

Synthesis, Characterization and Effect of Conductive Filler on Mechanical properties of thermosetting resin

V. T. Bhugul¹, G. N. Chaudhari²

Nano Technology laboratory, Department of chemistry,
Shri Shivaji Science College, Amravati (Maharashtra), India
1.vtbhugul@gmail.com 2 cgnrao@yahoo.com

Abstract: Conductive polymer polyaniline (PANI) and its composite with activated charcoal (AC) have been synthesized by in-situ polymerization technique and this composite is used as filler in unsaturated polyester resin. PANI-AC reinforced composite with supporting matrix of unsaturated polyester resin containing 5 to 30% PANI-AC have been used to study mechanical properties such as tensile strength, flexural strength, % elongation and young's modulus by standard methods. The PANI-AC composite samples were characterized by FTIR, SEM and XRD. The results indicated that amount of reinforcing agent ie PANI-AC plays a vital role in the properties of thermosetting resin.

Key words: Resin, Composite, Activated charcoal, Tensile strength, young's modulus, elongation.

1. INTRODUCTION

The heterogeneous mixture of two or more heterogeneous phases which are bounded together is called composite [1]. Recently composite material have been of interest because of their wide applications in many fields such as civil Engineering, industrial, defense, automobiles, space craft, packaging and biomedical applications due to their excellent thermal and mechanical properties [2-5]. The composite materials generally consist of four constituents such as matrix, reinforcement, accelerator, fillers or coupling agents. By permutation and combination of various fibers and polymers, a wide range of composite having unique properties for versatile applications as alternative to conventional materials like metal, wood etc. have been synthesized. Composites are materials that comprise strong load carrying material known as reinforcement imbedded in weaker material known as matrix [9]. Reinforcement provides strength and rigidity to the composite. Reinforcement is used with resin system to improve the mechanical properties of cured resin and to provide a usable product. The matrix or binder maintains the position and orientation of the reinforcement. Filler is the additives material which is used to enhance the thermal as well as mechanical properties and also for reducing the cost of the material and product. Various types material such as organic (wood flour, hull, carbon black, graphite etc.) and inorganic (asbestos, silica, talc powder, mica CaCO₃ etc.)

were used as fillers. The thermosetting polyester resin matrices have been used in the widest range of structures because of easy handling, cheap price, balanced thermal, chemical and mechanical properties. In this work unsaturated polyester thermosetting resin were used as matrix due to its good mechanical properties, relatively low cost and corrosion resistance.

Among the conducting polymers polyaniline (PANI) is one of the most studied intrinsically conducting polymers. PANI obtained high value in scientific community owing to its easy preparation, easy doping / dedoping, environmental stability and low synthesis cost, so PANI is probably the most important industrial conducting polymer today [5,6]. PANI useful in wide area of applications; such as a solar energy conversion, rechargeable batteries, electro chromic displays, electrochemical sensors capacitors, and active corrosion protector [7,8]. The processibility of PANI can be increased by making its composite with carbon black, metal oxides, or blends with conventional polymers like PVC, PVA, Nylon 6, Polyacryl amide etc. In present work the activated charcoal (AC) have been used to prepare PANI-AC composite using in-situ techniques with supporting matrix of polyester. The composite was characterized by FTIR, SEM and XRD characterization methods and the mechanical properties of PANI-AC composite with supporting matrix of polyester contains different wt % of composite were studied.

2. EXPERIMENTAL:

2.1. Materials:

The materials used for synthesis of composites include aniline monomer, Ammonium peroxodisulfate (NH₄)₂S₂O₈, HCl, Activated charcoal, Dimethyl sulphoxide (DMSO) and methanol, were purchased from Merck India Ltd. Unsaturated polyester, Methyl ethyl keton peroxide (MEKP), and cobalt octet were purchased from Wilson k. laboratories, Mumbai. aniline monomer from Merck was distilled and stored under 0⁰C before use.

