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Thermal and Mechanical Properties of Composites from unsaturated polyester filled with Cured Resol Novolac resin

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Abstract: The aim of this study was to investigate the thermal and mechanical properties of composites consist of unsaturated polyester(UP) as matrix material and different weight ratio of cured resol novolac resin (CRN) as filler, the result obtained from this study showed that the thermal stability of the composites increased as CRN resin content increase which was a logical consequence of the high thermal stability of phenolic resin compound from filler compared to that of unsaturated poly ester resin,,,on the other hand the mechanical properties, i.e tensile and flexural strength of UP/ filler composites were improved in modulus with increasing filler content

Keywords: CRN, commercial unsaturated polyester (UP) resin , filled composites, thermal and mechanical properties.

INTRODUCTION

Unsaturated polyester resin are extensively used in composite industry [1-3], because of their good mechanical properties, low coast and easy to use. Phenolic resin is known for their excellent thermal properties and chemical stability, also in the field of advanced composites is known for their excellent flame retardant and is excessively used in the rocket industry because of their ablative characteristics[4-6]. The mechanical properties of fillers filled composites varied considerably depending on physical, chemical and composition of materials, type of fillers. Popa *et al*,[7] emphasized the mechanical adhesion that represent the properties of material is correlated with interfacial bonding between the filler and the polymer matrix . Also Hsu *et al.*[8] proposed that the composites should have good adhesion

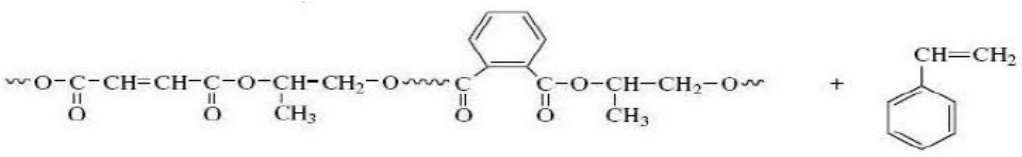
between filler and matrix, high modulus, low stress, minimal setting, low moisture absorption, fast cure and long life time. Amar *et al.*[9], studied thermal behavior of particulate filled polymer and the results showed that the increase in filler content lead to high thermal properties. Fu *et al.*[10] examined the effect of particle size, particle matrix adhesion and particle loading on composites, stiffness strength, toughness, it was noted that compressive strength and toughness were strongly affected by all three factors especially in particle-matrix adhesion. So the aim of this paper is to analyze the effect of CRN on thermal and mechanical properties of UP resin.

MATERIALS AND METHODS

Materials: The unsaturated poly ester (UP), commercially known as (RPPL-3111) and its hardener, methyl ethylketone peroxide (MEKP) was supplied by Revertex (Malaysia) sdn. Bhd, kluang. Johor. Malaysia. novolac resin was prepared according to the literature[11], formalin 35% and sodium hydroxide was supplied from Merck Co.

Specification of unsaturated polyester resin used in this study

SI.No.		Properties
1-	Appearance	Clear
2-	Specific gravity	1.12 @ 25C^0
3-	Acid value	28-30 (mg KOH/ g)
4-	Gel time	20-25 minutes @25C^0
5-	Volatiles	35-40%
6-	HDT	55 C^0 ISO; 75/1974
7-	Water absorption	30 mg ISO ;62/1980
8-	Viscosity	550-700 (cps) @ 25C^0



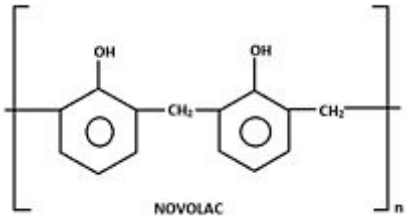
Chemical structure of unsaturated poly ester resin used in this study

Preparation Methods:

a-preparation of novolac resin: Phenol based novolac resin with mole ratio 1;06 phenol to formaldehyde was prepared using oxalic acid as catalyst by method similar to that adopted in previous article [11].The initial pH of the reaction mixture was 6.0, which reduced to avalue of 4.8 after 2 hrs at 120 C^0. Free formaldehyde content was checked after every 45 min to check the progress of the methlation reaction, after 3 hrs stopped the reaction and neutralized the reaction mixture by using 10% of phosphoric acid in order to separate the novolac product.

