

Structural Investigation of Semi Crystalline LDPE Nano-polymer

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Abstract

Low density polyethylene (LDPE) nano-polymers were subjected to a high power ultrasonic irradiation as a polymerization initiator, for different times (0, 5, 10 and 15 minutes). Characterization was performed on the non-irradiated and irradiated LDPE samples by measuring the low power ultrasonic wave velocities (Longitudinal and Shear) along with density measurements. X-ray diffraction (XRD) patterns revealed that the percentage crystallinity and crystalline size had changed significantly with exposure to ultrasonic irradiation. The XRD patterns showed, the usual peaks relative to the planes (110) and (200). The XRD parameters indicated the formation of LDPE nano-polymer and the increase in the degree of crystallinity, lattice constants (a & b) and crystallite size for nano-LDPE samples with exposure time from 0 to 10 min, while with exposure time up to 15 min they decreased. However, the results obtained by the X-ray diffraction have been confirmed by the ultrasonic wave velocities together with densities of the samples.

Keywords: LDPE; Ultrasonic wave velocities; X-ray; Ultrasonic viscosity

1. Introduction

Ultrasonic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding intermolecular interaction between the component molecules because they have diverse and important applications in several industrial and technological processes [1-3]. Moreover, this study also focuses on the behaviour of a non-polar molecule in a different polar environment. These liquid mixtures are of interest to organic chemists who want to know about the types of bonds, type of molecular interactions, etc. The values of ultrasonic velocity, density, viscosity and adiabatic compressibility as a function of concentration will be of much help in providing such information. Moreover, such studies are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes. The ultrasonic study can give the indication of complex formation through hydrogen bonding in the system. Recently researchers suggested that adiabatic compressibility also used for detecting hydrogen bond formation in solutions. The ultrasonic velocity measurement is a unique tool in characterizing the structure and properties of the system and provides significant information about the arrangement of matter in solutions. It also finds an extensive application in studying the nature of intermolecular forces. Accurate

knowledge of thermodynamic mixing properties such as adiabatic compressibility, intermolecular free length, free volume, internal pressure and molar volume and their excess values for mixtures of protic, non-protic and associated liquids has a great importance in theoretical and applied areas of research.

LDPE is a popularly used food stretch or shrinks wrap material owing to its versatile usability, affordability, and safety [4]. Also, polyethylene is the most widespread polymer in the world. It belongs to the family of the polyolefin. The annual production is approximately 80 million metric tons in 2008 [5]. Especially, low-density polyethylene is widely used in greenhouses as covering material due to its dielectric properties, durability [6], excellent chemical resistance [7-9], good resistance to cracking, low permeability to water vapor [10], low cost and easy manufacturing [6, 11].

The X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used by M. Hamouya et al. [12] to study the natural ageing of low-density polyethylene greenhouses covering films. His study by XRD showed the presence of the peaks relative to the planes (110), (200) and (020) and the emergence of the new peak at the angular range of 43.50- 43.60° corresponding to the plane (220) with different time.

The preferential oxidation of the amorphous phase relative to the crystalline phase is a result of the higher diffusion of oxygen within it. The peaks around this latter phase are due to oxidation processes. The results obtained by the infrared have been confirmed by observing the morphology of the samples with scanning electron microscopy technology [12].

Characterization of polymeric materials has been carried out by means of thermodynamic, mechanical and spectroscopic methods [13-16]. The ultrasonic velocity and the elastic properties are of the most important factors determining the polymers properties; several experimental methods have been used to estimate the static and dynamic viscoelastic properties. Further parameters such as ultrasonic absorption, ultrasonic viscosity, adiabatic compressibility, acoustic impedance and Rao's constant can be calculated. These parameters are useful in understanding the nature of interactions of polymers. Several earlier papers have addressed these problems of polymers in single solution.

The food industry is increasingly aware of the importance of developing new analytical techniques to inspect the complex structures of food and to monitor online their properties during the production processes. The main reason for this increase arises from the fact that ultrasonic technologies are nondestructive, rapid and easy to automate. In addition, they can easily be adapted to analyze optically opaque systems and the cost has been reduced due to the new electronic technologies.

The ultrasonic wave propagation in real media is accompanied by several phenomena, among which we mention: absorption [17], diffraction [18], and non-linearity [19]. As the physicochemical properties change from one medium to another, the intensities of the phenomena mentioned above change as well [20]. Therefore, the measurement of acoustic parameters (e.g. absorption coefficient or velocity) in a given propagation medium is of great interest since it can be exploited to control the quality of some foodstuff products, especially fluid.