2.2. Synthesis of polyaniline (PANI)

Polyaniline was prepared according to a procedure reported in literature after some modifications. In this procedure Ammonium peroxodisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ (12.3g, 0.054mol), was dissolved in 70 ml of 1M HCl in a 500 ml beaker and kept at 5°C using ice bath. Aniline (5 g, 0.054 mol), was dissolved in 75 ml of 1M HCl in another 500 ml beaker and also kept at 5°C . Then, ammonium peroxodisulfate solution was added slowly to the aniline solution over a period of 1 minute. The flask was left for 30 minutes, during which the temperature remained constant at 5°C . The solution started to take on a blue-green tint after one to three minutes, then became intense blue green with a coppery glint. After 30 minutes, the precipitate was collected on a Büchner funnel and flask using a water aspirator. The precipitate cake was washed portion wise (80 ml/portion) with deionized water until the filtrate became colorless. The liquid level in the filter should be constantly adjusted to be above the top of the precipitate. This prevented cracking of the precipitate cake, and hence avoid inefficient washing of the precipitate. In order to remove oligomers and other non-polymeric impurities the precipitate was washed thoroughly with methanol and deionized water. After washing, the precipitate remained under section for 10 minutes until significant cracking of the moist filter cake occurred. This cake was dried at $50\text{-}60^\circ\text{C}$ in an oven, powder in mortar and stored for processing, the yield was found about 92%.

2.3 Synthesis of activated charcoal reinforced blend of PANI- USPR

The activated charcoal particles were pretreated by boiling in 4 mol/dm^{-3} HNO_3 solution for 4 hours, then washed with deionized water until pH~ 7. The 0.1, 0.2, 0.3 and 0.4 gm amount of treated Activated charcoal (AC) was dispersed in 1 mol/dm^{-3} H_2SO_4 solutions by ultrasonic over 1 h, then the solution was transferred to magnetic stirring apparatus equipped with an ice bath. aniline monomer was then added to the above suspension of carbon particles. 20 mL of 1 mol/dm^{-3} H_2SO_4 solution containing APS (molar ratio ANI/ APS 1: 1.2) was slowly added to the suspension keeping constant magnetic stirring, at a reaction temperature of $0\text{-}5^\circ\text{C}$ for 15 min. After further 6 h stirring, the resulting green suspension was filtered and rinsed several times with distilled water and methanol until filter became neutral and colorless. The obtained powder was dried in a vacuum oven at 60°C for 24 hours.

The resulting composite were added in a 100 ml of USPR and thoroughly mixed half an hour to get homogeneous mixture and then methyl ethyl ketone peroxide (MEKP) was used as a hardener, as an amount of 1.5 wt % of USPR was added, the

mixture was then poured into the mould and kept it 5-6 hours for drying. After drying the blends were released from the mould in sheet form. Samples were prepared by addition of varying quantity of PANI-AC composite in USPR.

3. CHARACTERIZATION

The specimen synthesized were characterized by different standard methods such as optical, morphological, phase and structural characterization using FTIR, SEM and XRD analysis respectively. The mechanical properties such as tensile strength, tensile strain, percentage elongation and young's modulus of blend samples were determine by standard method with the help of universal testing machine.

4. RESULT & DISCUSSION

4.1 FT-IR analysis

FTIR spectroscopy is a very useful and convenient technique to detect the interaction developed between two or more components of a blend. The FTIR spectra USPR and of selected blend samples are shown in figure 4.1.1 and 4.1.2 respectively. Fourier Transform Infrared (FTIR) Spectra were recorded by a Shimadzu FI-8400 Fourier Infrared Spectrophotometer with the KBr pellet technique. The peak at 1720 cm^{-1} corresponding to carboxylic group on Activated charcoal particles, fig. 4.1.2(a) appears also on the spectra obtained for the PANI-AC composites with supporting matrix of USPR fig. 4.1.2(b), which differ from the spectrum of pure PANI Fig. 4.1.2(c). The spectra of the composites exhibit clear benzoid and quinoid ring skeleton vibrations of PANI macromolecules at 1470 and 1565 cm^{-1} , which can be seen at 1490 and 1588 cm^{-1} respectively in the case of pure PANI. The strong band at 1150 cm^{-1} was described by MacDiarmid as the "electronic-like band" and considered to be a measure of the degree of delocalization of electrons, thus, it is a characteristic peak associated to PANI conductivity.[1-12]. The FTIR spectra of the composites with supporting matrix of USPR show several obvious differences in comparison with the spectrum of pure PANI. First of all, the spectra of the composites have a higher strength ratio of the previously described peaks (Iquin/Ibenz) and a lower vibration frequency with respect to the spectrum of pure PANI. The fact that the relative intensity of the electronic-like band in the composites is much higher than in the pure PANI, indicates that the composites have a higher conductivity than pure PANI.