Properties of novolac prepared in this study

Form	Flakes
Phenol to formaldehyde ratio	1:0.63
Melting point	72-80 C^0
Free phenol	Less than one %



Chemical structure of Novolac resin

(b). Synthesis of resol-novolac resin (RN): Three necked flask equipped with mechanical stirrer, thermometer and reflux condenser, is charged with 100 gm of novolac powder and 250 ml formaldehyde solution, The reaction mixture is mixed vigorously and 10% sodium hydroxide solution is added in portions to control the pH to about 9 , temperature of the reaction is kept at (50-60) °C for 3hrs. The reaction mixture is cooled and neutralized with 10% phosphoric acid solution and then the organic layer past is separated and purified by washing several time with distilled water, then dissolved in ethanol in order to prevent polymerization and left in cool place.

(c). Synthesis of Cured resol –novolac resin (CRN): Cured resol novolac was prepared by thermal treatment specific weight of sample in oven with different temperatures and times (i.e 3hrs @ 70 ^{0}C, 3 hrs @ 120 ^{0}C, finally post cure 2hrs @ 170 ^{0}C), after this the sample was ready to use it as reinforced material.

Specimen preparation: Fabrications of specimens were prepared at different weight ratio, i.e, 0, 10, 20 and 30 % of CRN with 100, 90, 80 and 70 % of UP matrix mixed with 1 % of hardener. Compounded matrix with fillers has been done by using mechanical stirrer for 10 min. compounded material were poured into a flat surface mould and left to cure at room temperature for 24 hrs, Then post cure at 120 C^0 for 3 hrs.

Tensile test; The tensile strength test was performed according to ASTM D 5083, the test was carried out with a universal testing machine model Instron 3366 equipped with load capacity of 10 kN at a deformation rate of 5 mm/ min and a gripping length of 100mm. the relative humidity (RH) and temperature in testing were maintend at 50% and 25 ^{0}C respectively. The replication of 5 specimens for each sample was carried out.

Flexural test: Sample were prepared according to ASTM D790, which was 3mm thick,125 mm long and 10mm wide and then conditional at temperature of 25C^0, RH of 50% for minimum 40 hrs before testing. Flexural load on 3-point bending was used with recommended testing span to the depth ratio of 16:1.

Bending was conducted using a load cell of 5KN at 2.8 mm/min rate of loading. The replications of 5 specimens for each sample were carried out.

Thermal test: Thermogravimetric Analysis (TGA) & Differential Scanning Calorimeter (DSC) tests were performed concurrently using the Mettler Toledo TGA/DSC. The test were performed using aluminum pan at heating rate $10C^0$ /min in the temperature range from 0 C^0 to 100 ^0C, Nitrogen flow at a rate of 50 ml /min was kept throughout the experiments. Sample mass for each experimental was chosen between 6 and 12 mg

RESULT AND DISCUSSION

The effect of increasing filler contents (cured resol novolac), on the results of tensile strength, flexural strength, tensile modulus, flexural modulus and elongation at break of the composite system are presented in Table 1.

Table 1: the effect of filler contents on the mechanical properties of the UP/CRN composites

CRN content %	Tensile strength (Mpa)	Flexural strength (Mpa)	Tensile modulus (Mpa)	Flexural modulus (Mpa)	Elongation at break (%)
0	21.32	76.65	355	189	4.15
10	19.43	68.98	375	205	3.43
20	18.12	62.22	405	217	3.06
30	15.56	54.78	464	224	2.89

The relationship between tensile strength of UP/CRN composites with CRN loading is showing in **Figure 1**. The tensile strength value of pure UP was decreased by additional of CRN filler at 10, 20, and 30 % (19.43, 18.12 and 15.56 Mpa) respectively. The decreasing of tensile strength can be attributed to the physical properties of the filler and interaction of this filler with UP matrix which create a void that induced to the initiation crack in the composite and the initiation cracks were caused the tensile and flexural strengths of the composites were decreased. **Figure 2 .** also the large particle size of filler (200 micron) were caused decreasing of tensile strength of UP/ CRN composites and the agglomerated particles were reduced the compatibility of filler in UP matrix. On the other hand the incorporation CRN has improved the stiffness of the UP matrix, since the tensile modulus of composites increased as CRN filler loading was increased **Figure. 2**, it is well known that the incorporation of fillers has improved the stiffness of the UP composite[12].

