

## Synthesis, Characterizations and Study of Mechanical Properties for Blended Nanocomposites Biased on New Epoxy Resin

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### Abstract

This research discloses the development and synthesis of blended nanocomposites filled with titanium dioxide ( $\text{TiO}_2$ ). Hybrid polymer networks (HPNs) based on unsaturated polyester resin (UPR) and epoxy resins were synthesized by reactive blending. The optimum quantity from nano particles of titanium dioxide was selected and different wt. proportions 1%, 3%, 5%, and 7% ratios of epoxy are mixed with UPR resin. The mechanical properties of the blended nanocomposites were compared with those of the basis material (UPR and 3%  $\text{TiO}_2$ ) and with results of semi-interpenetrating UPR/Epoxy blends (semi-IPNs) for one type of new epoxy ( $\text{P}_2$ ) that were prepared. Epoxy resins show good compatibility with the UPR resin on blending, show improves in mechanical properties and tensile strength values are higher for blended nanocomposites, addition improvement in the impact resistance. Considerable enhancement of tensile strength is noticed at very low loading of Epoxy resin. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were employed to study the thermal properties of the resins. Morphological studies of the blended nanocomposites systems were ascertained using scanning electron microscope (SEM).

**Keywords:** blended nanocomposites, epoxy resin, tensile strength, unsaturated polyester

### Introduction

The first production of epoxy resin occurred simultaneously in Europe and in the United States in the early 1940s. Credit is most often attributed to Pierre Castan of Switzerland and S.O. Greenlee of the United States who investigated the reaction of bisphenol-A with epichlorohydrine [1]. Epoxy resins belong to the most important thermosetting polymers with a high crosslinking degree and that contain many hydroxyl groups. Epoxy resins available in a wide variety of properties that are unattainable with other thermoset resins, they are easily cured without evolution of volatiles or by -products by a broad range of chemical species. These polymers have brilliant characteristics such as good chemical and moisture resistance and high dielectric properties, epoxy resins are widely working in modern industries, as adhesives, coatings and paints, and packaging materials for microelectronic devices. It available in a wide variety of physical forms from low -viscosity liquid to high -melting solids and used to produce advanced composites matrices in which they usually act as the matrix, since they exhibit excellent adhesion to reinforcement, cure with low shrinkage, provide good dimensional stability and possess good mechanical properties [2-8].

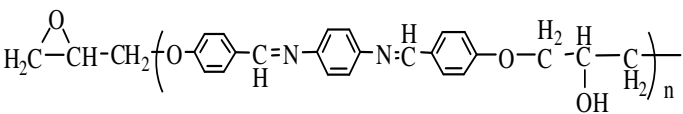
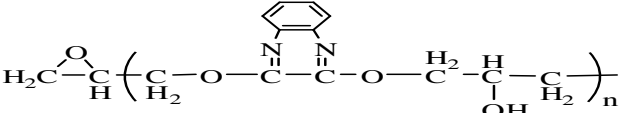
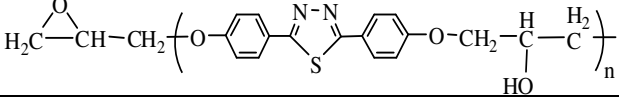
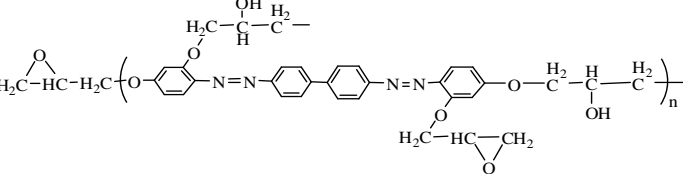
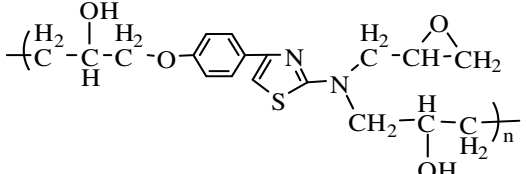
polyester resins (UPR) are comparatively hard and brittle materials and one of the important thermosetting materials used for the manufacture of glass-reinforced plastics and polymeric composites. These resins have wide spread use is due to their relatively low cost, comfortable of processing, high wetting properties with reinforcements, and good balance of properties. UPR are solutions of unsaturated polyester with unsaturated co reactant diluents like styrene [9].

Nanomaterials have recently gained a considerable amount of attention because of their unique physical and chemical properties and their importance in technological applications. because of their large surface -to-volume ratios, their properties, and structural stability are very different to those of their bulk counterparts. It have possess several advantages such as greater thermal stability increased strength, improved flammability properties, etc of polymer matrix.