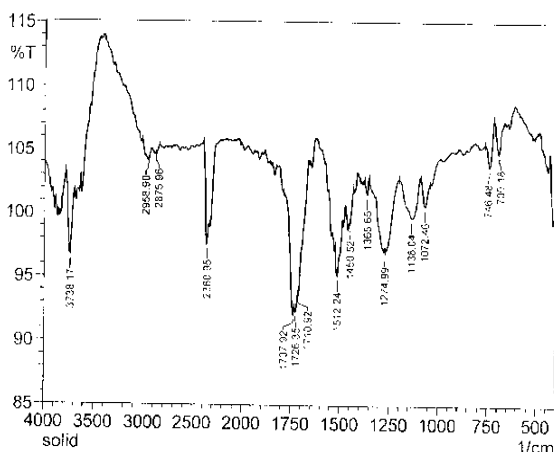


Figure 4.1.1 FTIR spectra of USPR

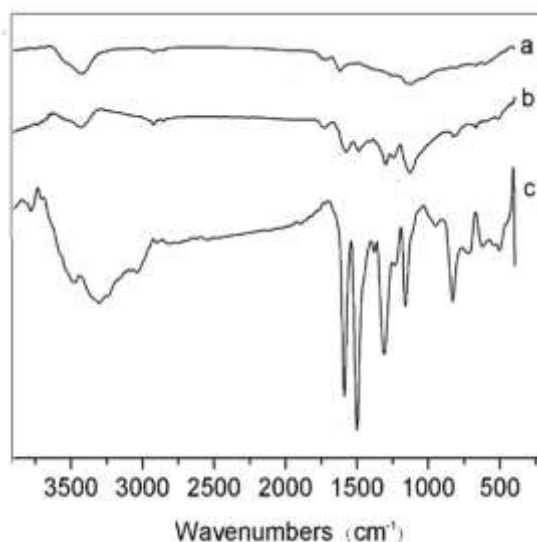


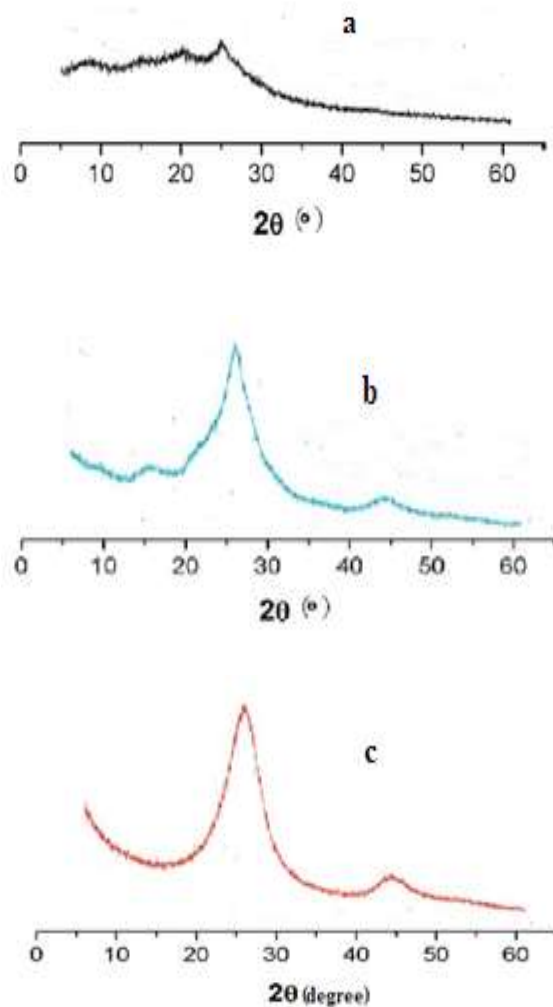
Figure 4.1.2 FTIR Spectra of (a) PANI and (b-c) for selected blend samples containing different wt % of filler.