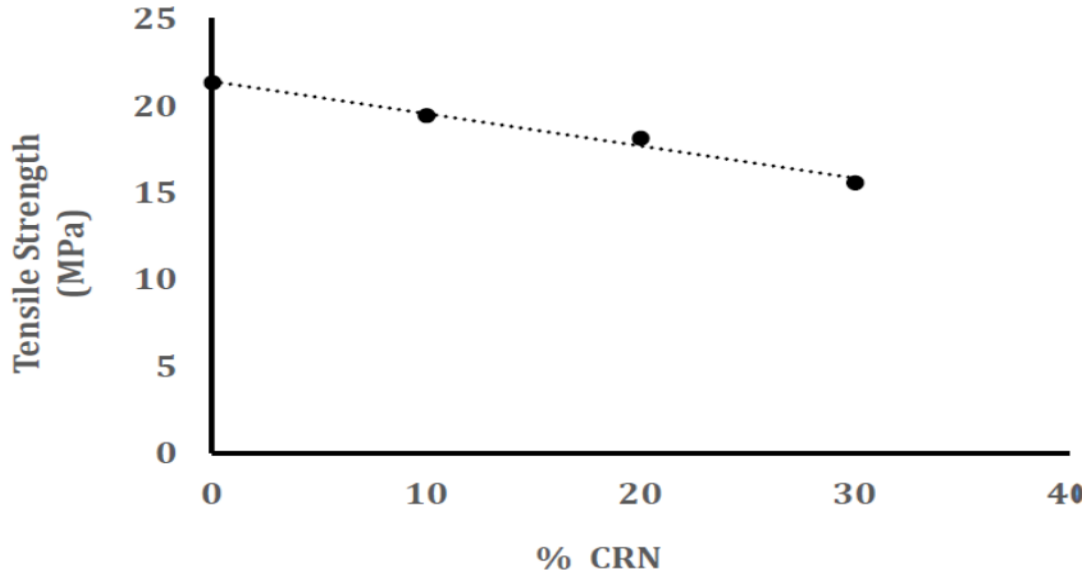


Figure 1: Effect of CRN filler on the tensile strength of UP/CRN composites

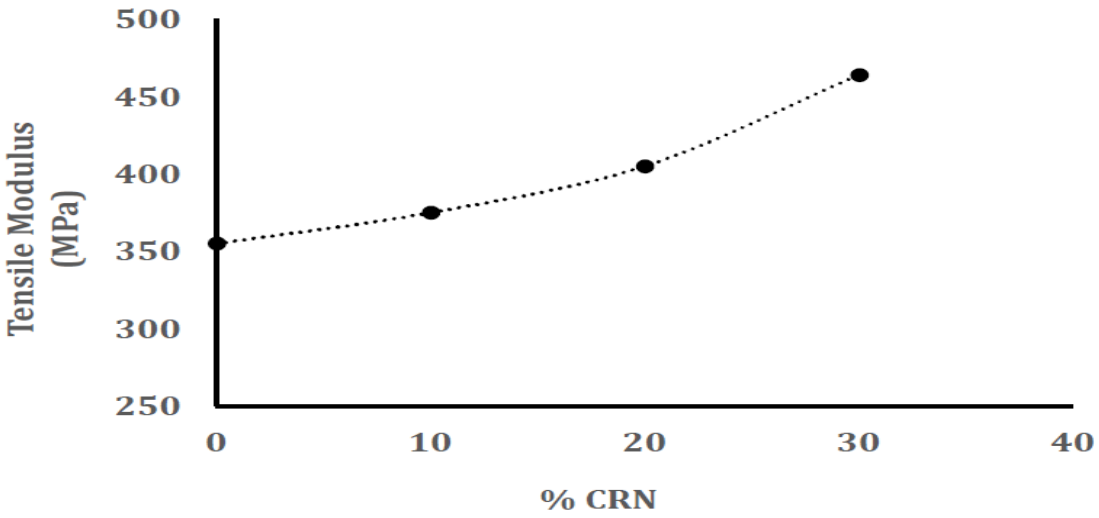


Figure 2: Tensile modulus of UP/CRN composite at different filler content

Figure (3) shows the effect of CRN loading on the elongation at break of UP/CRN composites. The addition of fillers caused the matrix to be losing its elastic properties, in other words, the material is more brittle, it was reported that the decrease in elongation at break of mica/epoxy composites was due to reduction of volume of the matrix[13].The rigidity of composites was also due to the restriction of the UP matrix mobility and deformability by the addition of filler content[14].

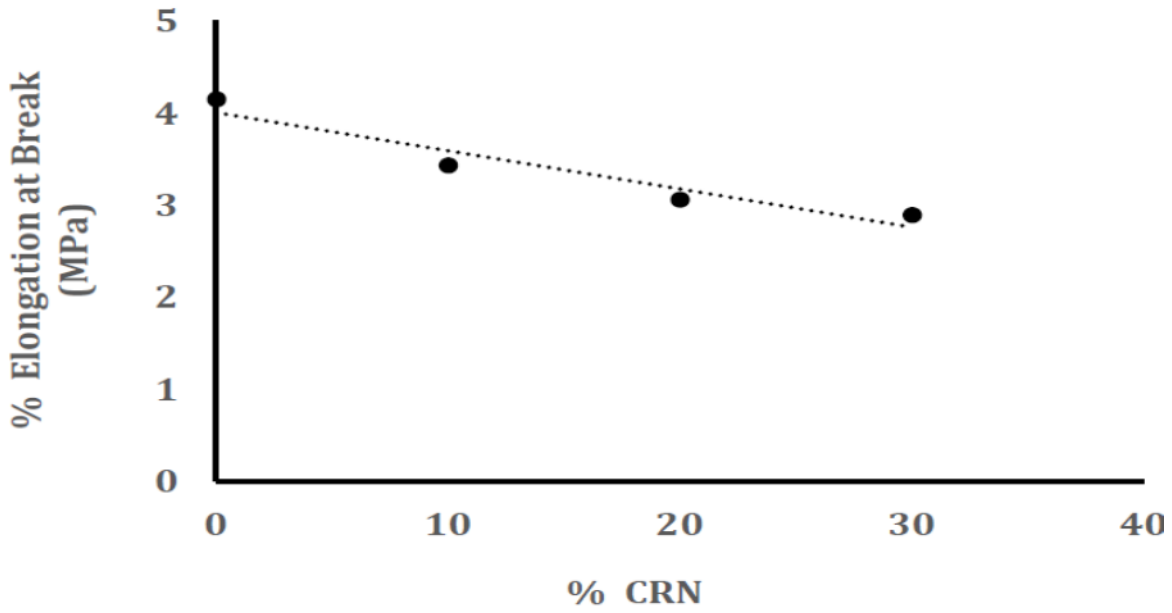


Figure 3: Effect of CRN loading on elongation at break of UP/CRN composites.

The flexural stress or strength was determined using athree point bending test is determined using athree point bending test is given by Eq, (1)

$$\sigma \max = (3p\max L) / (bh2)$$

Where the pmax is the maximum load at failure (N), L is the span in mm, b and h are the width and thickness of the specimen in mm, respectively.

The results of flexural strength of the composite UP/CRN are presented in **Figure (4).** In general the graph shows a decreasing trend as CRN filler loading is increased, the reason for this fact is that surface adhesion between UP matrix and CRN filler was rather poor, in the other words, there was less interfacial interaction between UP and CRN. The result of flexural modulus for different filler content of UP/CRN composites is shown in **Figure (5).** The modulus was increased with the addition of CRN filler, this due to the stiffness properties of the composites, the relative stiffness of material is indicated by its modulus. In the case of thermal study, **Figure (6)** shows the TGA thermogram of the specimens of composites with several filler content. The thermogram exhibits two mass loss steps; an initial mass loss was below 100 C^0 which was due to the gradual evaporation of moisture or water, and a second mass loss from approximately 150 to 500 C^0, which was due to the decomposition of the polymeric material. Also from the result in Table 2, the initial decomposition temperature (IDT) was increase with increasing percentage

of fillers; this due to highly aromatic content of the CRN fillers and this result also demonstrated that the thermal stability of UP/CRN composites was higher than net UP.

