

Synthesis and Characterization of Poly(styrene)-block-Poly(acrylic acid) and Organoclay Based Hybrid Composite Materials

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Abstract—Polystyrene (PS) and polyacrylic acid (PAA) are organic and synthetic polymers. Generally, a composite needs a matrix and reinforcement. Montmorillonite (MMT) is used as reinforcement to form a hybrid matrix by ultra-sonication. Block polymers of PS and PAA were first synthesized and then hybrid nanocomposite material of synthesized block polymeric matrix was fabricated by incorporating organoclay as reinforcement through 6 and 12 hours of ultra-sonication. The characterizations of the hybrid nanocomposite material were done by UV-visible and infrared (IR) spectroscopy, which confirm the successful synthesis of PS and PAA block polymer. The UV-visible spectroscopic measurements revealed that hybrid composite material is different from PS-block-PAA and that absorbance increases on increasing concentration. After successful ultra-sonication the hybrid composite is analyzed through scan electron microscopy (SEM) regarding surface morphology, distribution, uniformity, porosity, matrix compatibility, and matrix reinforcements. Sonication (for 6 hours) demonstrates a heterogeneous porous surface and an increase in roughness and porosity of surface morphology at different optical zooms.

Keywords—poly(acrylic acid); poly(styrene); block polymer; montmorillonite (MMT); exfoliation

I. INTRODUCTION

A polymeric composite material is made out of two distinct parts, network and filler. It is also called fortification or dispersed stage [1, 2]. It might come in the form of strands (fibers), sheets or particles. However, sometimes extra mixtures are utilized. The properties of composites depend on size, shape, orientation, relative amount, distribution of particles, constituent phase, and geometry of dispersed phase [3]. The dispersed medium is liable for further structure improvement.

In order to improve the interaction between filler and matrix, compatibilizers can be added which have expressive effect on material cohesion and properties. Due to their unique advantages composite materials are used in various technical applications [4]. The combination of synthetic or natural inorganic filler makes up polymer matrix composites (PMCs). PMCs comprise resins as matrix. Metal matrix composites (MMCs) can enhance properties like tensile strength, yield stress and high impact resistance. MMCs usually are alloys of Al and Mg using silicon carbide fibers [5]. Polymers have been with us and other species from the beginning, they formulate the basic building blocks of life [6]. Polymers like polyethylene, PS, plastics and nylon are obtained by synthetic methods. The polymeric products are widely abundant in nature [7, 8]. Nano scale structuring material has unique properties. The physical and chemical properties of nano scale materials significantly differ from the ones at large scale. Filler alternative additive nanoparticles utilized within polymers for different impacts are an expanded investment [9]. Regarding physical structure, nanofillers might be characterized into their substance nature, yet they are arranged in view of the particle states. Constituents have at least one dimension in the nanometer scale [10]. The collaboration amongst nanoclays and polymers can deliver two sorts of nanocomposites. The primary type possess intercalated nanocomposites, which are framed because of the infiltration of polymer chains between the layers of the clay, shaping a multilayer structure with rotating layers of polymer and clay [11].

II. MATERIALS AND METHODS

It is logical to investigate spectrum and quantum properties regarding ionized electronic conduction of fabricated high sub-

atomic weight novel composite and nanocomposite materials. It is fundamental to acquire and investigate optical and quantum analysis with expanded ultraviolet and close infrared spectroscopy. The hybrid composite material of Polystyrene-block-Polyacrylic acid (PS-b-PAA) is characterized by FT-IR, SEM and UV-Visible spectrophotometer. Analyses are done in order to know the shifting of functional groups and main bond vibrations and to accumulate and confirm the nano-fabrication.

A. UV-Visible Spectroscopy

UV-visible spectroscopy is a valuable apparatus to scan the natural atoms that incorporate in saturated and unsaturated compounds like aromatic compound, alkanes, alkenes, alkynes, ketones and aldehydes for various distinct wavelengths. It delivers change from pre-synthesis to post-synthesis [13].

B. FT-IR Spectroscopy

Polymers and composite materials would be also examined by FT-IR spectroscopy. The limitation and utilitarian of instrument is in terms of vibrational frequencies of single wavelength to various wavelengths of polymers and composite materials. Bonding and circulation of polymerized and co-polymerized monomeric units in chains is done with the aid of hydrogen bonding [15]. All the inner and outer composition can be revealed by the FT-IR technique. The created cross-linked and polymer and nano-composite blocks are identified in terms of wave numbers and bands of vibrations.