The chemical and physical combination methods and properties of Polymer mixtures or blends have of great practical and academic regard for widely usable in industry field and because they supply a suitable route for the modifications of properties to meet specific needs. An Interpenetrating polymer network (IPN) is a polymer involving two or more networks which are at least partially interlaced on polymer scale but not covalently bonded to each other [10]. Several studies on IPNs revealed improved mechanical properties. [10,11] In recent years, chemical modification by reactive blending of UPR and other thermosets via semi interpenetrating polymer networks (IPNs) and hybrid polymer networks (HPNs) has been reported. Blending of epoxy resin and polyesters resulting in IPNs [12-14] has been extensively studied. The main objective of this investigation is to study the modifying effect of epoxy resins on UPR. In the present study, HPNs based on unsaturated polyester, epoxy resins and  $\text{TiO}_2$  have been prepared by reactive blending.



**Table 1: Summary of compounds structure and melting points .**

Compound NO.	RESIN	M.P.
Resin 1		>300
Resin 2		>300
Resin 3		>300
Resin 4		>300
Resin 5		>300

**The optimum quantity from titanium dioxide**

The optimum quantity from Titanium dioxide (TiO<sub>2</sub>) was determined by means of measurement properties when mixing different percentage (1,3, 5, 7%) from nano material with unsaturated polyester were mixed together by ultrasonic set for 2 hours at room temperature, than add methyl ethyl ketone peroxide 2% part by weight to the mixture and mixed mechanical stirrer for 5 min., we found that 3% is optimum quantity. Table 2 illustrated the results of mechanical properties for (UPR/TiO<sub>2</sub>).

**Table2: Summary of properties of UPR+ (1,3,5,7) % TiO<sub>2</sub> modified**

Poperty	UPR/ TiO <sub>2</sub> (1%)	UPR/ TiO <sub>2</sub> (3%)	UPR/TiO <sub>2</sub> (5%)	UPR/TiO <sub>2</sub> (7%)
Tensile strength(MPa)	48.2	53	51.7	51
Hardness(ShoreD)	79.5	83.5	83.2	84.1
Impact strength(KJ/m <sup>2</sup> )	4.25	6	5.24	5.04

**Preparation semi-interpenetrating blend (S-IPNs)**

For one type of new epoxy P<sub>2</sub> preparation semi-interpenetrating blends (UPR/Epoxy). Testing tensile, hardness and impact strength properties have been carried out for (semi-IPNs) the data are listed in Table 3.

**Table 3; Summary of properties of S-IPNs [UPR with (1,3,5,7) wt% epoxy resin (P<sub>2</sub>)]**

Property	UPR/(1%)wt Epoxy	UPR/(3%)wt Epoxy	UPR/(5%)wt Epoxy	UPR/(7%)wt Epoxy
Tensile strength (MPa)	59.4	61	61.7	60.04
Impact strength (KJ/m <sup>2</sup> )	5.13	5.65	6.25	7.25
Hardness(ShoreD)	75	80.4	81.7	82.6
Elongation	10.8	10.2	9.3	8.43

**Preparation of polymer blend and composite [B<sub>1</sub>-B<sub>5</sub>]**

Unsachreated poly ester, epoxy resin in varying amounts (1,3,5,7%) and optimum quantity from titanium dioxide (TiO<sub>2</sub>) (3%) were mixed together in a suitable flask, and mixture was placed in a high intensity ultrasonic bath for 2 hrs at ambient temperature conditions ,used ice bath to avoid temperature rise during the sonication process .

Then curing agent methyl ethyl ketone peroxide (2% ) part by weight was added to mixture, the mixture was stirred well with mechanical stirring to give a homogeneous mixture, the mixture poured into mold of iron with dimension (15×5)cm<sup>2</sup> and thickness 0.4 cm and stay for overnight. The first curing was done at room temperature followed by a second curing step at 120° C for 2 hours. When the solidification process is finished the sample was cut down in to standard dimensions.

### Testing

The FTIR spectrum of UPR/TiO<sub>2</sub> and blended nanocomposites were taken using bromide discs on a Shimadzo (IR prestige-21) FTIR spectrophotometer. <sup>1</sup>H NMR spectra were carried out by company: Bruker, model: ultra-shield 300MHz origin: Switzerland, and Bruker model: ER-av-400MHZ, origin: Switzerland are reported in ppm (δ), DMSO was used as solvents. The mechanical testing, tensile strength, elongation, hardness and impact strength were taken for UPR and blended nanocomposites, The tensile and elongation properties were tested on Jianqiao Testing Machine Equipment (ASTM D 638-89), A shore D Durometer was used for measuring surface hardness TH210 (ISO 868) and Charpy impact test achieved by the use Machines Testing .Inc., Amityville, New York.

