Journal of Engineering and Applied Sciences 11 (12): 2557-2560, 2016
ISSN: 1816-949X
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Ultrasonic Irradiation: A Novel Approach for Conductive Polymer

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Abstract: Conducting Polymers (CPs) were first produced in the mid-1970 as a novel generation of organic materials that have both electrical and optical properties similar to those of metals and inorganic semiconductors but which also exhibit the attractive properties associated with conventional polymers such as ease of synthesis and flexibility in processing. CPs has many attractive applications in the field of sensors, fuel cells, capacitors and for a number of biological and medical applications. This review provides brief information on synthesis techniques of CPs, ultrasonic irradiation in particular. The manuscript first introduces different types of CPs, their unique properties and their synthesis. Then specific information is provided on the basic of ultrasonic irradiation, parameters which influence the ultrasonic irradiation and effect of ultrasound on polymer properties. Also a couple of case studies have been discussed.

Key words: Ultrasonic irradiation, conductive polymers, electrical conductivity, sensors, manuscript

INTRODUCTION

In the last decades, Conductive Polymers (CPs) such as polyaniline, polypyrrole and their derivatives have been widely investigated (Leonelli and Mason, 2010; Price, 1996; Jones and Holder, 2000). The use of conducting polymer has several advantages: intrinsic conductive, cheap, easy to prepare and fabricate, good specific capacitance. They also exhibits excellent stability, good conductivity and are biocompatible. Because of these properties, they have found many applications in fields as sensors (Jones and Holder, 2000; Price, 1996; Mason and Lorimer, 2002), fuel cells (Santos *et al*., 2009) batteries (Lodeiro and Martinez, 2009; Athawale *et al*., 2008), capacitors and anti-corrosive coatings.

Therefore, the development of CPs for different applications has received much attention. Polyhetero cycles such as PolyPyrrole (PPy), PolyThiophene (PT), Polyaniline (PANI) and Poly (3,4-EthyleneDioxythiophene (PEDOT), developed in the 1980's have since emerged as another class of aromatic CPs that exhibit good stabilities, conductivities and ease of synthesis (Price, 1996; Mason and Lorimer, 2002). However, conducting polymers are not molten in nature and generally are insoluble in common solvents and the nanoparticles are easily aggregated due to their high surface energy, so it is difficult to prepare conducting polymer/inorganic nanoparticle composites by conventional blending or mixing in solution or melt form (Price, 1996).

Ultrasonic irradiation technology has been widely used in chemical synthesis. When an ultrasonic wave passes through a liquid medium, a large number of microbubbles form, grow and collapse in a very short time of about a few microseconds, an effect that is called ultrasonic cavitation. Sono-chemical theory calculations and the corresponding experiments suggested that ultrasonic cavitation can generate local temperatures as high as 5000 K and local pressures as high as 500 atm, with heating and cooling rates >109 K sec^{-1}, a very rigorous environment. Therefore, ultrasound has been extensively applied in dispersion, emulsifying, crushing and activation of particles (Price, 1996). Ultrasonic irradiation is considered a green energy source because of shorter reaction times and higher yields in comparison with thermal energy sources and also we can fabricate compounds in nano-scale with this method. Due to these advantages, recently chemists have focused their attention on this type of energy source. The results reveal that compared with traditional synthetic techniques, ultrasonic synthesis is a simple, cost effective and environmentally friendly approach to synthesize (Liu *et al*., 2002). The chemical effects of ultrasound

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derive primarily from acoustic cavitation. Bubble collapse in liquids results in an enormous concentration of energy from the conversion of the kinetic energy of the liquid motion into heating of the contents of the bubble. The high local temperatures and pressures, combined with extraordinarily rapid cooling, provide a unique means for driving chemical reactions under extreme conditions. The basic parameters that make ultrasonic irradiation function are cavitation and ultrasound which are explained as.

MATERIALS AND METHODS

Cavitation: The sound can be transmitted through any physical medium by waves that compress and stretch the molecular spacing of the medium through which it passes. In Fig. 1, "a" represents a displacement x-graph, "b" the condition of transient cavitation while, "c" the stable cavitation and "d" represent the pressure P-graph. As the ultrasound cross the medium, the average distance between the molecules will vary as they oscillate about their mean position. When the negative pressure caused for an ultrasonic wave crossing a liquid is large enough, the distance between the molecules of the liquid exceeds the minimum molecular distance required to hold the liquid intact and then the liquid breaks down and voids are created. Those voids are the so-called cavitation bubbles (Mason and Lorimer, 2002; Santos *et al*., 2009)