C. Scanning Electron Microscopy (SEM)

SEM is a helpful system to examine the surface morphology of a composite material. SEM runs through a PC program, the pictures of SEM are seen on CRTs arranged at electronic reassurance in addition to EFI pictures [16].

D. Ultra Sonication

Ultra sonication is a process which converts electrical signals into physical vibrations. Ultra sonication is mostly done by sonicator devices which work on a mechanism in which sound waves are converted into mechanical waves. Sonication has various impacts on physical and chemical properties. Sonication can be utilized to speed disintegration, by breaking intermolecular associations. It is particularly helpful when it isn't attainable to mix the given substance, as with NMR tubes [12].

E. Centrifuge

A centrifuge is deployed for the detachment of particles of matter whether it is solid, liquid or gas. A centrifuge works on the application of centrifugal force for the sedimentations of heterogeneous mixture. It is a device for isolating particles from a solution as indicated by their size, shape, thickness, density, medium consistency, and rotor speed. In a mixture, particles whose thickness is higher than that of the dissolvable sink and particles that are lighter than it glide to the top. The more prominent the distinction in density, the speedier they move. If there is no distinction in thickness (isopycnic conditions), the particles remain steady [14].

F. Chemicals and Reagents

Following chemicals were utilized without sterilization. Refined water was utilized for arrangement of tests.

- Polystyrene 99% pure
- Poly acrylic acid 99% pure
- MMT nanoclay
- Tetra hydrofuran (THF) (solvent) 98%

G. Synthesis of PS-b-PAA \ MMT Clay Composite

For the synthesis of PS-b-PAA and MMT clay based hybrid composite materials, 3g of PS were dissolved in 30ml of THF and were shaken till the viscous nature of solution increased. Ten ml from the resulting solution were mixed with 10ml of PAA and the mixture was sonicate for 30 minutes to form the block polymer of PS-PAA. The appearance of light brownish color justifies the reaction proceedings. After careful monitoring we added 1g of MMT clay in the brownish colored solution under continuous stirring for 1 hour. The solution was sonicated for 6h to 12h. In spite of the fact that the specimens were gathered for different hours (3, 6, 9 and 12 hours), to get an even checked trial contrasts and for successful incorporation 6 hours and 12 hours ultra-sonicated arrangements were sufficient to indicate clear nanofabrication. After ultra-sonication the color consistently changes to white colored solid as well as white viscous solution formed that came about because of development of composite via reinforcement and matrix. The nanocomposite hybrid material changes its properties and behavior with the designed structure. It was additionally affirmed with the assistance of FT-IR and SEM results.

III. RESULTS AND DISCUSSION

A. Spectrophotometric Study & UV-Visible Measurement

The qualitative studies of PS-PAA and their hybrid composite material by incorporation of MMT organoclay, were studied by UV-Visible spectroscopy which gives strong indication for the successful incorporation of organoclay in the matrix. The pure block copolymer of PS-PAA was scanned in 300nm-700nm and its maximum absorbance was found at 479nm. After, the different solutions of composite material i.e, 10%, 20%, 30%, 40%, and 50% were scanned at 479nm to determine absorbance. It was found that the absorbance increases with the increase of concentration, almost in linear relation, except minute deviation observed due to expected impurities during the preparation of the solutions. The results are depicted in Table I. Results show that absorbance increases with the increase of concentration of hybrid composite material (Figure 1). This indicates the formation of hybrid composite material between block copolymer of PS-PAA and organoclay. Hybrid composite material should differ from its polymer matrix and on increasing concentration the absorbance should increase in linear relationship.

TABLE I. PS-PAA CONCENTRATION AND ABSORBANCE

| Concentration % of HCM | Absorbance | λ_{max} |
|------------------------------|------------|-----------------|
| 10% | 0.769 | 479nm |
| 20% | 0.834 | |
| 30% | 0.918 | |
| 40% | 1.091 | |
| 50% | 1.423 | |
| Pure block co-polymer PS-PAA | 1.178 | |