## RESULTS AND DISCUSSIONS

### Spectroscopic identification

polycondensation was successfully conducted between epichlorohydrin and M<sub>1</sub>, M<sub>3</sub>, M<sub>4</sub>, M<sub>11</sub> or M<sub>12</sub> using aq. NaOH incentive as shown in Scheme 1. The pure polymer and blended nanocomposite after post curing were studied by FTIR spectrum. The FTIR spectra of the purified epoxy prepolymer of polymer [P<sub>1</sub>-P<sub>5</sub>] showed the characteristic C-O band in oxirane ring and ether linkages formed can be seen in Table 4 presents the principal FTIR stretching vibrations for the epoxy resins. Comparing the FTIR spectrum of UPR/TiO<sub>2</sub>, blended nanocomposites [B<sub>1</sub>] and polymer P<sub>1</sub> can be seen in Fig. 1 the FTIR of blend polymer [B<sub>1</sub>] showed appearance good peak for C=O stretching band at 1722 cm<sup>-1</sup> besides to other characteristic bands of polymer [P<sub>1</sub>]. The <sup>1</sup>H NMR spectrum (in DMSO as a solvent) for polymer [P<sub>2</sub>] showed the following signals: signals in the region δ (7.23-7.60) ppm for aromatic protons and OH proton. Many signals in the range δ (3.91-5.35) ppm for aliphatic protons of CH<sub>2</sub> methylene groups. The <sup>1</sup>H NMR spectrum (in DMSO as a solvent) for [P<sub>3</sub>] showed: a singlet signal at δ 8.87 ppm for proton of OH group, double of doublet signals at δ (7.32-8.06) ppm that could be attributed to aromatic protons and a signal at δ 5.76 ppm for one proton of CH group. Another signal at δ (4.312-4.44) ppm due to four protons of 2CH<sub>2</sub>O groups.