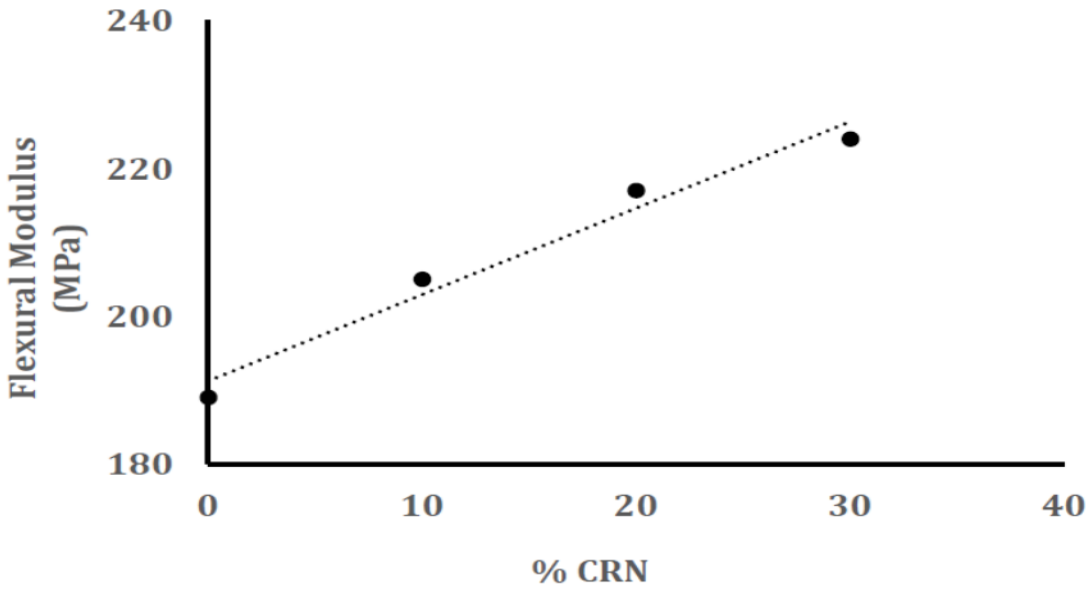


Figure 5: Effect of filler content on the flexural modulus of the UP/CRN

Table 2: Initial decomposition temperature of UP/CRN composites from TGA

Composites	IDT of 5 % mass weigth loss ^{0}C
Net UP	293
UP/CRN 10%	356
UP/CRN 20%	375
UP/CRN 30%	401

The thermal degradation of UP took place through random chain scission and a radical chain mechanism. The maximum mass loss temperature of unsaturated polyester filled with cured resol novolac is shown in **Table 3.**

Table 3 : Tempreture of max weigth loss, Tmax C^0

Composites	IDT of 5 % mass weight loss C^0
Net UP	436
UP/CRN 10%	460
UP/CRN 20%	468
UP/CRN 30%	476