Ultrasonic cavitation in liquid-solid systems also produces high-energy phenomena. The physical effects primarily responsible for such enhancements include improvement of mass transport from turbulent mixing and acoustic streaming, the generation of surface damage at liquid-solid interfaces by shock waves and micro jets, the generation of high-velocity inter-particle collisions in slurries and the fragmentation of friable solids to increase surface area. Cavitation near extended liquid-solid interfaces is very different from cavitation in pure liquids (Athawale *et al*., 2008). Near a solid surface, bubble collapse becomes non-spherical, driving high-speed jets of liquid into the surface (Fig. 1) and creating shockwave damage to the surface. Because most of the available energy is transferred to the accelerating jet, rather than the bubble wall, this jet can reach velocities of hundreds of meters per second. In addition, shockwaves created by cavity collapse in the liquid may also induce surface damage and the fragmentation of brittle materials. The impingement of micro jets and shockwaves on the surface creates the localized erosion responsible for ultrasonic

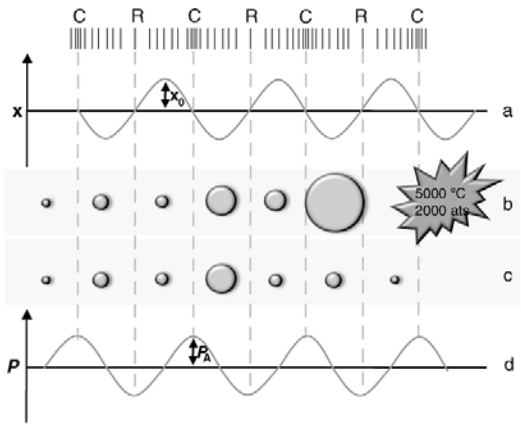

Fig 1: Creation of stable cavitation bubbles, creation and collapse of transient and stable cavitation bubbles (Santos *et al*., 2009)

cleaning and many of the sono-chemical effects on heterogeneous reactions (Suslik and Price, 1999).

Ultrasound in polymer synthesis: According to Price (1996), ultrasound produces a significant acceleration in the cationic polymerization of cyclic siloxanes to give commercially important silicone resins. Polymers that resulted from sonication processes may give a narrower polydispersity's but higher molecular weights as compared to those from normal conditions (Suslick and Price, 1999). The more efficient the dispersion of the acid catalyst throughout the monomer the faster the polymerization process, leading to a higher homogenous reaction and hence less distribution of chain lengths.

Effects of ultrasound on polymer properties: The effects of ultrasound on polymer can be both physical and chemical aspects. Irradiation of liquids with ultrasound can cause only physical changes from acoustic streaming, such as rapid mixing and bulk heating. There are always accompanied by the cavitation even though it is not always necessary for these effects. Some of the physical changes induced by ultrasound in polymer systems include the dispersal of fillers, the encapsulation of inorganic particles, particle size modification in polymer powder and welding and cutting of thermoplastics (Suslick and Price, 1999).

RESULTS AND DISCUSSION

Morphology: According to Rapra, the composition and morphology of a particular polymer with another substance (dispersed phase) will influence the properties of the mix such as physical and mechanical properties.

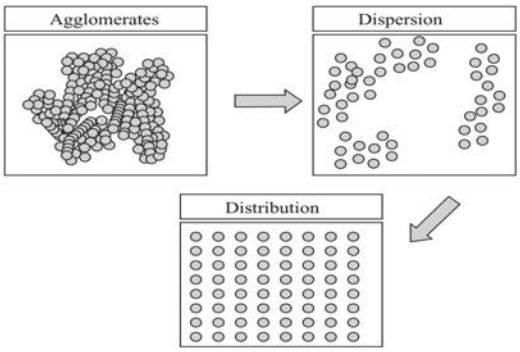

Fig. 2: Mixing steps of dispersion and distribution

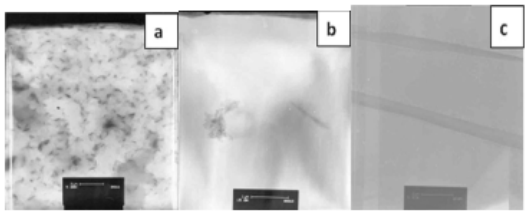

Fig. 3: Image of polypyrrole nanofibers by transmission electron (Athawale *et al*., 2008)

The quality of the mix will be dependent upon how well the plastic has been dispersed and how the filler is distributed in the plastic that gives the homogenous compound as the result. Two mixing steps have shown in (Fig. 2) in a way to get the best homogenous compound. Base on the experiment done by Athawale *et al*. (2008), the morphology images have shown as in Fig. 3 and 4. Figure 3 shows the TEM micrographs of the polypyrrole nanofibers that recorded at different time, nanofibers formed after complete addition of the oxidizing agent, after 2 h sonication and after aging the sample for 8 days. Figure 3a shows the presence of particles size ~13 nm as well as fibers with diameter ~13 nm and length ~21 nm. This image proved that the fibers formation was initiated before sonication. After the sonication as the reaction progresses the size of the fibers is seen to increase with the length extending up to ~35 nm and diameter ~17 nm. On the Fig. 3c, the length of the fiber was increase further to ~1536 nm; however, there are no changes in diameter since the growth is only in longitudinal direction (Athawale *et al*., 2008).