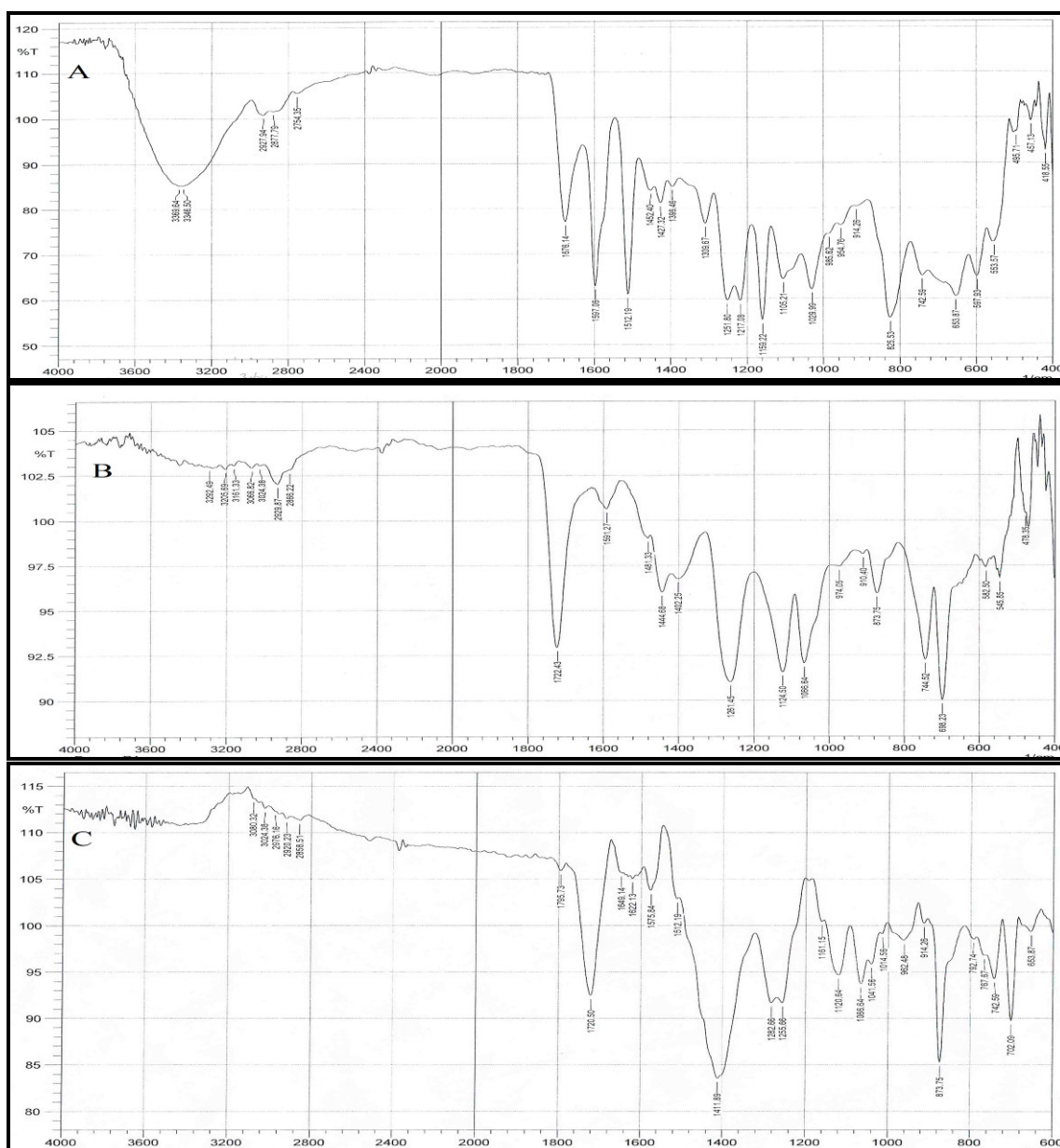


Table 4: Summary of identification of infrared bands for epoxy resins

Polymer No.	OH cm <sup>-1</sup>	C-Hcm <sup>-1</sup> aromatic	C-H cm <sup>-1</sup> aliphatic	C=N cm <sup>-1</sup>	C=C cm <sup>-1</sup>	N=N cm <sup>-1</sup>	C-O-C cm <sup>-1</sup>	oxarin asym.,sym.
P <sub>1</sub>	3369	3060	2927 -2840	1676	1597	—	1251	1217,914
P <sub>2</sub>	3394	3047	2960-2760	1649	1595	—	1269	1240,918
P <sub>3</sub>	3400	3030	2931, 2879	1603	1595	—	1238	overlap with ether, 952
P <sub>4</sub>	3400	3060	2935, 2879	—	1597	1460	1246	overlap with ether, 914
P <sub>5</sub>	3315	3010	2978, 2873	1665	1604	—	1240	overlap with ether, 939

### Mechanical properties

#### Tensile properties

Tensile properties of the composites are mostly affected by the materials, method, specimen condition and preparation, and also by percentage of the reinforcement [18]. Illustrated the results of the tensile tests of the

composite at different weight percentages of epoxy resins, at room temperature were shown in Table 5, most tensile strength values are significantly higher compared to that of the UPR with 3%TiO<sub>2</sub>. Tensile strength with 3 %w of epoxy which exhibited the greatest improvement of tensile strength compared to other ratio of epoxy. Figure 2 shows that the strength decreases with further increase in weight percentages of epoxy. The improvement in tensile strength over that of the base material is due to a higher degree of cross-linking by the interpenetration of networks and chain extension. At higher percentages, many epoxy chains may go uncross-linked, and this leads to a plasticising effect and thus weakening the matrix[9]. Table 6, Figure 3 shows that the elongation at break decreases with increased of epoxy concentration.

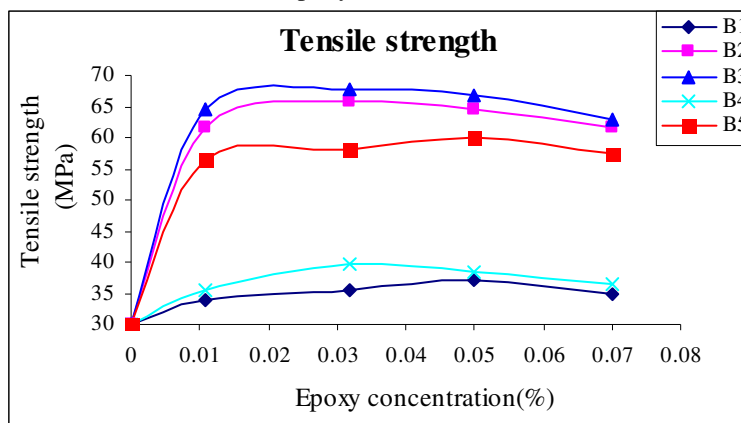


Fig. 2. Tensile strength of blended nanocomposite samples versus epoxy concentration (%)

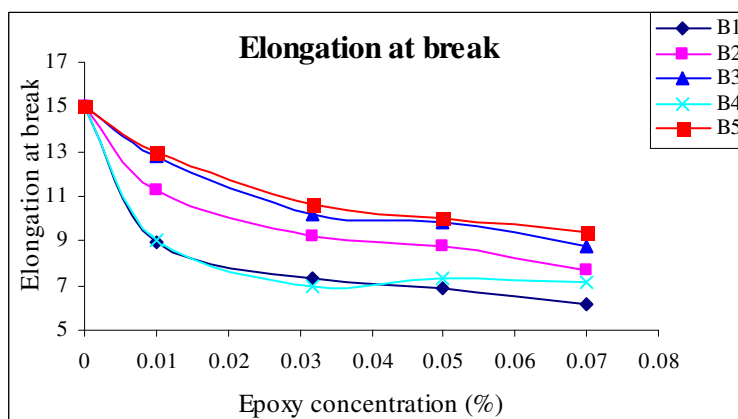


Fig.3. Elongation at break of blended nanocomposite samples versus epoxy concentration (%)

Table 5: Summary of Tensile strength propertie of blended nanocomposites with (1,3,5,7) wt% epoxy resins.

