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SYNTHESIS AND THE STUDY OF TENSILE PROPERTIES OF POLYANILINE-POLYESTER (UNSATURATED) COMPOSITES USING ACTIVATED CHARCOAL AS FILLER.

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Abstract: This work deals with the synthesis of polyaniline, unsaturated polyester resin and PANI-USPR composites using Activated carbon black as filler in stable dispersion form using non aqueous medium by in-situ technique. The composites thus synthesized were characterized by FT-IR, UV-Visible and scanning electron microscope. In spectrometric study the peak positions indicates an intermolecular hydrogen bonding between amine group of PANI and carbonyl group of USPR. In synthesized composites, the tensile properties are found to be improved by loading of filler. The SEM study of composites revealed that in PANI-USPR composite activated charcoal particles dispersed evenly. The tensile properties such as tensile strength, percentage elongation and young's modulus of composites significantly affected by addition of filler content in composite.

Keywords: PANI, USPR, Composites, Tensile properties.



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INTRODUCTION

Composites are the materials which consist of a combination of two or more materials in which the individual components retain their separate identities [1]. These are also defined as a heterogeneous mixture of two or more heterogeneous phases which were bonded together [2]. Recently composite and blend materials have been of interest because of their wide applications in many fields such as civil, industrial, military, space craft, automobiles, packaging and biomedical applications mainly because of their excellent thermo-mechanical properties [3-6]. Among the conducting polymers, polyaniline and its co-polymers have been widely used to study due ease of its protonic acid doping in the emeraldine form and its environmental stability in both doped and undoped forms. The doping methods of polyaniline by protonic acid were discussed in previous chapter. As per the previous discussion conductivity of polyaniline (PANI) depends on the degree of protonation of the material unlike other conducting polymers. The processibility of PANI has been achieved by making conductive composites or blends of PANI with conventional polymer like polystyrene (PS), unsaturated polyester resin (USPR), polyvinyl acetate (PVAc), polyvinyl chloride (PVC) wherein the composites retain the thermo-mechanical properties of the conventional polymer and conducting polymer. Great interest has been focused on synthesis and characterization of polyaniline-unsaturated polyester (PANI-USPR) blend in non aqueous medium with the use of in-situ polymerization technique. This blend may combine the desired properties of two components, the electrical conductivity of PANI with the physical and mechanical properties of polymeric matrix [5, 6]. Polyester matrices have been in use for the longest period in the widest range structures because of easy handling, balanced mechanical and chemical characteristics and cheap price. Polyesters cure with the addition of a catalyst such as peroxide resulting in an exothermic reaction, which can be initiated at room temperature.

In present work, unsaturated polyester resin was preferred due to their good range of thermo-mechanical properties, low cost, corrosion resistance and low molecular weight. Therefore, polyesters were suitable for variety of applications and are adaptable to the fabrication of large structures. [7-9]. The conductive polymers can be used as fillers in conventional polymers to obtain composite with excellent thermo-mechanical properties. In this part of research conducting polymer polyaniline was used for the preparation of PANI-USPR composite which is morphologically porous matrix and has improved thermal stability. The PANI-USPR composites with various weight percentage of PANI synthesized by in-situ method were characterized using various characterization techniques such as, UV, FTIR and SEM to find the utilization of synthesized composites. The compressive strength, tensile strength and percentage elongation, such tensile properties of blend was also studied.

2. Experimental

2.1 Materials Used

The aniline monomer, Ammonium peroxy-disulfate (APS) and Dimethyl sulfoxide (DMSO) purchased from Merck, India. Unsaturated polyester resin from Wilson K. Laboratories, Mumbai were used as received. HCl, Methyl ethyl ketone peroxide (MEKP). Cobalt octet was used as a hardener purchased from S.D. Fine Chemicals, India. All chemicals were of analytical grade and used as received.

2.2 Synthesis of polyaniline Emeraldine salt

For the synthesis of polyaniline (ES), Ammonium peroxodisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) (12.3 g, 0.054 mol), was dissolved in 70 ml of 1M HCl in a 500 ml beaker and kept at 5°C using ice bath. Aniline was purified by double distillation at reduced pressure (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 peroxy-disulfate 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 Buchner funnel and flask using a water aspirator. The precipitate cake was washed portion wise (80 ml/portion) with de-ionized 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 de-ionized water. After washing, the precipitate remained under section for near about 10 minutes until significant cracking of the moist filter cake occurred. This cake was dried at 50-60°C in an oven, powder in mortar and stored for processing, the yield was found about 92%.