The figure 4.1 shows the FTIR spectra of USPR by comparing this spectra with spectra obtained for blend samples, it is observed that the carbonyl stretching at 1726 cm^{-1} for the USPR shift to lower frequency of 1710 cm^{-1} for blend samples with activated charcoal fillers as a results of intermolecular hydrogen bonding.

4.2 X-Ray diffraction study

X-ray Diffraction (XRD) measurements were obtained on a Rigaku Rotaflex X-Ray diffractometer using a $\text{Cu K}\alpha_1$ X-ray source operating at 40 kV and 30 mA, at a scan rate of $0.1^\circ/\text{min}$. Figure 4.2 shows the XRD patterns of PANI (a) , AC (b) and different samples. For the AC particles (a), the diffraction peaks are observed at $2\theta = 26.2^\circ$ and 42.5° , corresponding to C(002) and C(100) crystal faces[11]. For PANI macromolecules (f), the crystalline peaks appear at

$2\theta = 8.8^\circ, 15.0^\circ, 20.4^\circ,$ and 24.9° , corresponding to (001), (011), (020), and (200) [13] crystal planes in PANI emeraldine salt form. The XRD data for the composites (b–c) reveal crystalline peaks including all the evidences already obtained for the pure PANI and AC particles. As the PANI content increases, more and more PANI macromolecules cover the surface of the AC particles, and the specific peaks of pure PANI become better visible, whereas the diffraction peaks corresponding to the carbon particles get weaker. Evidences show that a thin polymer layer effectively covers the surface of the AC particles. On the basis of SEM morphological characterizations, no substantial differences can be directly observed among the samples.



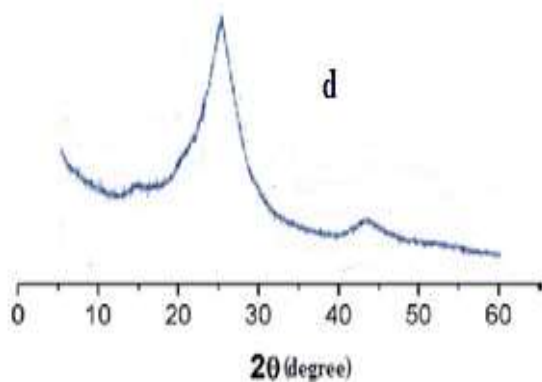


Figure 4.2: XRD patterns of PANI,(a) & samples (b-d) for different wt% loading of filler

4.3 SEM analysis

Figure 4.3 shows the morphology of Activated charcoal particles (a) and PANI-AC composites with supporting matrix of USPR (b, c) the AC particles disperse evenly. After AC compounded with PANI in a composite using USPR as supporting matrix, polymer coat onto the carbon particles. From this evidence, we conclude that in low quantity of aniline monomer, the AC particles were coated with PANI by in- situ deposition of the formed conducting polymer, oligomer, or anilinium cations from the non aqueous medium because of the electrostatic attraction of the carboxylic anion. The change in surface morphology were observed with increasing loading (wt %) of AC in polymer matrix. At lower content of AC , the uniform granular dense interconnected morphology attributed to the homogeneous dispersion of AC particles in to the blend sample. At higher content of AC particles , porous granular morphology accumulates with voids are observed.