The aim of this work is to investigate the structure and properties of LDPE with ultrasonic irradiation.

2. Experimental Methods

The LDPE samples were prepared as liquids by mixing 5 g of LDPE, 0.25 g clay in 400 ml xylene. The mixture of every sample was heated to 80 °C. X-ray diffraction of the prepared samples was investigated by

x-ray diffraction using Brucker X-ray diffractometer. All diffraction patterns were recorded between $1 < 2\theta \leq 30^\circ$, the $\Delta\theta$ was 0.01° and time interval was 4 seconds.

The mixtures were subjected to high power ultrasonic irradiation using Branson sonifier (S-450D & 400W) at different irradiation times (0, 5, 10, 15 minutes). The high power ultrasonic irradiation technique, was used to break the polymer chains to nano sized polymer latex particles [21 - 23].

The ultrasonic velocities in the liquid mixtures were measured using pulse-echo method (USN 60 Flaw detector) and the Krautkramer transducer, operating at a frequency of 2MHz (central frequency of 0.7 MHz and bandwidth of 1.4 MHz) as shown in Fig. 1. The uncertainty of the measurements is 10 m/sec. Using an oscilloscope (60 MHz time base oscilloscope, Philips, Netherlands) direct measurement of the time required for the pulses to travel twice the length of the specimen is possible, to allow immediate calculation of the ultrasonic wave velocity as given in the following equation [21]:

$$V = 2L/\Delta t \quad (1)$$

where L is the liquid length and Δt is the time interval. The ultrasonic absorption coefficient (α) and ultrasonic viscosity (η_u) are given in the form;

$$\alpha = (20/2L) \log (A_n/A_{n+1}) \quad (2)$$

$$\eta_u = (\rho\alpha V^3)/(26.3f^3) \quad (3)$$

where A_n/A_{n+1} is the ratio between two successive echoes A_n , A_{n+1} , ρ is the density of the liquid and f is the ultrasonic frequency. The uncertainty of the measurements of ultrasonic absorption and viscosity are ± 0.01 dB/cm and ± 0.03 mPa.s respectively. The experimental measurements were performed for all examined liquid samples having varied densities at ambient temperature 25°C. Each experiment was repeated three times and through three days consecutively, and the median was chosen as an end result.

Table 1: Variation of XRD peak intensities, 2 theta, inter-planner distances (d) and planes for every sample with ultrasonic irradiation times.

Irradiation time (min)	Peak Intensity	2 Theta (degree)	d (hkl) (Å)	Plane (hkl)
0	3043	21.414	4.14616	110
	839	23.691	3.75255	200
5	2690	21.387	4.15131	110
	860	23.673	3.75541	200
10	1319	21.255	4.17688	110
	621	23.555	3.77396	200
15	2038	21.365	4.15555	110
	702	23.656	3.75802	200

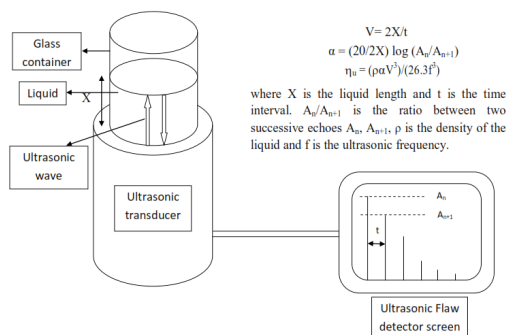


Fig. 1: Plot diagram for the ultrasonic pulse echo technique for measurement of ultrasonic velocity and ultrasonic absorption coefficient.

3. Results and discussions

The X-ray diffraction patterns for all LDPE samples at different ultrasound irradiation times, were recorded and shown in Fig. 2 and Table 1. The XRD patterns showed the characteristic peaks corresponding to orthorhombic crystalline planes (110) and (200) [12]. It can be seen from this figure, that the intensity of the peaks decreases with increasing irradiation time from 0 to 10 min and then increased at irradiation time 15 min.