2.3. Synthesis of PANI-USPR composite

For preparation of USPR supported PANI by in-situ method, 0.1-0.4 ml of purified aniline was added to 10 ml of 2M solution of HCl in DMSO which was then cooled at 5°C to this solution 1g of USPR was dissolved. 0.06 M ammonium peroxodisulfate solution was prepared separately in 1 ml acidic DMSO and then added drop wise over 20 minutes to the above reaction mixture with constant stirring, a 1:12 mol ratio of aniline to Ammonium peroxydisulfate was maintained. Polymerization was allowed to proceed at 5°C for about 8-24 hours with occasional stirring. The

USPR supported PANI composite was isolated by using excess methanol as the precipitant; the isolated product were dried under vacuum. The yield was found to be 89.8 %. For preparation of different samples, the content of PANI in USP was taken 5,10,15 and 20% . The residue obtained was converted in to fine powder and formed pellets. The synthesized samples were named as PANI-USP/5, PANI-USP/10, PANI-USP/15 and PANI-USP/20.

2.4. Synthesis of activated charcoal reinforced composite of PANI- USPR

The activated charcoal particles were pretreated by boiling in 4 mol/dm⁻³ HNO₃ solution for 4 hours, then washed with de-ionized 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 H₂SO₄ solutions by ultrasonic over 1 hr., 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 H₂SO₄ 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 0–5°C for 15 min. After further 6 hrs. 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 hrs.

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 hrs. 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.

6.3 Characterization

The optical, morphological, phase and structural characterization of synthesized samples were characterized by different conventional techniques, such as SEM, UV-Visible, FTIR. The mechanical properties such as tensile strength, tensile strain, percentage elongation and young's modulus of composites were determine by standard method with the help of universal testing machine.

3. Result and Discussion

3.1 UV-Visible Spectra

The Figure 1 shows UV-visible spectra of acid doped PANI and PANI-USPR composite using activated charcoal as a filler prepared in non aqueous medium (DMSO). The USPR shows no significant absorption peak in figure 1(iii), the 310 nm peak for PANI, curve (i), corresponds to excitation of the amine group of benzenoid segment of PANI and the peak at 418 and 870 nm corresponds to polaron/bipolaron transition in the chain molecules of PANI [10]. The UV-Visible spectrum of USPR supported PANI-USPR selected composite sample (15%) shown in figure 1(ii), the curve shows a much subdued peak at 300 nm which indicates an intermolecular hydrogen bonding between amine group of PANI and the residual carbonyl group of USPR.

Further broadening of the 418 peak for PANI over the region of 360-450 nm for PANI-USPR blend is a consequence of structural modification of PANI due to the presence of USPR. UV-Visible spectra of samples were carried out using Shimadzu UV-1008 spectrometer.

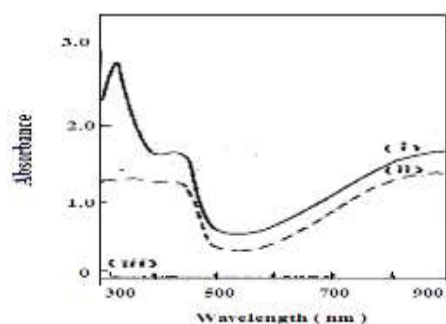


Figure 1. UV-Visible spectra of (i) PANI (ES), (ii) Blend & (iii) USPR

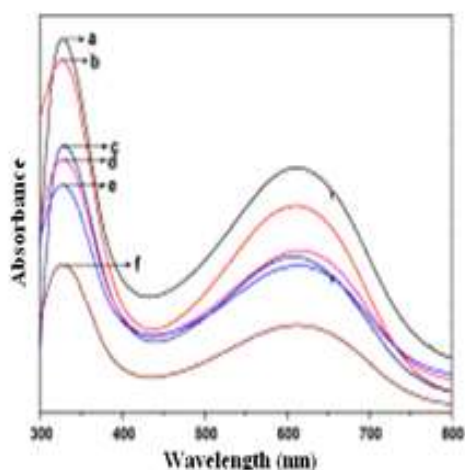


Figure 2. UV-Visible spectra for samples using AC fillers

(a) PANI (ES), (b-e) for samples containing different wt% of AC& (f) for AC

3.2 Fourier Transform Infrared Analysis (FTIR)

The UV-Visible spectra of selected samples of PANI-USPR composites using activated carbon filler are shown in Figure 2 (b-f)