COMPOUND NO.	UPR+3% TiO <sub>2</sub> +1%P	UPR+ 3% TiO <sub>2</sub> +3%P	UPR+ 3% TiO <sub>2</sub> + 5%P	UPR+3% TiO <sub>2</sub> + 7%P
Blend <sub>1</sub>	33.8	35.6	37.1	34.8
Blend <sub>2</sub>	61.5	65.7	64.5	61.6
Blend <sub>3</sub>	64.4	67.6	66.9	63
Blend <sub>4</sub>	35.6	39.7	38.5	36.3
Blend <sub>5</sub>	56.5	58	60	57.5

Table 6: Summary Elongation property of blended nanocomposites with (1,3, 5,7) wt% epoxy resins

COMPOUND NO.	UPR+3% TiO <sub>2</sub> +1%P	UPR+ 3% TiO <sub>2</sub> +3%P	UPR+ 3% TiO <sub>2</sub> + 5%P	UPR+3% TiO <sub>2</sub> + 7%P
Blend <sub>1</sub>	8.9	7.3	6.9	6.2
Blend <sub>2</sub>	11.3	9.25	8.8	7.65
Blend <sub>3</sub>	12.8	10.2	9.8	8.75
Blend <sub>4</sub>	9	7	7.3	7.12
Blend <sub>5</sub>	13	10.6	10.05	9.35

### Impact properties

Increasing of impact strength value with increased weight percentages of epoxy resin as in Table 7, figure 4 is a few this is due to the rigid aromatic rings which make up the polymer backbone [17] and may be arise binet bonds due to the presence of polarity groups that lead to low degree of molecular flexibility and absorb the energy of impact.

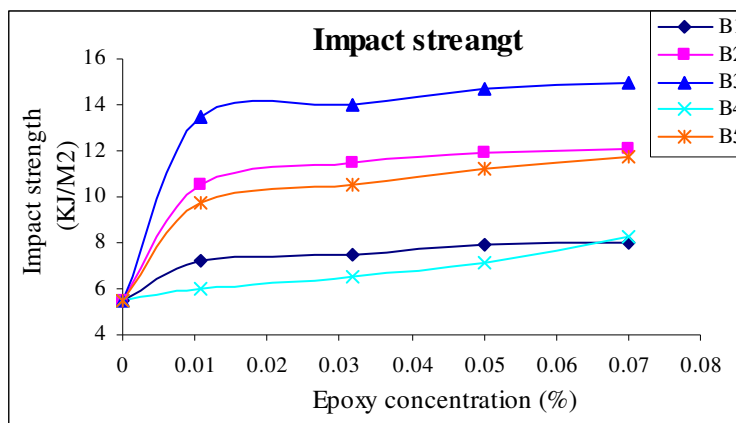


Fig.4.Impact strength of blended nanocomposite samples versus epoxy concentration

Table 7: Summary of Impact strength property of blended nanocomposites with (1,3,5 ,7) wt% epoxy resins

COMPOUND NO.	UPR+3% TiO <sub>2</sub> +1 %P	UPR+ 3% TiO <sub>2</sub> +3%P	UPR+ 3% TiO <sub>2</sub> + 5%P	UPR+3% TiO <sub>2</sub> + 7%P
Blend <sub>1</sub>	7.25	7.5	7.88	8
Blend <sub>2</sub>	10.5	11.5	11.9	12.1
Blend <sub>3</sub>	13.5	14	14.7	15
Blend <sub>4</sub>	6	6.5	7.12	8.25
Blend <sub>5</sub>	9.75	10.5	11.2	11.7

### Hardness properties

Hardness value is increase with increased weight percentages of epoxy resin as in Table 8, figure 5 this is due to the rigid aromatic rings which make up the polymer backbone [17]. This means increasing the proportion of epoxy (%) working to impede the movement of dislocations inside the material basis and this is what hinders the occurrence of the plastic deformation and thus will improve the hardness material .

