Ultrasonics in the Field of Conducting Polymers: A Review

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Abstract: *A critical review on the important role of ultrasonic in the field of conducting polymers is presented in this paper. The literature survey gives many positive reports regarding the effect of ultrasonic on the polymerization of conducting polymers. The use of ultrasonic irradiation while polymerization gives enhanced electrical conductivity, morphology and (crystallinity) structure of conducting polymers. During the last thirty years, many workers have studied aqueous and non-aqueous polymer solutions by ultrasonic methods and have tried to get information on the behavior of polymeric chains in an ultrasonic field. Some reports give the detailed account of the study of ultrasonic velocity and attenuation in polypyrrole solutions, and the variation of these quantities with concentration and temperature. Also the ultrasonic velocity and attenuation in conducting polypyrrole in the form of pellets of fine powder have been investigated. Chuang Peng et al have reported that due to the low dispersibility of CNTs in water, ultrasound has been applied to achieve a better dispersion of CNTs in aqueous solution before and during chemical polymerization. Their results have shown that the crystallinity of polyaniline synthesized using the ultrasonic method is much higher than that synthesized by stirring. However, polyaniline with higher crystallinity does not possess higher conductivity. It has also been reported that the polymerization of 3,4-ethylenedioxythiophene (EDOT) by Iron(III) chloride in 1 M sulfuric acid is accelerated by the irradiation of ultrasound, and thus results in higher yield; without changing the molecular bonding patterns of PEDOT, the ultrasound caused emulsification by the rapid motion of the molecules which resulted in efficient mixing. The effects of the ultrasound on the polymerization causes rapid mixing in multiphase systems, the formation of free radicals, and mechanical shocks. The ultrasonic irradiation has considerable effect on the morphology and conductivity of blends obtained. The conductive blends that were synthesized under ultrasonic irradiation showed higher conductivity as compared to the blends synthesized via magnetic stirring. Maximiano V. Ramos et al have reported the preparation of conducting polymers with carbon black filler by ultrasonic mixing for gas sensor application. The composite sensors were exposed to different types of gases and the resulting changes in the resistivity were recorded. The effects of ultrasonic mixing and sensitivity of the composite sensor to various organic gases have been examined at length.*

Keywords: Ultrasonic, Polyaniline, Polypyrrole, PEDOT, CNTs.

1. Introduction

Electrically conducting polymers (CPs) such as polyacetylene, polypyrrole, polythiophene, PEDOT and polyaniline have been the subject of intensive research due to their useful electronic properties and for their application in optoelectronic and display devices, and as active electrode materials in primary and secondary batteries. The factor that has motivated much of the researcher's work on the synthesis of conducting polymers is the need to find newer materials having a wide range of physical properties such as flexibility and processibility, and conductivity close to that of metals to suit many technological applications [1].

Now researchers are in interest to make some innovative techniques which may show positive effects on polymerization, morphology, crystallinity, dispersibility and electrical conductivity of CPs. In this sense many expertise has been done to become CPs as versatile basic material in their field of application. Many expertise have been referred in the present review regarding the importance of ultrasonic in the field of CPs. Some of these are discussed in the present review.

2. Ultrasound in the Field Conducting Polymers:

Maximiano V. Ramos et al reported [**2**] that the conductive polymers with carbon black filler were prepared for gas sensor application utilising ultrasonic mixing. The composite sensors were exposed to different types of gases and the resulting changes in the resistivity were recorded. The effects of ultrasonic mixing and sensitivity of the composite sensor to various organic gases were examined [**2**]. Previous investigations have shown that ultrasonic treatment results in the formation of homogeneous mixtures of both powders [3] and liquids [4]. In this paper, the effect of ultrasonic mixing of CB and polymer powders on the percolation limit of their composites is presented. The composites prepared by this method are tested for their effectiveness for organic gas sensing applications [**2**].