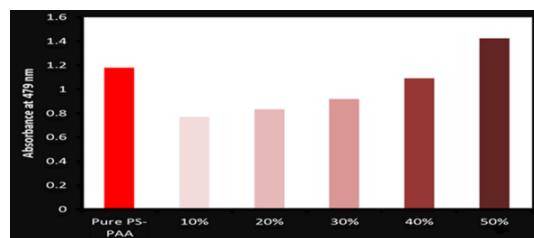


Fig. 1. UV-Visible spectroscopy results

B. FT-IR of PS-b-PAA

FT-IR spectrum of PS-b-PAA shows peak at 2985cm^{-1} for CH_3 symmetric stretch vibrations (Figure 2). The peak at 1721cm^{-1} corresponds to $\text{C}=\text{O}$ stretching, confirming the presence of PAA which was initially present in PAA at 1696cm^{-1} and $\text{C}=\text{C}$ aromatic peaks in phenyl ring of polystyrene were initially present at 1601cm^{-1} - 1458cm^{-1} which was shifted to 1640cm^{-1} - 1451cm^{-1} . This confirms that both characteristic peaks of acrylic and styrene are present in the block of composite material. There also exist $\text{C}-\text{O}$ for carboxylic acid at 1275cm^{-1} - 1175cm^{-1} and the broadening of peaks at $>3000\text{cm}^{-1}$ justifies the presence of H-bonding.



Fig. 2. FT-IR spectrum of PS-b-PAA

C. FT-IR of 6 Hour Sonicated Hybrid Composite

FTIR spectrum was recorded after 6 hours sonication of the hybrid composite. The spectrum shows the characteristic peak at 1031cm^{-1} for $\text{Si}-\text{O}$ stretching of tetrahedral silicate layers of the surface modified clay. The appearance of this peak shows that polymeric chains are separated due to the incorporation of nano clay. This can also be justified by the significant decrease in the intensity of $\text{Si}-\text{O}$. The peaks at 2925cm^{-1} - 2850cm^{-1} are for $-\text{CH}$ asymmetric and symmetric stretching respectively, while the peak at 1703cm^{-1} for $\text{C}=\text{O}$ stretching shows the existence of PAA. This confirms the configuration of nanocomposites (Figure 3).

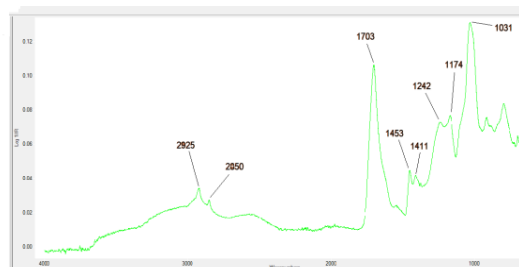


Fig. 3. FT-IR of 6 hour sonicated hybrid composite

D. FT-IR of 12 Hour Sonicated Hybrid Composite

After 12 hour sonication of hybrid composite, FTIR shows difference in the peak positions. The peaks at 2915cm^{-1} and 2853cm^{-1} are for sp^2 and sp^3 $\text{C}-\text{H}$ stretch and the peak at 1707cm^{-1} for $\text{C}=\text{O}$ stretching. The peak at 1015cm^{-1} is attributed to $\text{Si}-\text{O}$ stretching of MMT. The peak of MMT is still visible in the hybrid composite; showing that MMT has been dispersed in the polymeric matrix. As the hybrid composite was prepared through sonication, MMT has not been intercalated in the polymer matrix but rather exfoliated (Figures 4 and 5).

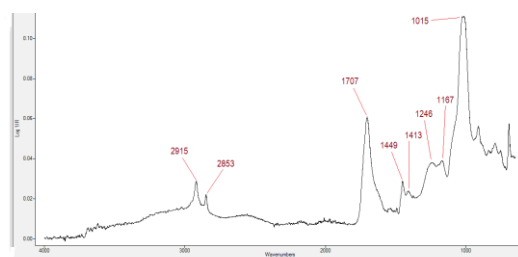


Fig. 4. FT-IR of 12 hour sonicated hybrid composite

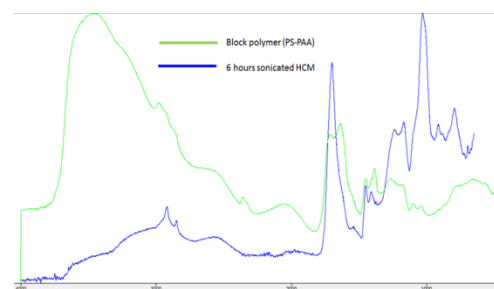


Fig. 5. Comparative FT-IR of block polymer PS-PAA & 6 hour sonicated hybrid composite material

E. IR Characterization of Composite Material Comparative

The appearance of peak at 1031cm^{-1} is attributed to $\text{Si}-\text{O}$ bond, which is a characteristic peak for organoclay. The successful incorporation of organoclay can be seen by observing the decrease in H-bonding. The two layers of block are strongly merged with H-bonding. After incorporation of organoclay between two layers of block, an obvious decrease in H-bonding is observed.