FT-IR spectroscopy is a very useful and convenient technique to detect the interaction developed between two or more components of a composite. The FT-IR spectra selected composite samples is shown in figure 3. 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. 3(a) appears also on the spectra obtained for the PANI-AC composites with supporting matrix of USPR Fig. 3(b), which differ from the spectrum of pure PANI Fig. 3(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 [36,37]. 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 ($I_{\text{quin}}/I_{\text{benz}}$) and a lower vibration frequency with respect to the spectrum of pure PANI. The fact that the relative intensity of the electronic-like band ($I_{\text{e-}}/I_{\text{quin}}$) in the composites is much higher than in the pure PANI, indicates that the composites have a higher conductivity than pure polyaniline.

Comparing FTIR spectra of USPR with spectra obtained for composites, it is observed that the carbonyl stretching at 1726 cm^{-1} for the USPR shift to lower frequency of 1710 cm^{-1} for composites with activated charcoal fillers as a results of intermolecular hydrogen bonding.

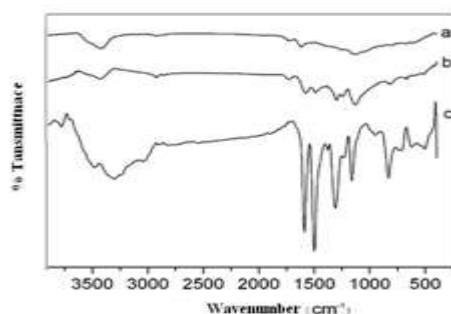


Figure 3. FTIR Spectra of (a) PANI and (b-c) for selected blend samples

3.3 Scanning Electron Microscope Analysis (SEM)

Figure 4 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.

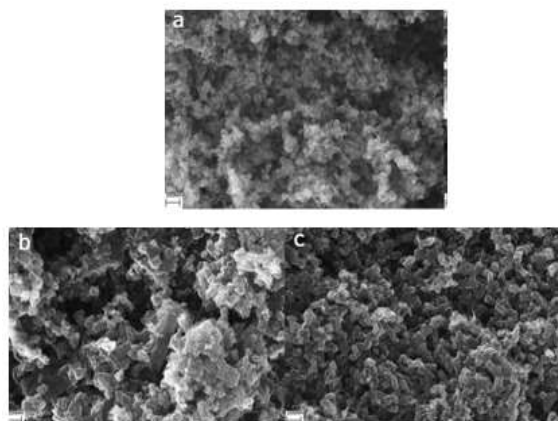


Figure 4. SEM images of (a) PANI (b & c) PANI-USPR (10 at % & 30 at % of AC)

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 composites. At higher content of AC particles, porous granular morphology accumulates with voids are observed. Due to porous granular morphology such composites can be used for gas and humidity sensor.

4. Study of Tensile Properties

For measurement of Tensile properties such as Tensile strength, Tensile stress, % Elongation and Young's modulus, the samples of composites 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 hr. The in-situ composite of PANI-USPR was prepared in non aqueous medium and in this composite different Wt. % of activated charcoal (AC) fillers were added and curing of sample takes place by addition of cobalt octet and methyl ethyl ketone

peroxide (MEKP) as initiator and hardener respectively. The MEKP concentration in excess of 3 % result in degradation of mechanical properties as well as glass transition temperature, therefore MEKP concentration was selected as 1.5 wt.% for the study of mechanical properties of composites. 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;

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

Tensile properties of synthesized composites are studied by use of universal testing machine (ASTMD 882 method). Table 1 shows tensile properties of blend with AC fillers and figure 5.1, 5.2 and 5.3 shows effect of fillers on tensile strength, % elongation and young’s modulus respectively.