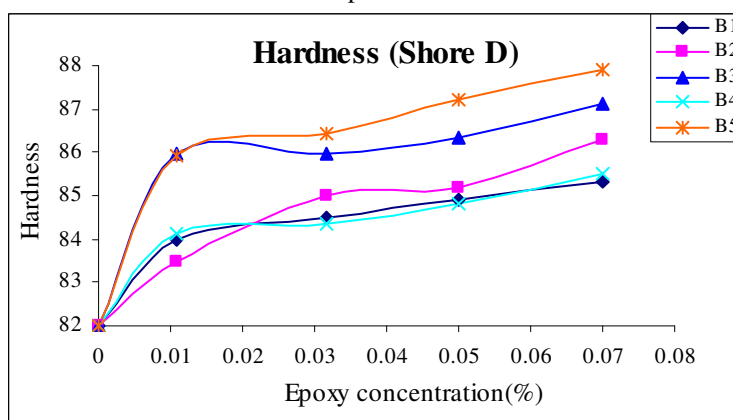


Fig. 5. Hardness of blended nanocomposite samples versus epoxy concentration.



**Table 8: Summary of Hardness property of blended nanocomposites with (1,3,5,7) wt% epoxy resins**

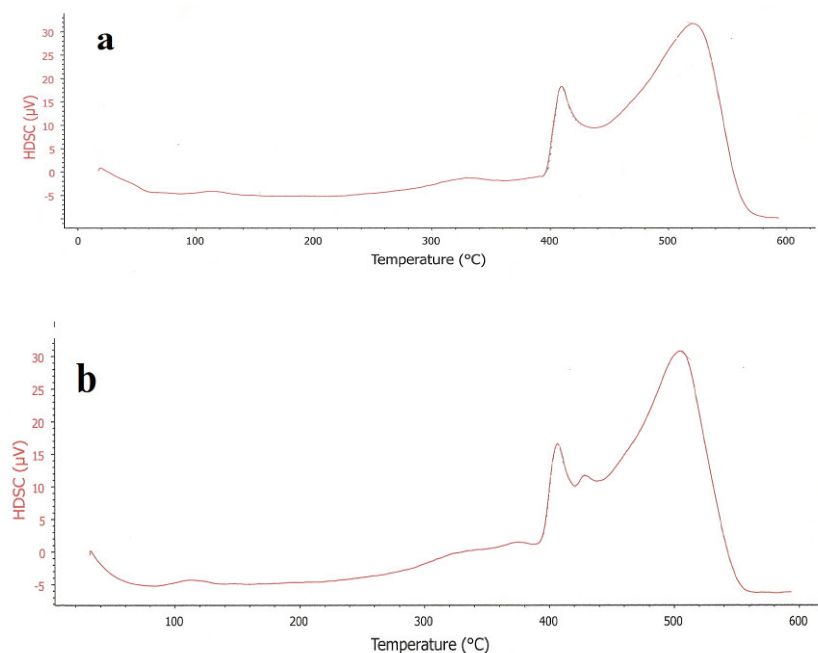
COMPOUND NO.	UPR+3%TiO <sub>2</sub> +1%P	UPR+ 3%TiO <sub>2</sub> +3%P	UPR+ 3%TiO <sub>2</sub> + 5%P	UPR+3%TiO <sub>2</sub> + 7%P
Blend <sub>1</sub>	83.98	84.51	84.92	85.33
Blend <sub>2</sub>	83.49	84.98	85.2	86.3
Blend <sub>3</sub>	85.95	85.97	86.36	87.12
Blend <sub>4</sub>	84.11	84.34	84.8	85.53
Blend <sub>5</sub>	85.9	86.44	87.2	87.9

**Thermal studies**

DSC scan for the blended nanocomposites after curing are shown in Figure 6, the blended nanocomposites has marginally better thermal stability as shown in Table 9 and Figure 7. UPR has a glass transition temperature T<sub>g</sub> of (63°C). Reactive blending with 3% Epoxy results in a homogeneous blended nanocomposites with a single T<sub>g</sub> (72°C) for blend 3.

