimen of recipe #4*

The GRP strip prepared from UPR of recipe No. 4, according to ASTM standard 3039, beared a load of 491N, the corresponding tensile strength was 7.74N/mm<sup>2</sup>, elongation was 6.49%, extension was 8.25mm, before breakage.

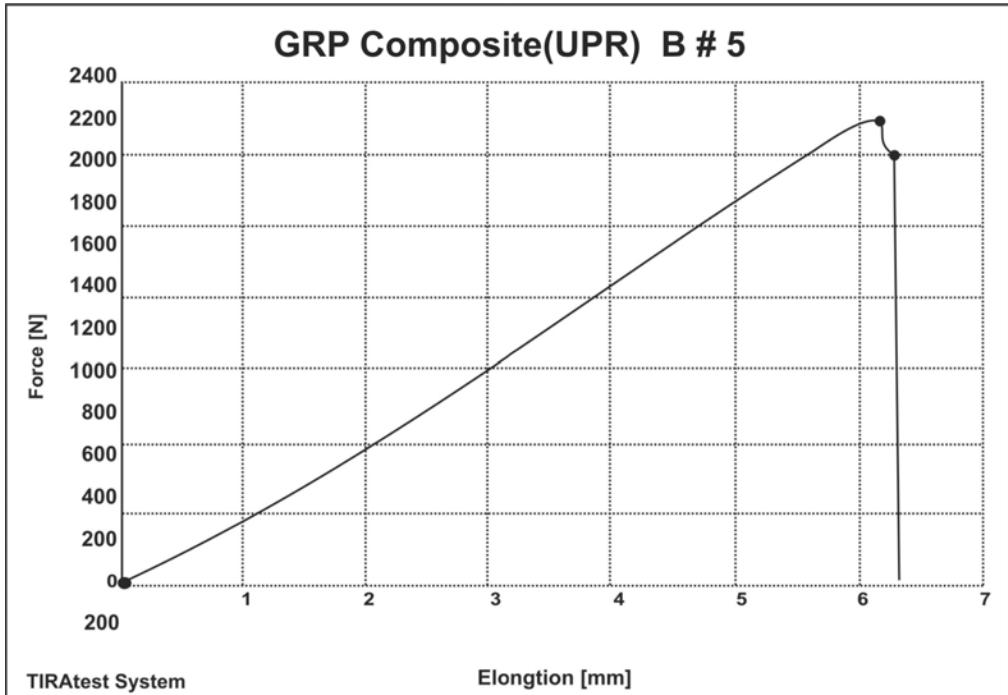
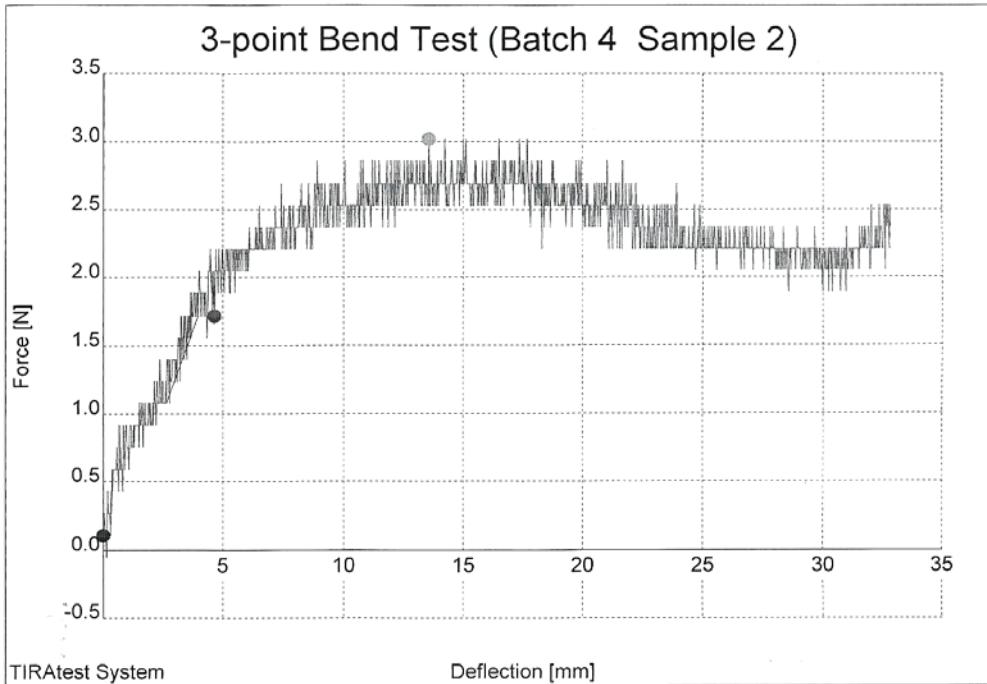


Figure 7: UTM Result from Specimen of Recipe # 5

The GRP strip produced from UPR of recipe No. 5, *having no phthalates*, according to ASTM standard 3039, beared a load of 2208N, the tensile strength was 34.79N/mm<sup>2</sup>, elongation was 4.83%, and the extension was 6.14mm, before breakage.