Table 1. Tensile properties of specimens

Sample Code	Wt % AC	Tensile Strength peak load	% Elongation at break load	Yield Stress	Young’s Modulus
PANI-AC-USPR-1	0%	453.28	6.70	323.07	5220.94
PANI-AC-USPR-1	10%	614.77	8.40	612.14	6285.13
PANI-AC-USPR-1	20%	515.60	6.70	513.40	8285.13
PANI-AC-USPR-1	30%	480.32	6.40	431.42	9841.68
PANI-AC-USPR-1	40%	517.96	6.00	514.94	9021.40

Unit- Kg/cm²

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.

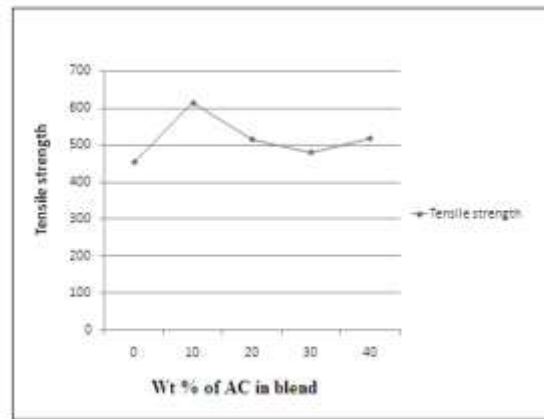


Figure 5.1. Effect of AC filler on Tensile strength of blend

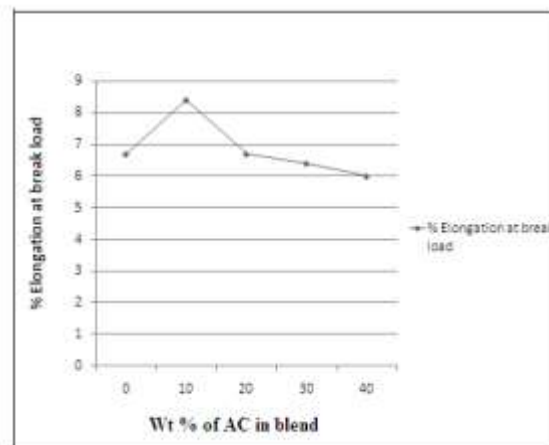


Figure 5.2. Effect of AC filler on % Elongation of blend

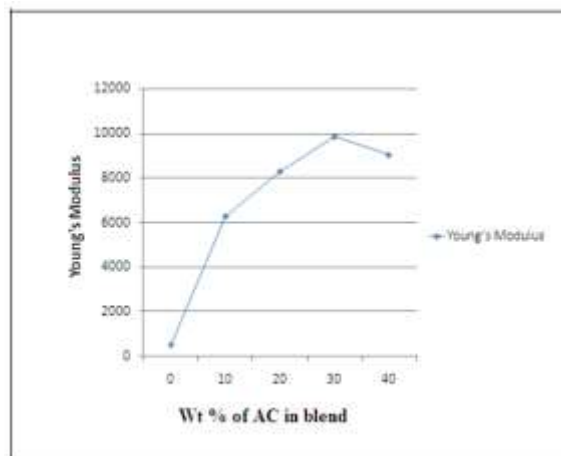


Figure 5.3. Effect of Wt % of AC in blend on young's modulus

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.

5. CONCLUSION

The Composites of conducting polymer PANI with unsaturated polyester resin (USPR) with supporting matrix of activated charcoal was synthesized by in-situ technique. The specimens containing different wt. % of activated charcoal and PANI were analyzed for their structure, surface morphology and tensile properties. The UV- Visible spectrum shows the possibility of an intermolecular hydrogen bonding between amine group of polyaniline and the residual carbonyl group of polyester resin. The broadening of the 418 nm peak for PANI over the region of 360-450 nm for PANI-USPR blend is a consequence of structural modification of PANI due to presence of USPR.

The tensile properties such as tensile strength, % elongation and young's modulus of PANI-USPR blend have been affected by addition of AC particles. The blends have shown significant decrease in tensile strength with respect to wt. % of AC filler. This decrease in tensile strength may be attributed to change in effective cross sectional area brought about by AC as filler in dispersed phase, gain there is marginal decrease in % elongation. The young's modulus of blend increases up to 30 % wt. of AC and decreased on further increasing wt % of AC particles. This

indicated that, there may be reduction in stiffness of the blend sample. At this loading AC particles may acts as lubricating agents facilitating ductility in blend.

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