G. Madhu Sudhana et al reported [**6**] that the poly ortho toluidine (POT) was synthesized by oxidative chemical polymerization method in the absence and in the presence of ultrasonic irradiation using potassium dichromate as an oxidant and hydrochloric acid as a dopant. The POT prepared in the presence of ultrasonic irradiation (POT-Us)

showed better results even at lower concentrations [**5**]. Ultrasound can lead to new chemical reaction and improve the reaction rate, and thus opens up a new chemistry i.e. sonochemistry (Mason & Lorimer, 1988). Especially, high intensity ultrasound not only can accelerate the heterogeneous liquid–liquid chemical reactions, but also can break the aggregation and reduce the particle size due to its dispersion, crushing, emulsifying and activation effect, and thus has a better control on the morphology of particles, especially on the hard solid particle such as PANI. Suslick et al. (1996) first reported the sonochemical preparation of metallic nanoparticles. It has been reported that aggregates of nano silica can be broken apart and be redispersed in the aqueous medium, and thus the long-term stable polymer/nano silica composite latex can be prepared through ultrasonic irradiation (Wang et al., 2001; Xia et al., 2001) [**6**].

i) Effect on Polymerization

Some studies on the effect of ultrasound on the polymerisation products were carried out. It was found that the crystallinity of polyaniline synthesized using the ultrasonic method is much higher than that synthesized by stirring. However, polyaniline with higher crystallinity does not possess higher conductivity [**8**]. It was also reported that the polymerisation of 3,4-ethylenedioxythiophene (EDOT) by Iron(III) chloride in 1 M sulfuric acid was accelerated by the irradiation of ultrasound, and thus resulted in higher yield; without changing the molecular bonding patterns of PEDOT, the ultrasound caused emulsification by the rapid motion of the molecules which resulted in efficient mixing [**9**]. Generally, the effects of the ultrasound on the polymerisation are believed to be rapid mixing in multiphase systems [**10**], the formation of free radicals, and mechanical shocks [**8**, **11**].

In-situ electrochemical co-deposition of CNTs with the three most important conducting polymers, namely, PPy [**12**, **13**], PANI [**14**], and PEDOT [**15**], has been achieved. Due to the low solubility of EDOT monomers in aqueous solution, PEDOT–CNT was deposited from a metastable emulsion of acetonitrile and water containing EDOT + 0.3 wt% CNTs pretreated with ultrasound [**15**]. The PEDOT–CNT film was deposited from a mixture of 5 ml acetonitrile and 5 ml water containing 0.25 M EDOT + 0.3 wt% CNT. After 10 min ultrasonic treatment, this mixed solution formed a metastable emulsion which could last long enough for the electrochemical deposition of thin films [**15, 7**].

Different ratio of CB and PMMA powders were subjected to ultrasonic mixing using a Vibra Cell (Sonic and Materials Inc.) ultrasonic mixer. The homogeneous powder mixture was then dissolved in acrylonitrile solution [**2**].

Ultrasound enhances the polymerization rate of aniline that is usually very slow under conventional stirring in inverse microemulsion and promotes the diffusion of HCl molecules and improves the degree of doping. In the polymerization of PANI using certain amount of HCl, (NH4)2S2O8 aqueous solution were sequentially added into the CTAB n-hexanol solution, aniline monomer was added to the formed microemulsion under ultrasonic irradiation, the color of the microemulsion turned colorless after 1–3 min, then changed

as the following sequence: light blue, blue, blue-green, green, dark green. The time when the color of the microemulsion turns dark green, t_{dark} , are summarized in Table 1. Compared to the inverse microemulsion polymerization of aniline under conventional stirring, t_{dark} observed in ultrasonic assisted inverse microemulsion polymerization are much shorter as shown in Table 1, Clearly, ultrasound greatly enhance the polymerization rate, mainly because ultrasound accelerates the diffusion of aniline molecules into the water pool [**6**].