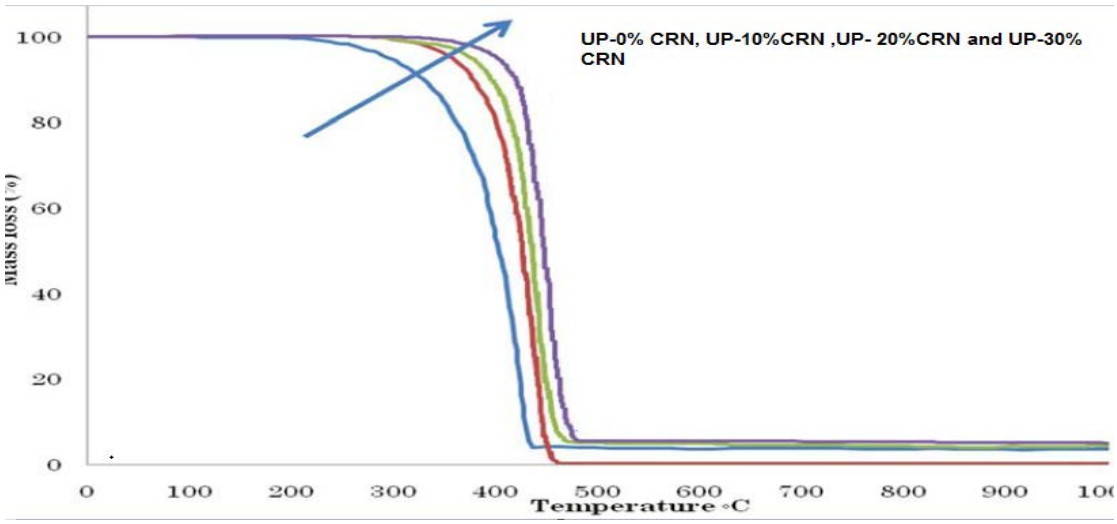


Figure 6) :TGA Thermograms of (a) UP100/0 CRN, (b)UP90/CRN10, (c)UP80/CRN20 and(d) UP70/CRN30

The result based on DSC are shown in figure (7) , there is confirmed by run in the inert condition (nitrogen atmosphere), which does not reveal any exothermic effect, the increasing in the filler content , relatively more exfoliated particles are formed, char forms more and increase the thermal stability. The addition of filler content up to 30 % slightly increases the glass transition temperature, Tg of UP matrix from 185 to 191 ^{0}C

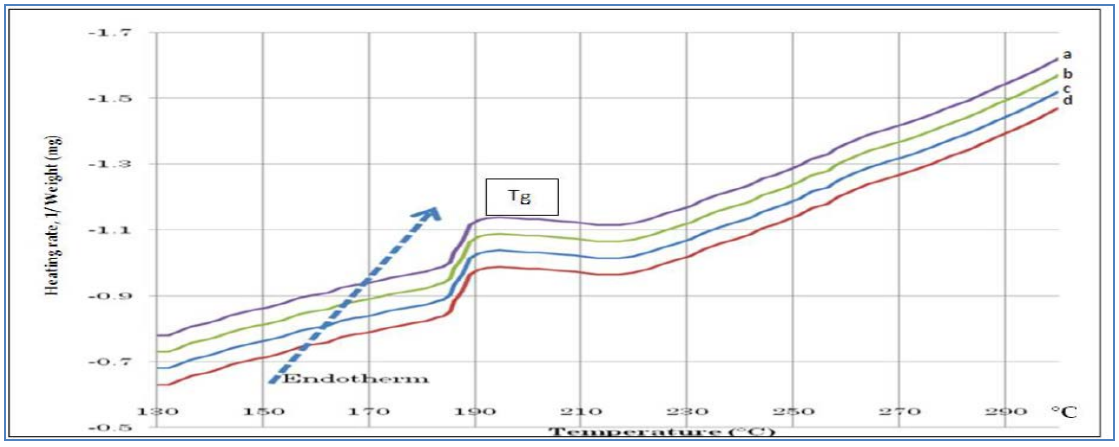


Figure 7: DSC curves of (a) UP100/0 CRN, (b) UP90/CRN10, (c) UP80/CRN20 and (d) UP70/CRN30

CONCLUSION

The incorporation of CRN fillers in UP matrix was improved in modulus but lack of tensile and flexural strength of the prepared composites due to the low surface intraction,However the stiffness of the composites relatively increased as the percentage of CRN increase, The thermal stability of these composites were increased as the CRN increased and the tempreture of maximum mass loss in the trend of UP70/CRN30 (476 C^0) > UP80/CRN20(468 C^0) > UP90/CRN10 (460 C^0)>UP100% (436 C^0).The DSC studies showed glass transition temperature of UP/CRN composites slightly increase from 185 C^0 to 191C^0 with the addition of filler content up to 30 % .

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