F. SEM Analysis of PS-PAA Hybrid Composite (6-Hour Ultra-Sonication)

SEM study of PS-PAA hybrid composite incorporated with MMT reveals that the morphology of hybrid composite material shows porous surface. Circulation and position of lattices over the surface show the unjumbled spines with somewhat rocky shape (Figure 6). It further reports the nanofabrication with reference to the successful incorporation of organoclay over the composite material with different interfacial faces and edges.

G. SEM Analysis of PS-PAA Hybrid Composite (12-Hour Ultra-Sonication)

SEM study of PS-PAA hybrid composite material

incorporated with organoclay reveals that the morphology of hybrid composite material shows porous surface. Circulation and position of lattices over the surface are like inside curved concaves with phase separation as shown in Figure 7.

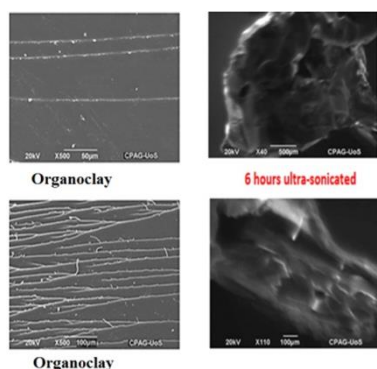


Fig. 6. SEM images of organoclay and 6-hour ultra-sonicated PS-PAA composite material

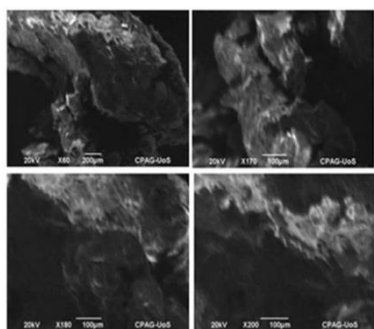


Fig. 7. SEM images of 12-hour ultra-sonicated PS-PAA hybrid composite material

H. SEM Analysis Comparative

Surface morphology declares the even distribution of organoclay (MMT) with PS-b-PAA composite material. SEM shows the phase separation and permeable surface of the hybrid composite material. MMT has diffusive properties at elevated temperatures. The material turns out to be significantly more grounded because of expanded support. To synthesize the composite material, filaments and layers of MMT are evenly adsorbed with help from the ultrasonic bath. Organic polymers with physically blended MMT have circulation, similarity of lattices with unjumbled spines and some-what rocky shape while, after 12 hours they show the inside curved concaves. With the assistance of SEM we decipher the morphological examinations at various optical zooms. The novel composite materials should be analyzed with SEM to elucidate the surface morphology, porosity, transport and network similitude which had been refined successfully. SEM pictures show permeable and penetrable surfaces (Figure8).

SEM pictures disentangle the morphological surface territories and the physical adsorption occurring through the shedding between the layers of block copolymer and MMT organoclay.

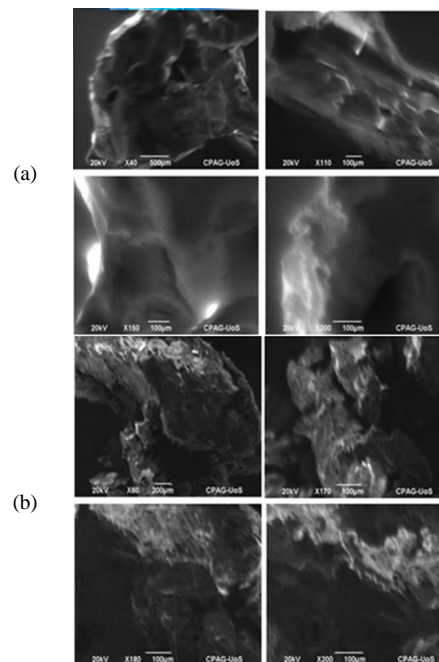


Fig. 8. Comparative 6-hour (a), and 12-hour (b) SEM analysis of hybrid composite

IV. CONCLUSIONS

Polymeric composite materials of PS-b-PAA ultrasonicated with MMT had been combined through 6-hour and 12-hour ultrasonication at various interims. The composite material was subjected to UV-visible to confirm the finished structure. The antecedents and novel composite materials were studied by infrared and SEM techniques. The FT-IR spectrum confirms the incorporation of organoclay in the polymeric structure of PS and PAA with MMT. SEM pictures deciphered the surface morphology, porosity, circulation and similarity of framework and support in it, which had been accomplished effectively.

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