Table 1: t_{dark} during inverse microemulsion of aniline by ultrasonic methods and conventional methods

[water]/[surfactant] ω	t_{dark}^{*} (min) Ultrasound	Conventional stirring
5.42	9	23
6.33	8	14
7.59	7	9
9.49	5	5
12.65	4	4
18.98	3	—
31.40	1	—
No surfactant	0.5	—

ii) Effect on characterization

In case of POT-Us, on its FTIR spectrographs, the bands at 1155cm-1 seem to be very intense and broad in the spectra of the sample prepared in presence of ultrasonic irradiation compared with its absence. This band is vibrational mode of B – N+H = Q or B–N+°H–B (B: Benzenoid, Q: Quininoid unit) and may be attributed to the existence of positive charge and the distribution of the dihedral angle between the benzenoid and quinioid rings [**19**]. Therefore this could be considered that the polytoluidine prepared in the presence of ultrasonic irradiation has higher doping level than its absence. The UV-Vis spectra of POT and POT-Us were examined in DMSO. It has been observed that absorption for the polymer prepared in the presence of ultrasonic irradiation is higher at longer wavelength than that for the polymer prepared in its absence [**5**].

The UV–vis absorption spectra of diluted colloid dispersions of PANI nanoparticles obtained through ultrasonic method, the absorption peak of PANI obtained appears at the shorter wavelength compared to that of PANI prepared in aqueous solution due to the solvent effect (Cui, 1994). The ratio of absorbance at 860 and 300 nm was lower for sample obtained through conventional stirring, indicating the doping level of PANI is lower, and the polarons of PANI prepared by conventional method are more localized than that of PANI colloid dispersion by ultrasonic methods. This was because ultrasonic cavitations promote the diffusion of HCl molecules into the PANI chain [**6**].

iii) Effect on CP films and Morphology

In in situ polymerization of aniline in the presence of starch solution, ultrasonic irradiation has detrimental effect on polyaniline size and shape [**16**, **17**]. It is well known when the size of polyaniline granules is in the range of nanoscale, higher conductivity would be obtained. Figures 1a and 1b show scanning electron micrographs of PANI/starch blends prepared under ultrasonic irradiation. From these figures, it can be deduced that PANI/starch has granular structure in

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these blends and polyaniline is well dispersed in the starch matrix. Ultrasonic irradiation of polymerization medium leads to production of polyaniline with greater dispersion and smaller particles size [16].

Ultrasound enhances the polymerization rate of aniline that is usually very slow under conventional stirring in inverse microemulsion and contributes to produce spherical nanoparticles [6].
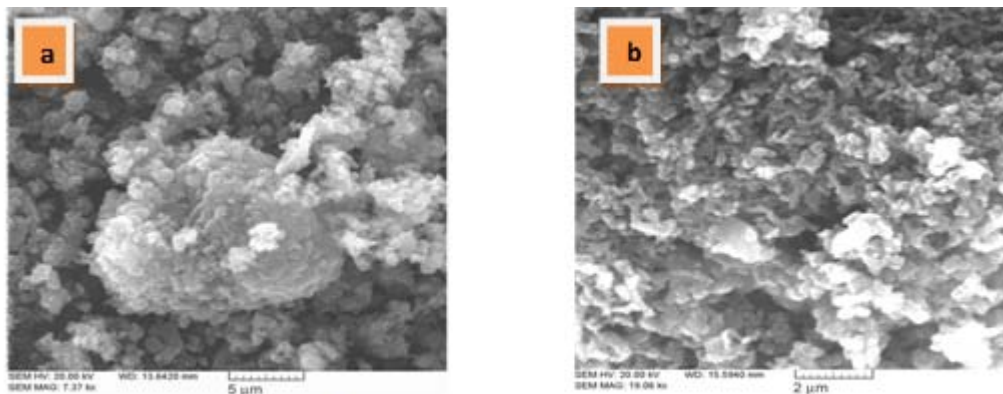

Figure 1: SEM Micrographs of PANI/starch blend at different magnifications: (a) ×734 and (b) ×1906.