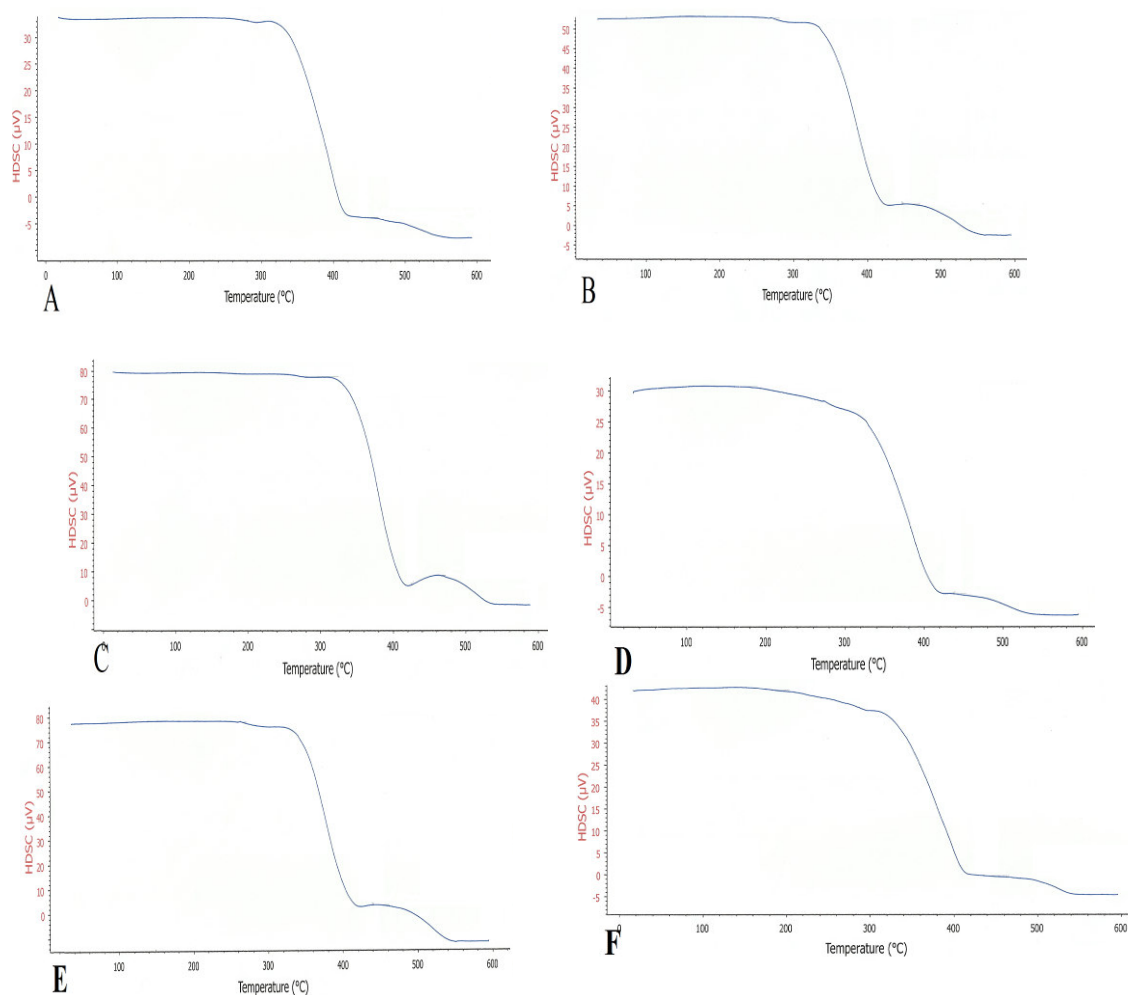
**Table 9: Thermal properties-TGA of blended nanocomposites (3wt% epoxy resin)**

Blend NO.	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
UPR/TiO <sub>2</sub>	281.1	409.1	389.2	8.52%
Blend <sub>1</sub>	268.9	404	386.5	12.50%
Blend <sub>2</sub>	263.5	379.7	405.3	12.00%
Blend <sub>3</sub>	197	405.8	371.6	9.14%
Blend <sub>4</sub>	192	406.2	365	14.65%
Blend <sub>5</sub>	264.9	395.6	372	9.65%