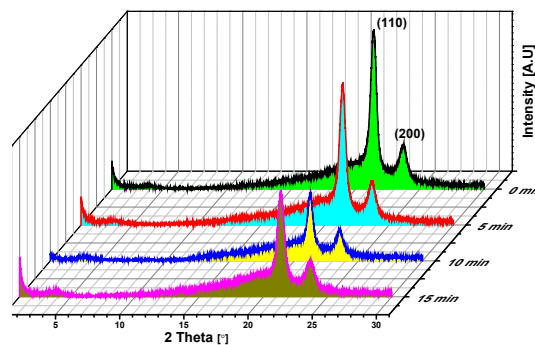


Fig. 2: X-ray diffraction patterns for LDPE samples at different irradiation times.

The variation of the calculated lattice parameters (a) and (b) were shown in Fig. 3 and Table 2. They increased with increasing the irradiation time up to 10 min, which means the increase in the inter-molecular distances, while they decreased at 15 min.

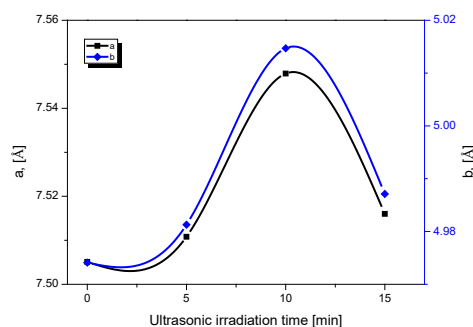


Fig. 3: Variation of lattice constants (a & b) for LDPE samples at different irradiation times.

Fig. 4 showed also the variation of crystallite size and the inter-chain distance, they showed the same behaviours as those of the lattice constants confirming the effect of the ultrasound irradiation in the formation of nano-LDPE (see Table 2). Mourad et al. [12] had reported that the increase in crystallite size is due to the further crystallization of small crystals and vice versa.

Table 2: Representation of crystallinity degree (%), lattice constants (a&b), full width at half maximum (FWHM), crystallite size (L) and inter-chain distance (D) with ultrasonic irradiation times.

Irradiation time (min)	Crystallinity degree (%)	a (Å)	B (Å)	FWHM	L (Å)	D (Å)
0	37.9	7.5051	4.9741	0.552	146.4	5.1853
5	36.4	7.5108	4.9813	0.537	150.5	5.1918
10	30.6	7.5479	5.0147	0.477	155.9	5.2236
15	35.7	7.5160	4.9871	0.590	137.0	5.1970

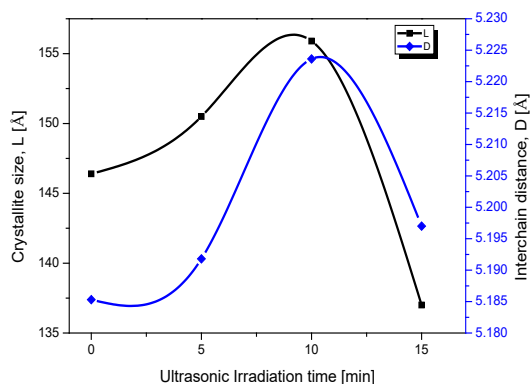


Fig. 4: Variation of the crystallite size and inter-chain distance for LDPE samples at different irradiation times.

Generally, the ultrasonic wave velocity depends on distance between atoms or molecules [21 & 24]. Therefore, the decrease in both (longitudinal and shear) ultrasonic wave velocities with the increase in ultrasonic irradiation time from 0 to 10 min as shown in Fig. 5 and Table 3, confirms the increase in inter-chain distances D and free length L_f (i.e. the increase in the distances between molecular surfaces). While the increased velocities at 15 minutes irradiation, interpret the decreased inter-chain distances. The change in ultrasonic velocity behaviours represents the good interaction throughout the entire composition range due to the chemical reactions between the constituents [21-24].

Table 3: Representation of density, both ultrasonic wave velocities (longitudinal and shear), ultrasonic absorption coefficient (α), ultrasonic viscosity, Poisson's ratio (σ), cross-link density (N_c) and free length (L_f) with ultrasonic irradiation times.