The better surface homogeneity of thin film of polythiophene was examined by SEM when their polymerization takes place in the ultrasonic field of 47 kHz. During the ultrasonic irradiation, the microagitation effect and the cavitations enhance the diffusion rate of monomer and dopant, and it seemed to result in a more homogeneous and thicker polythiophene film [18].

Metal electrodeposition has long been known to be enhanced in various ways by ultrasound [19, 20]. Conducting polymers of the polypyrrole type may be considered to be electrode coatings, and improved morphology and other enhancements in polythiophene electrodeposition under insonation in the 20 –40 kHz frequency range have been shown [21]. More recently ultrasound has been seen to influence polyaniline electrodeposition [22]. We found that 20 kHz insonation using a cleaning bath interfered with polypyrrole formation at the electrode, but use of an 850 kHz higher-frequency bath allowed the formation of good polymer films on the electrode [23]. [15]These films had finer structural features and a denser morphology than silent ones [19].

Polyaniline (PANI) has been fabricated by a combination of interfacial polymerisation and ultrasonic irradiation method. The morphology of as fabricated PANI exhibits the coexistence of nanoparticle agglomerates and nanofibres. It is proposed that the ultrasonic irradiation combined with interfacial polymerisation could effectively shape the PANI morphology [24].

500 kHz ultrasound was shown to have very interesting effects on PPy elaborated with various counter-ions: perchlorate (ClO4 [-]), p-toluenesulfonate (TS[-]) and molybdate (MoO4 [2-]). All these electroactive species move into the polymer film by diffusion, to ensure the electroneutrality. Specific electrochemical behavior was evidenced for sonicated PPy/MoO4 [2-] as well as unique ions reparation within the organic matrix. Ultrasound leads to higher number of growth centers leading eventually to thinner and more homogeneous surface structure for thick deposits. Ultrasound is thus useful to control surface structure properties of such films. Changes in polymer growth for

sonicated films were highlighted by Atomic Force Microscopy (AFM) while Scanning Electron Microscopy (SEM) showed thinner and more homogeneous surface structure for PPy elaborated under ultrasound. Much more compact structure for sonicated films is likely to be the cause of change in rate-determining steps during PPy reduction process. Very interesting ion-sieving behavior was attributed for PPy/MoO4 [2-] films elaborated under ultrasound [25].

iv) Effect on Structure and Crystallinity
Consequently, some studies on the effect of ultrasound on the polymerisation products were carried out. It was found that the crystallinity of polyaniline synthesized using the ultrasonic method is much higher than that synthesized by stirring. However, polyaniline with higher crystallinity does not possess higher conductivity [8, 7].

Polymerization of aniline by ultrasonic irradiation using HCl as dopant occurred in the confined nanoreactor in microemulsion and strengthens the hydrogen-bonding of amine and imine of PANI molecular chains, which improves the degree of crystallinity [6]. In the ultrasonic assisted inverse microemulsion polymerization the confined nanoreactor, i.e. water pool, strengthens the inter- or intrachain H-bonding in the PANI, leading to a more compact structure with a high degree of crystallinity. Ultrasonic irradiation not only enhances the polymerization rate of aniline which is usually very slow under conventional stirring in inverse microemulsion, but also has a better control on the morphology of PANI compared to conventional stirring. Polymerization of aniline occurred in the confined environment, strengthens the hydrogen-bonding of amine and imine of PANI molecule chains, increases the degree of crystallinity. A decrease in particle size can lead to more effective doping, higher degree of crystallinity, and enhanced conductivity, however, too small particle size can produce some lattice defect, more localized electron and lower conductivity [6].