**Figure (6) . DSC of a: UPR and b: blended nanocomposites B<sub>3</sub>**

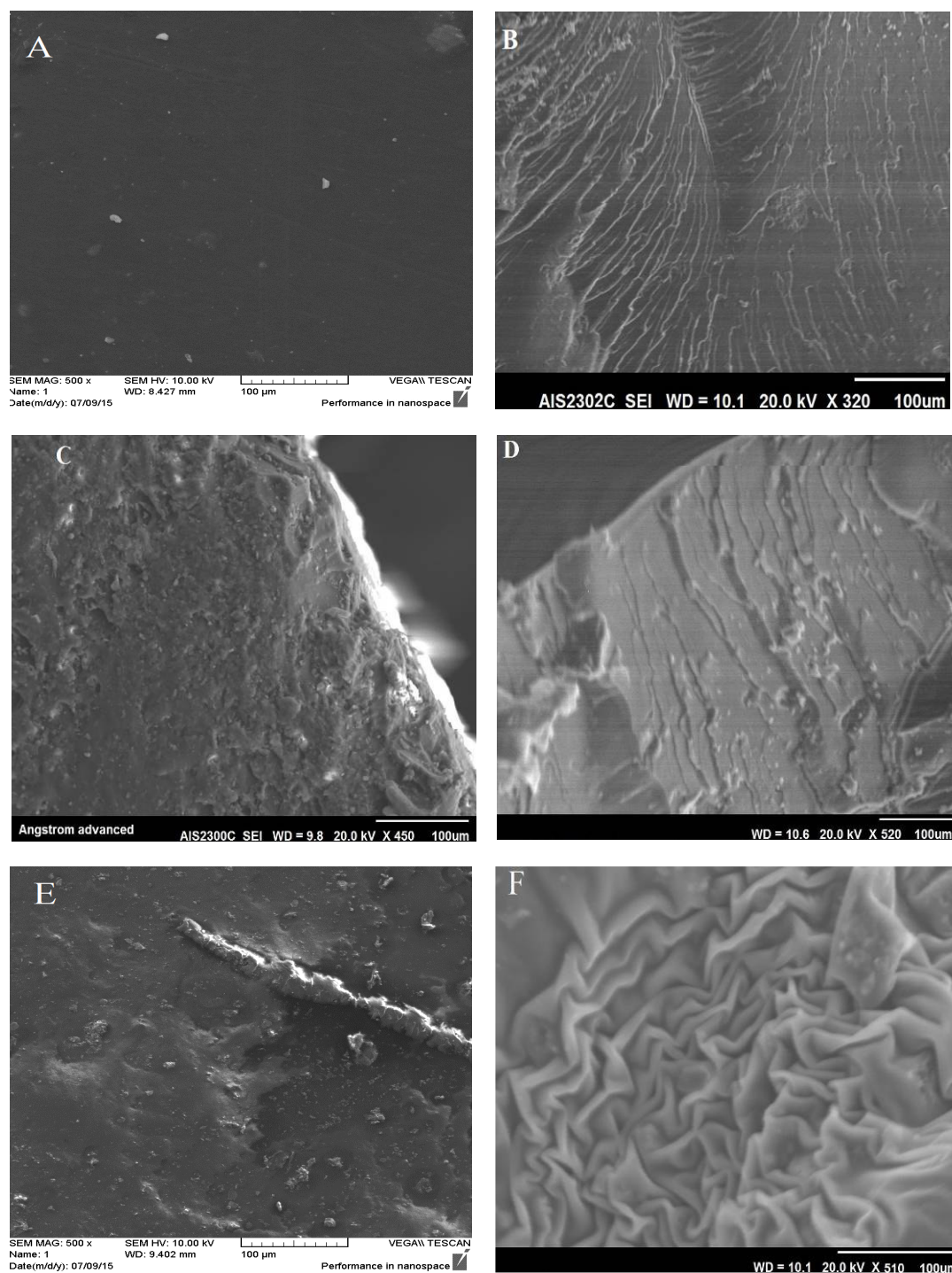




**Figure (7).** TGA of UPR and blended nanocomposites, A:UPR, B:blend 1,C: blend<sub>2</sub>, D: blend 3, E:blend 4,F: blend 5.

### Morphological Studies

The epoxy compounds have better miscibility with the polyester and lead to various morphologies Figure 7 shows micrographs for the UPR/TiO<sub>2</sub> and blended nanocomposites. The UPR/TiO<sub>2</sub> showed homogeneous surface and containing some narrow breaking paths. The comparing five of hybrid systems; these shows that hybrid fracture surfaces of the blends (b,c,d,e,f) indicate extensive crazing and shows that hybrid with b had the fracture paths are branched and less continuous than in the case of the UPR/TiO<sub>2</sub> and the hybrid with c and e had a slightly rough surface. But the hybrid with d and f they are also discontinuous, convoluted, twisted and showed parallel structures in towed undulant crest which indicate to the stretching that takes place prior to fracture. The mechanical properties of the blended systems are strongly dependant on the morphology of the dispersed epoxy resins.



**Fig. 8. Scanning electron micrographs of fracture surfaces (A) UPR, (B) HPNs<sub>1</sub>, (C) HPNs 2, (D) HPNs 3 (E) HPNs 4 F) HPNs 5.**

## CONCLUSIONS

Epoxy prepolymer was successfully prepared, epoxy resins are highly miscible with UPR, (B<sub>3</sub>) is far superior to all other epoxy resins considered in this investigation for blending with UPR. Tensile property show maximum improvement at about 3% by wt. Epoxy concentration. The increase in hardness has been achieved with simultaneous increase in tensile strength for all epoxy resin blends. The improvement in impact resistance has been seen, blended nanocomposites show substantial improvement in thermal stability. Epoxy resins in general can be used as modifiers for UPR at low percentages.

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