Irradiation time (min)	Density (kg/m ³)	U_l (m/s)	U_s (m/s)	α (dB/cm)	Viscosity (Pa.s)	σ	N_c	L_f (Å)
0	704	1603	816	1.61	41.2	0.325	0.550	8.243
5	809	1473	739	1.56	34.2	0.332	0.507	8.484
10	885	1298	626	1.24	18.1	0.348	0.417	9.557
15	817	1465	739	1.50	33.1	0.329	0.522	8.445

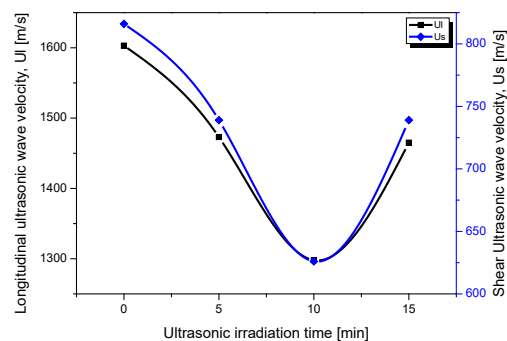


Fig. 5: Variation of both (longitudinal and shear) ultrasonic velocities for LDPE samples at different irradiation times.

Moreover, Fig. 6 showed the variation of both ultrasonic absorption coefficient and ultrasonic viscosity for all nano-LDPE samples. They decreased with increasing the irradiation time from 0 to 10 min, correlating with the decrease in ultrasonic wave velocities. At 15 min irradiation time, they increased due to the decrease in inter-chain distances (see Table 3). Huayue Wu et al. [25] had synthesized a nano-sized flake carboxymethyl cassava starch (CMCS) with high degree substitution under ultrasonic irradiation. The substitution degree of carboxymethylation and sonication time had a great influence on the morphology and the size of CMCS. Xiong Liang et al. [26] had plasticized the ultra-high molecular weight polyethylene (UHMWPE) semi-crystalline polymer using ultrasonic irradiation. They reported that the (UHMWPE) consists of nascent and melt-recrystallized phases and that energy concentrated at particle interfaces as a result of high-frequency friction, compressive deformation, and ultrasonic radiation led to rapid diffusion and interpenetration of the chain segment. Shaohua Chen et al. [27] had

investigated the influence of ultrasonic irradiation on the conformation and crystallization behaviors of two isotactic polypropylene samples with similar molecular weight and average isotacticity, but different stereo-defect distributions. The ultrasonic treatment induced a decrease in the degree of crystalline perfection and a wider distribution range of the crystalline perfection of polypropylene.

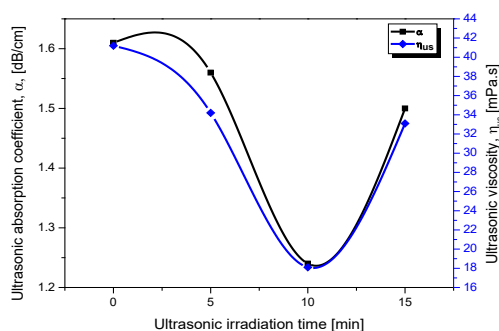


Fig. 6: Plot of the ultrasonic absorption coefficient and ultrasonic viscosity for LDPE samples at different irradiation times.

According to Rao [28], Poisson's ratio (σ) depends on the dimensionality of the structure and cross-link density. The cross-link density (N_c) was calculated according to Higazy & Bridge [29] using the following the equation:

$$\sigma = 0.28(N_c) - 0.25 \quad (4)$$

Therefore the decrease in Poisson's ratio as shown in Fig. 7 caused the decrease in cross-link density with the increase in ultrasonic irradiation time from 0 to 10 min. Further, the increase in cross-link density at 15 min confirms the polymer degradation at this time of irradiation.

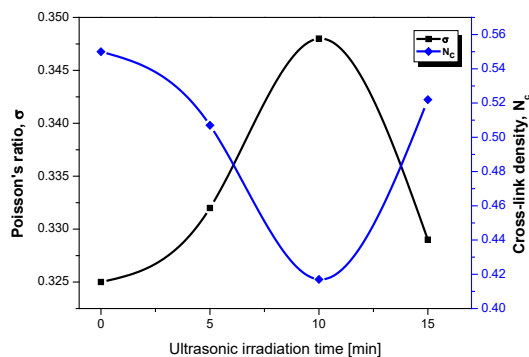


Fig. 7: Dependence of Poisson's ratio and cross-link density for LDPE samples at different irradiation times.

This behavior proved by ultrasonic measurement via decreasing in free length L_f (the distances between molecular surfaces).

Such results confirm indicate the formation of nano-LDPE using high power ultrasound at different times as polymerization initiator.

4. Conclusion

This research study showed the effect of the high power ultrasound to initiate the polymerization of LDPE in the nano-size. The results predicted the effect of ultrasound on the structure of these polymer samples. Also, the results of XRD and ultrasonic wave velocities were found to be in good agreement with each other.

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