If the sonication treatment is too aggressive and/or too long, CNTs can be easily and seriously damaged, especially when a probe sonicator is employed. The Raman spectroscopy

confirmed that ultrasonication of CNTs for a long time resulted in a significant increase in the intensity of D band (representing disordered sp3 carbon on CNTs), suggesting the generation of defects on CNT surface [26, 27]. In extreme cases, the graphene layers of CNTs are completely destroyed and the nanotubes are converted into amorphous carbon nanofibers [28]. The localized damage to CNTs deteriorates both the electrical and mechanical properties of the CNT/polymer composites [26].

v) Effect on Dispersion
Ajit Khosla reported [29] that the typical methods for dispersion of nanoparticles in the polymers are physical dispersion and chemical dispersion. Physical dispersion involves the separating agglomerates of nanoparticles, nanorods, or a bundle of CNTs, which are tied up or clumped up together by the van der Waals forces. Three main physical dispersion mechanisms are commonly used: 1) ultrasonic agitation, 2) shear mixing and 3) ball milling. The most popular mechanism is ultrasonic agitation, in which the nanoparticles first stirred in a solvent and then exposed to ultrasonic waves/irradiations. In tjhis technique, two different ranges of ultrasonic waves can be used. The first range is of 20-24 KHz, in which the composite is placed in the ultrasonic bath and agitated for a specified time depending on the type of nanoparticle [29]. The second range of ultrasonic wave (~ 42-50 kHz) is used, in which an ultrasonic probe (a horn) is immersed into the composite. While using the second range, the probe is operated in pulsed mode, which provides mixing by repeatedly allowing the sample to resettled under the probe after each burst. The shock waves generated by ultrasonic pulses leads to collision between nanoparticles. Because of this the agglomerated nanoparticles are eroded and split by the collision. Major problem with the ultrasonic agitation is that the immense local heat is produced and hence it is recommended to use the ultrasonic bath or the probe in pulse mode. In case of CNTs, it has been observed that the prolonged exposure of ultrasonic waves can damage them.Among all physical dispersion methods, the ultrasonic agitation is mostly preferred, because it is quick, easy to use, and dispersion degree is acceptable as compared to other physical methods [29].

Due to the low dispersibility of CNTs in water, ultrasound has been applied to achieve a better dispersion of CNTs in aqueous solution before and during chemical polymerization [7].

The conductive blends that were synthesized under ultrasonic irradiation showed higher conductivity compared to the blends synthesized via magnetic stirring. This effect can be interpreted by the fact that, ultrasonic irradiation of polymerization medium leads to production of polyaniline with greater dispersion and smaller particles size [16].

Ultrasonication is the act of applying ultrasound energy to agitate particles in a solution for various purposes. In the laboratory, it is usually achieved using an ultrasonic bath or sonicator. It is the most frequently used method for nanoparticle dispersion. The principle of this technique is that when ultrasound propagates via a series of compression, attenuated waves are induced in the molecules of the medium through which it passes. The production of these shock waves promotes the ''peeling off'' of individual nanoparticles located at the outer part of the nanoparticle bundles, or agglomerates, and thus results in the separation of individualized nanoparticles from the bundles [30]. Ultrasonication is an effective method to disperse CNTs in liquids having a low viscosity, such as water, acetone and ethanol. However, most polymers are either in a solid or viscous liquid state, which requires the polymer to be dissolved or diluted using a solvent to reduce the viscosity before dispersion of CNTs [26].

Table 2 compares the characteristics of various CNT dispersion techniques, which can serve as a general guideline for the selection of appropriate dispersion technique to prepare CNT/polymer nanocomposites. It should be noted that the techniques for CNT dispersion are not limited to those described above. Many of the recent studies are often based on the use of a combination of aforementioned techniques, such as ultrasonication plus ball milling [31], and ultrasonication plus extrusion [32, 33]. In addition, researchers should bear in mind that there is no almighty tool to achieve perfect dispersion of different CNTs in different types of polymer matrices. Many factors, such as physical (solid or liquid) and chemical (thermoplastic or thermoset) states of polymer matrix, dimensions and content of CNTs to be added, availability of techniques and fabrication processes, should be taken into account when selecting a proper technique for CNT dispersion [26].