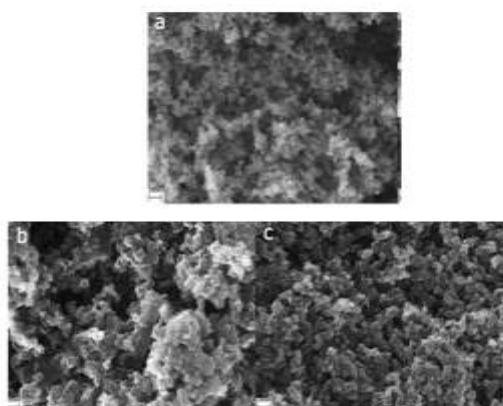


Figure 4.3 SEM images of (a) PANI (b & c) PANI-USPR (10 at % & 30 at % of filler)

5 Mechanical Properties

For measurement of mechanical properties such as Tensile strength, Tensile stress, % Elongation and

Young’s modulus, specimen samples of blends with activated charcoal filler loading are prepared. Initially the moisture present in activated charcoal was removed by keeping it in hot air oven at 70 °C temperature for 1 hour . The in-situ blend of PANI-USPR blend was prepared in non aqueous medium and in this blend different Wt % of activated charcoal fillers were added and curing of blend takes place by addition of MEKP and cobalt octet as initiator and accelerator respectively. The test specimens in the form of thin sheet of width of narrow section 4.4 mm, distance between grips 50 mm, total length of specimen 110 mm, thickness of specimen 2.05 mm. The tensile strength at break point calculated by dividing the maximum load in Newton’s by the original minimum cross sectional area of the specimen in square meters. % Elongation was calculated by using following formula;

$$\text{Elongation at break} = \frac{(\text{Change in the gauge length at break/ yield}) \times 100}{\text{original gauge length}}$$

Mechanical properties are studied by use of universal testing machine (ASTMD 882 method). Figure 5.1, 5.2 and 5.3 shows effect of fillers on tensile strength, % elongation and young’s modulus respectively.

The figure 5.1 shows the behavior of tensile strength of in-situ blend using AC fillers , in this case there is decrease in tensile strength is observed. This decrease in tensile strength may be attributed to change in effective cross sectional area brought about by AC as filler in dispersed phase.