The same sample was observed after a period of ~60 days under TEM, the fibers could not be visualized to their fullest length. Therefore, the sample was analyzed under SEM as seen in Fig. 4 where the length is show to extend beyond ~1700 nm.

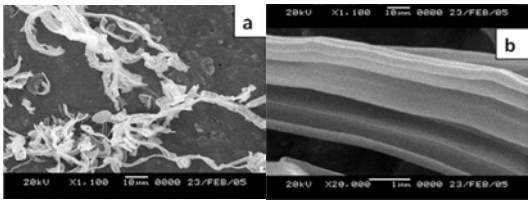

Fig. 4: Image of polypyrrole nanofibers by scanning electron micrographs at two different magnifications: a) 100x and b) 20000x (Athawale *et al*., 2008)

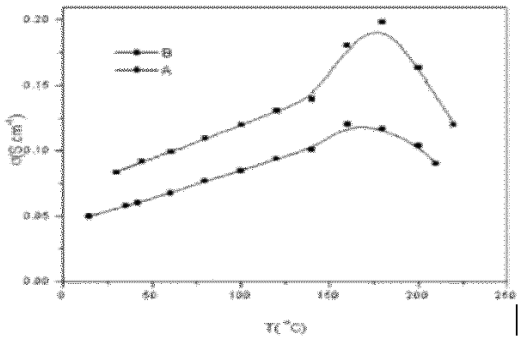

Fig. 5: Electrical conductivity of PANI samples: a) Polymerized by electromagnetic stirring; b) Polymerized by ultrasonic irradiation (Liu *et al*., 2002)

Electrical conductivity: In a study by Liu *et al*. (2002) PANI samples were synthesized by an ultrasonic irradiation synthesis method and by a magnetic stirring process. The electrical conductivity is shown in (Fig. 5) and it has been observed that the value of conductivity for PANI synthesized by stirring is much smaller than PANI synthesized by ultrasonic irradiation (Liu *et al*., 2002). This result may attribute to the fact that the ultrasound increases the mass transfer of reactants and hence enhance the rate of chemical reaction while polymerization.

In another study by Nazarzadeh biodegradable conductive blends based on polyaniline/starch were prepared by ultrasonic irradiation and were compared with normal stirring technique. The electrical conductivity results of the blends, of various ratios of aniline to starch (w/w%) by ultrasonic irradiation or magnetic stirring are presented in Table 1. The results shows, the higher the polyaniline content in the blends the higher the conductivity as well. Also, the blends that were synthesized using ultrasonic irradiation showed higher conductivity compared to the blends synthesized via magnetic stirring. This higher values of conductivities

Table 1: Conductivity results of PANI/starch synthesized under ultrasonic irradiation and magnetic stirring (Ehsan *et al*., 2011)

Blend serial No.	Ratio of monomers in feed (aniline/starch)	Conductivity (S/cm) by ultrasonic irradiation	Conductivity (S/cm) by magnetic stirring
1	1/1	2.07	2.00
2	1/2	1.90	1.78
3	2/1	2.18	2.13

were interpreted based on the fact that, ultrasonic irradiation of polymerization medium leads to production of polyaniline with greater dispersion, smaller particle size.

CONCLUSION

A novel approach, i.e., ultrasonic irradiation, was reviewed and its basic were explored. This brief review highlighted the preparation and synthesis of conducting polymers and the effect of ultrasonic irradiation on morphology and electrical conductivity, as reported by earlier researchers. The morphological analysis shows that ultrasonic irradiation have improved the dispersion and distribution of nano-fibers. The aggregation of nano fibers in the aqueous solution can be broken down under ultrasonic irradiation. Other case studies shows, ultrasonic irradiation contributes to the increase in the electrical conductivity compared with conventional stirring. Therefore, ultrasonic irradiation provides us a new approach to prepare conductive polymer composites/blends.

ACKNOWLEDGEMENT

Researchers are grateful to Ministry of Higher Education of Malaysia for the MIS scholarship to researcher 1.

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