Uniform dispersion can be achieved using various types of mechanical methods, including ultrasonication, shear mixing, calendaring, ball milling, stirring and extrusion. Selection of a proper method or a combination of several methods as well as their processing conditions has to be based on the desired properties of end products because use of these methods causes, to largely different degrees, mechanical damage to CNTs and their breakage into smaller pieces [26]. Table 3 summarizes recent studies on the effects of ultrasonocation on CNT dispersion and functionalization of CNT nanocomposites made from thermosets and thermoplastics.

vi) Effect on Electrical Conductivity
The conductivity results of the blends, of various ratios of aniline to starch (w/w%), by ultrasonic irradiation or magnetic stirring are presented in Tables 4 and 5, respectively. Our results demonstrate that the higher the polyaniline content in the blends structure there is an increase in conductivity as well. Also, the conductive blends that were synthesized under ultrasonic irradiation showed higher conductivity compared to the blends synthesized via magnetic stirring. This effect can be interpreted by the fact that, ultrasonic irradiation of polymerization medium leads to production of polyaniline with greater dispersion and smaller particles size [16]. The thin film of CPs like polythiophene shows enhance electrical conductivity when their polymerization takes place in the ultrasonic field of 47 kHz. 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 [18].

Table 2: Comparison of various techniques for CNT dispersion in polymer composites

Technique	Factor Damage to CNTs	Suitable polymer matrix	Governing factors	Availability
Ultrasonication	Yes	Soluble polymer, low viscous polymer or oligomer, monomer	Power and mode of sonicator, sonication time	Commonly used in lab, easy operation and cleaning after use
Calendering	No. CNTs may be Aligned in matrix	Liquid polymer or oligomer, monomer	Rotation speed, distance between adjacent rolls	Operation training is necessary, hard to clean after use
Ball milling	Yes	Powder (polymer or monomer)	Milling time, rotation speed, size of balls, balls/CNT ratio	Easy operation, need to clean after use
Shear mixing	No	Soluble polymer, low Viscous polymer or oligomer, monomer	Size and shape of the propeller, mixing speed and time	Commonly used in lab, easy operation and cleaning after use
Extrusion	No	Thermoplastics	Temperature, configuration and rotation speed of the screw	Large-scale production, operation training is necessary, hard to clean after use

vii) Effect on Application Ability of CPs

Conductive polymers with carbon black filler were prepared for gas sensor application utilising ultrasonic mixing. The composite sensors were exposed to different types of gases and the resulting changes in the resistivity were recorded. The effects of ultrasonic mixing and sensitivity of the composite sensor to various organic gases were examined [2].

The antibacterial activities of the POT and POT-Us were investigated against *S.aureus* (gram positive) and *E.Coli* (gram Negative) and their zone of inhibition are given in table 6 at the concentration of 50, 75 and 100μg/mL.[27,28,29]. It was found that zone of inhibition was highest for polymer prepared in presence of ultrasonic irradiation than its absence [5].

In case of cytotoxicity of POT and POT-Us, it has been found that at 24 hours the E_{C50} values of the POT is 240μg/mL whereas for the polymer in presence of ultrasonic radiation it is lesser than 125μg/mL. Hence it is evident that cytotoxic activity was exhibited by the POT-Us at lower concentration than in their absence. This could be attributed due to increased oxidation at the polymeric surface and enhanced decomposition of oxidant. At lower concentration polymer prepared in presence of ultrasonic radiation was found to have good toxicity against liver cancer cells [5].

Table 3: Effect of Ultrasonication on CNT functionalization in CNT/polymer nanocomposites

Matrix		Dispersion technique	Functionalization technique	CNT content
Thermo-plastic	PI	Ultrasonication	Acid treatment	7.0 wt.%
	PP	Ultrasonication and stir	Undecyl radicals attachment	1.5 wt.%
	PS	Probe ultrasonication	Butyl attachment	0.25 wt.%
	PVA	Ultrasonication and stir	Polymer grafting	2.5 wt.%
Thermo-set	PMMA	Ultrasonication	Polymer grafting	0.10 wt.%
	EP	Probe ultrasonication	Surfactant treatment	0.25 wt.%
		Ultrasonication	Organic silane	0.25 wt.%
	PU	Ultrasonication	Acid treatment	10 wt.%