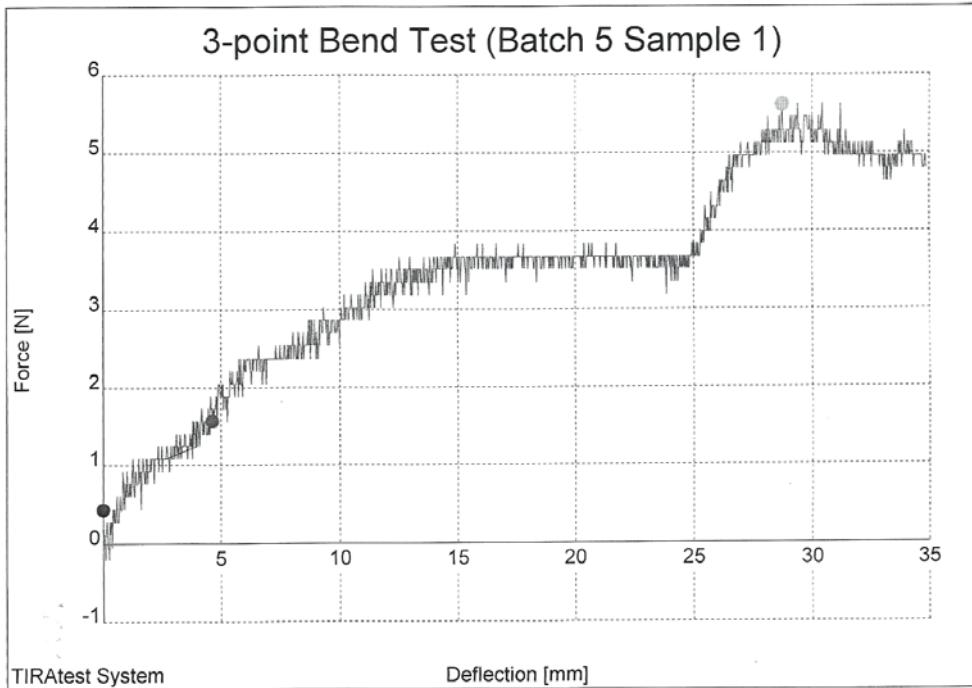


	Comm.1	Comm.2	Date	Time	FH N	RbB N/mm <sup>2</sup>	AbB %	fAbB mm
4	x		03.04.13	14:35	3.02	1.1	10.24	13.55

	FB N	RbR N/mm <sup>2</sup>	AbR %	fAbR mm	E N/mm <sup>2</sup>	A1 N	A2 N
4	x	0.00	0.0	0.00	23.05	1.72	0.00

Figure 8: Flexural Strength of Specimen prepared in accordance with ASTM 3479 from UPR of Recipe # 4 measured on UTM TIRA 2810.



	Comm.1	Comm.2	Date	Time	FH N	RbB N/mm <sup>2</sup>	AbB %	fAbB mm
2	x		03.04.13	13:42	5.61	2.0	21.71	28.74

	FB N	RbR N/mm <sup>2</sup>	AbR %	fAbR mm	E N/mm <sup>2</sup>	A1 N	A2 N
2	x	0.00	0.0	0.00	5.76	1.57	0.00

Figure 9: Flexural Strength of Specimen prepared in accordance with ASTM 3479 from UPR of Recipe # 5 measured on UTM TIRA 2810.

## CONCLUSIONS

This may be concluded from the results of recipes number 2 to 5, explicitly shown in Table 7, that phthalate free status of UPR has been achieved in recipe No. 5. Measurement of tensile strengths and flexural strengths of GRP strips prepared from resins of recipes Nos. 2 to 5, according to ASTM 3039 on UTM TIRA 2810 to monitor the mechanical properties shows tensile strength of 34.79 MPA for recipe No. 5, in comparison to 12-15 MPA, tensile strength of one of the UPRs grade (Mikeal 2000). Further improvement in mechanical properties is possible with continuous research and development. Phthalic anhydrides contributes, hardness and stiffness to cured resins, because of their compact aromatic ring structures pertaining to benzene molecules, when

they are replaced by longer chain adipic acid, fumaric acid and maleic anhydride molecules (because phthalates are carcinogenic), the compromised rigidity and stiffness can be increased by the use of higher percentage of Di ethylene glycol, Ethylene glycol and neo pentyl glycol, which lead to increased branching of resulting polyesters contributing to enhanced mechanical properties of UPR. (Abbas, A et al., 2009).

Table 7 Summary of Tests Conducted

Recipes	Weight of Batch (gram)	%age of Phthalates	GRP Strips prepared ASTM 3039	Force Applied (N)	Tensile Strength (N/mm) <sup>2</sup>	Elongation	Extension (mm)
1	3185.	21.283%	Batch gelled.	-	-	-	-
2	3208.	8.416%	2.5*25.4*127	1285.69	20.25	4.10%	5.21
3	2960.	6.759%	//	1354.98	21.34	5.25%	6.67
4	2920.	1.712%	//	491.21	7.74	6.49%	8.25
5	2825.	0	//	2208.88	34.79	4.83%	6.14

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