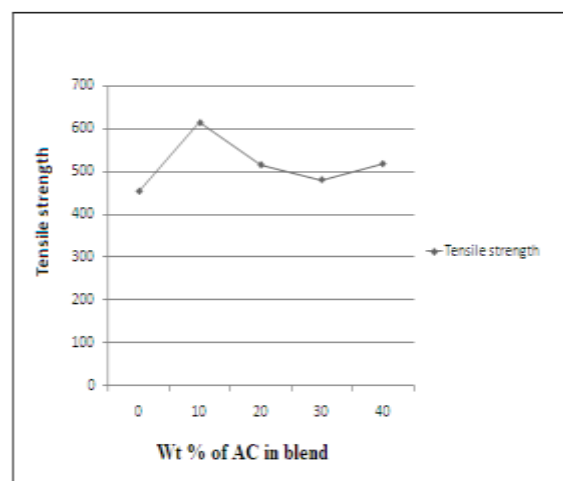


Figure 5.1 Effect of filler on Tensile strength of blend

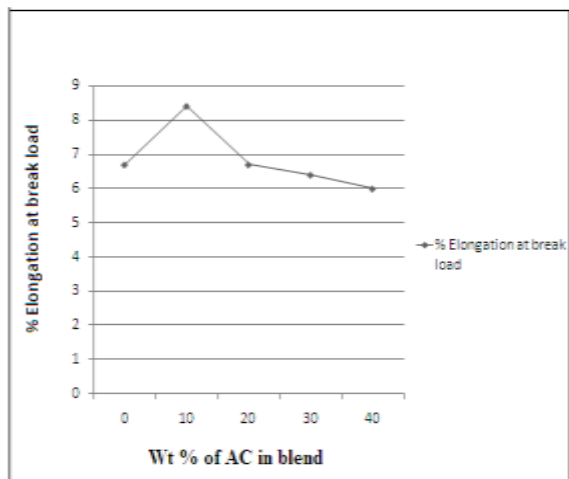


Figure 5.2 Effect of filler on % Elongation of blend

Figure 5.2 shows the % elongation of blend, there is marginal decrease in % elongation is observed. Figure 5.3 shows young's modulus of in-situ blend in which there is increase was observed up to 30 at % of AC and decreased on increasing wt % of AC. This decrease in modulus values at higher loading indicates that there may be reduction in stiffness of the blend sample. At this loading AC particles may acts as lubricating agent facilitating ductility in the composite/ blend at higher loading.

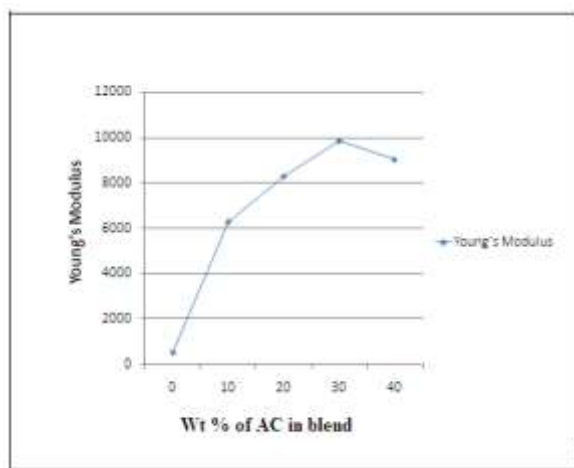


Figure 5.3 Effect of Wt % of filler in blend on young's modulus

6. CONCLUSION

The PANI-USPR blend was synthesized by in-situ method and PANI-AC composite with supporting matrix of USPR also synthesized in non aqueous medium by the same technique. The carbonyl stretching at 1726 cm^{-1} for the USPR shift to lower frequency of 1710 cm^{-1} for blend samples with activated charcoal fillers as a results of intermolecular hydrogen bonding. XRD and SEM analysis shows that a thin polymer layer effectively covers the surface of the AC particles and no

substantial differences was directly observed among the samples.

The tensile strength and % elongation of specimen samples decreases with increase of filler loading while young's modulus increases with loading of filler.

REFERENCES

1. A. Kelly. Concise Encyclopedia of composite materials. Elsevier science ltd. Amsterdam, 1994.
2. A. Kafi, M.Z. Abedin, M D H Beg, M.A. Khan, study on the mechanical properties of jute/ glass fiber reinforced unsaturated polyester hybrid composites, *Jn. of reinforced plastic and composites*, vol 25, 575-588,2006.
3. R. A. Khan, M.A. Khan, S. Sultana, M.N. Khan Q. T. H.Shubhra and F. G. Noor, *J. Reinforced plast compo*, 29, 466- 476,2010.
4. A. K. Bledzki, and J. Gassan, *J. Prog polym Sc.* 24, 221-274, 1999.
5. F.W.J. van Hattum, F. Regel and M. Labordus *Plast rubber composites*,40- 93(99) 2011.
6. N. Shah and N. Banarji, *Appl. Polym Sc.* 62, 1199-1204, 1996.
7. D.E.Tallman, G. Spinks, A.Dominis, G.G. Wallace, *J. Solid state electro chem.* 2002,685.
8. B.Wessling J. Posdorfer, *Electrochem Acta*, 1999,44,2139.
9. J.M.Lawther and H. Ldholt, *Comprehensive polymer materials*, . Elsevier Ltd. 2000.
10. Harada, M.; Adachi, M. *Adv Mater* 2000, 12, 839
11. Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. *J Am. Chem. Soc* 2001, 123, 3838.
12. Yu, Y. J.; Che, B.; Si, Z. H.; Li, L.; Chen, W.; Xue, G. *Synth. Met* 2005, 150, 271.
13. Wang, C.; Waje, M.; Wang, X.; Tang, J. M.;Haddon, R. C.;Yan, Y. *Nano Lett.* 2004, 4, 345.