Table 4: Conductivity results of PANI/starch synthesized under ultrasonic irradiation

Composites	Ratio of monomers in feed	Conductivity
1	1-Jan	2.07
2	2-Jan	1.9
3	1-Feb	2.18

Table 5: Conductivity results of PANI/starch Synthesized under magnetic stirring

Composites	Monomer feed ratio (aniline/starch)	Conductivity
1	1-Jan	2
2	2-Jan	1.78
3	1-Feb	2.13

viii) Effect on NGM

Temperature and ultrasound effect on the nucleation and growth mechanisms (NGM) of *poly (ortho-toluidine)* (POT) was investigated. Synthesis conditions at temperatures between 263 and 303 K were optimized with and without ultrasonic irradiation. The nucleation induction time increases, as occurs when ultrasound is applied during the electro-polymerization. This effect was ascribed to kinetic factors rather than to film conductivity. Also, these results explain the important effect of ultrasound on the NGM, because these variables directly affect solubility, a determining factor in electro-polymerization. In this case a 40 kHz ultrasonic perturbation was also employed during the potentiostatic electro-polymerization approach. When ultrasound is applied, precipitation on the electrode surface takes much longer and at the same time, the obtained current is much lower than in the absence of this radiation. This can be understood by assuming that ultrasound affects oligomes solubility in the high density oligomeric region, HDOR, increasing it, and therefore it takes longer to reach saturation and subsequent oligomer nuclei deposition [34].

It revealed that ultrasound irradiation had no effect on the nucleation mechanism of the polymeric phase. Thus the ultrasound effect is to increase oligomer solubility and, consequently, to decrease the degree of saturation present in the region close to the electrode, *i.e.* the HDOR. Ultrasonic irradiation caused the induction time to noticeable increase due to oligomers solubility being affected [34].

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ix) Effect on particle size

Polyaniline (PANI) and other conducting polymers such as polythiophene, polypyrrole, and poly (methylaniline) have great potential in numerous technological applications. These materials can exist as bulk films or as dispersions but a common problem with the latter is particle aggregation which limits the range of applications. Conducting-polymer synthesis using pulsed sonoelectrochemistry has been reported despite the fact that oxidation of the horn surface can generate an insulating layer when the sonoelectrode is used in oxidation process. Ganesan *et al*. [35, 36] reported the synthesis of PANI nanomaterial by oxidative polymerization using the sonoelectrode as anode. In this synthesis a constant potential pulse of +1V vs Ag/AgCl/3M NaCl was applied to the sonoelectrode in an aqueous solution of aniline in HCl. After 2 h, the formation of PANI nanostructures was confirmed by UV-Vis and TEM micrographs showed particles with a diameter of 2-4 μm made up of very small nanoparticles of average size 20-40 nm [35]. Mahito *et al.* [37] reported the synthesis of nano poly(methylaniline) by the use of a pulsed sonoelectrochemical method, but in this case the anode was a platinum electrode placed face to face with the ultrasound emitting surface of a horn. This arrangement overcame the drawback related to the use of an ultrasound horn in oxidation process. Poly(methylaniline) synthesis was achieved at a constant potential pulse of 0.75 V vs. SCE to the platinum electrode in an aqueous solution of methylaniline in HClO4. PNMA microspheres were obtained and their size distribution depended on the electric pulse width. Thus for a pulse width of 40 s the average size was 1.4 μm, whereas for 90 s the average size was 2.4 μm [35].

A new method, i.e. ultrasonic assisted inverse microemulsion polymerization has been reported to prepare advanced conducting polymeric nanomaterials. The method is especially useful for preparation of zero dimension PANI nanoparticles because the preparation of conductive PANI needs to be in strong acid medium and PANI is an easily aggregated substance [6].

The TEM micrographs of PANI nanoparticles in the colloid dispersions prepared by ultrasonic assisted inverse microemulsion polymerization. The spherical uniform polymeric nanoparticle can be produced, and the sizes are 10 ~15 nm at (water/surfactant) ω = 5.42; 20~30 nm at ω = 6.33; 20~50 nm at ω = 7.59; 30~60 nm at ω = 9.49 respectively, and it is increased with the increase of ω value. Ultrasound cavitation can produce immense shockwave and rapid microstream, so it has the dispersing, pulverizing, emulsifying function, and has been used to produce smaller and uniform latex particles. Ultrasound can produce a new dynamic balance between collision and breaking of particle, leading to a better control on the morphology of particle and size reduction of particles [6].

Table 6: Antibacterial Activity of POT and POT-Us

Concentration (μg/mL)	*S.auereus* gram (+ve) mm		*E.coli* gram(–ve) mm	
	POT	POT-Us	POT	POT-Us
100	20	20	7	8
75	15	15	6	7
50	12	13	6	6

x) Fabrication of Nanoparticle - doped electrically-conducting polymer

Fabrication of PDMS based electrically nanocomposte with nanoparticles such as grapheme, CNTs and silver nanoparticles involves following five steps and shows the importance of ultrasonic waves while this fabrication [29].

i) The desired quantity of nanoparticles is distributed in an organic solvent, such as heptanes or toluene, via high frequency ultrasonics employing a horn tip probe in pulse mode (10 sec. on and 15 sec. off) for a total time of two minutes.

ii) The base elastomer/monomer is added to the nanoparticle-organic solvent emulsion, followed by high-frequency agitation.

iii) The polymer curing/crosslinking agent is added in the ratio 10:1; i.e. 10 parts of base elastomer/monomer and 1 part of curing agent (Dow Corning Inc., USA). It is important to add curing agent after the high-frequency ultrasonic process as a lot of heat is produced during ultrasonication process, which can start to solidify (cure) the nanocomposite during mixing.

iv) The prepared PDMS-based nanocomposite is shear mix until the organic solvent evaporates.

v) The prepared nanopcomposite is placed in a vacumme for 30 minutes to remove air bubbles.

3. Conclusion

In case of PANI/starch conductive blend and polythiophene polymerization the ultrasonic irradiation shows considerable effect on the morphology, crystallinity and electrical conductivity of CP and obtained blends. The results have shown that CB/PMMA composite has potential for detecting gas vapors. The use of ultrasonic mixing to prepare the composite has improved the homogeneity of the composite mixture and results in lower percolation rate for CB. The CB/PMMA composites should be tested with various types of gas vapors at different concentration and obtain a kinetic model of the gas detection system.

If the sonication treatment is too aggressive and/or too long, CNTs can be easily and seriously damaged, especially when a probe sonicator is employed. Ultrasonication of CNTs for a long time resulted in a significant increase in the intensity of D band (representing disordered sp3 carbon on CNTs), suggesting the generation of defects on CNT surface. Ultrasound irradiation causes the increment in solubility of oligomers while electro polymerization of POT

CPs prepared in the presence of ultrasonic irradiation is more efficient than its absence. So the polymers prepared in the presence of ultrasonic irradiation can pave way for their application in various fields. It was found that antibacterial zone of inhibition was highest for polymer prepared in presence of ultrasonic irradiation than its absence. The cytotoxic activity was exhibited by the POT-Us at lower concentration than in their absence. At lower concentration polymer prepared in presence of ultrasonic radiation was found to have good toxicity against liver cancer cells. Also it has been possible to prepare CPs in nanoparticle size using sonoelectrochemical method.

Metal electrodeposition has long been known to be enhanced in various ways by ultrasound Electrodeposition of CPs like PPy and polythiophene under insonation shows improved morphology in the 20 - 40 kHz frequency range. Use of an 850 kHz higher-frequency bath allowed the formation of good polymer films on the electrode. These films had finer structural features and a denser morphology than silent ones.

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