



Trade Science Inc.

ISSN : 0974 - 7443

Volume 7 Issue 1

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ 7(1) 2012 [1-8]

Characterization and structural study of chlorinated polyethylene production in suspension phase

M.R.Razmirad, A.Moradi*

Chemical Engineering Dept., Shahid Bahonar University of Kerman, P.O.Box 76175-133, Kerman, (IRAN)

E-mail : Moradi@mai.uk.ac.ir; alimoradi2006@yahoo.com

Received: 24th December, 2011 ; Accepted: 11th January, 2012

ABSTRACT

In this research the radical chlorination reaction of polyethylene has been carried out in an aqueous slurry process via chlorination of high-density polyethylene under a moderate pressure, using chlorine gas and UV irradiation. These processes were performed in two-stage subsequently. First step was at low temperature below the crystalline melting point, and the second was above that temperature. Three types of chlorinated polyethylene were produced that were included 6.5, 12 and 34 percent by weight of high-density polyethylene. These three types of chlorinated polyethylene were characterized by Fourier transform infrared (FTIR) spectra and were compared with polyethylene and polyvinyl chloride. The comparisons of these spectrums show the progress of reaction. The content of chlorine was confirmed by an elemental analyzing technique namely flask combustion method (DIN EN ISO 1158) and the results interpreted accordingly. The results of screening analysis on product were reported too.

© 2012 Trade Science Inc. - INDIA

KEYWORDS

Chlorinated Polyethylene (CPE);
Radical Chlorination;
Screening Analysis;
Structure Characterization;
FTIR.

INTRODUCTION

Chlorinated polyethylene (CPE), has various degree of chlorination from 10% to 70%, it has also several applications such as property modifier in blends with many other polymers (especially polyvinylchloride (PVC)), wire and cable covering, adhesive, floor tile, membrane and also as a multiple pose thermoplastic elastomer^[1-4]. The physical and mechanical properties of CPE highly depend on degree of chlorination, microstructure of polymeric chain, method of production, polyethylene (PE) type and solvent. The rate of the chlorination strongly depends on method of production. As more and more chlorine atoms are substituted on the polymeric chain, the crystalline fractions of PE

gradually reduce and convert to a softer and more flexible product. At low chlorine content, the CPE product is still hard and has a powdered form while above 10% of chlorination the elasticity and flexibility of product is increased progressively and about 35%-40% chlorination it takes a thermoplastic elastomer form. Above 55% chlorination, the hardness and toughness of polymer again starts to increase^[5-13].

There are many types of chlorination process such as, the solution phase, suspension phase and bulk phase. In the method of solution phase the chlorine atoms are substituted along the back bone of polymer randomly and homogeneously and the obtained CPE has noncrystalline structure. Most of industrial units produce various kinds of CPE's in the solution phase using a single

Full Paper

solvent such as CCl_4 or a mixture of solvents^[5-13]. Chlorination reaction in the suspension phase mostly happens on the surface of the polymer particles and so the structure of procured product is blocky and non-uniform^[1-4, 10]. Both of these methods are usually carried out under a moderate pressure. Radical chlorination of polyethylene films in the heterogeneous solid-gas phase is another method of reaction that has been studied more recently^[14-15]. The polymer films that are chemically modified in this way have already found some interesting applications such as membrane technology^[16].

Some authors have used the infrared spectroscopy technique to analyze the molecular structure of chlorine containing polymers. These articles have been presented either to interpret the appeared peaks in the IR spectra, or to elucidate the distributions of chlorine atoms on the polymeric chains, for instance distinguishing of random or blocky regions^[17-21].

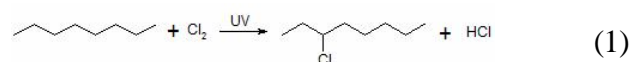
Carrying out the reaction chlorination of HDPE in suspension phase which was less studied in the articles before could be comprises many new results. Production of CPE in aqua's phase, achieving to chlorine percent based on a standard method, determining size distribution before and after chlorination, interpretation of instrumental analyzing results such as Fourier transfer Infra red spectroscopy and many other new results could help to improve technology of CPE production.

In this research many reactions have been carried out under pressure in aqueous slurry at different conditions such as reaction temperature, high density polyethylene and their concentrations and type of initiators (UV irradiation). Some new results were achieved.

EXPERIMENTS

Reaction scheme

The overall reaction of radical chlorination of polyethylene is as follow:

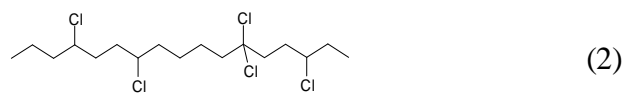


Since the reaction take place in suspension phase the non homogeneity will be observed at the polymeric chain and at the morphology of polymer.

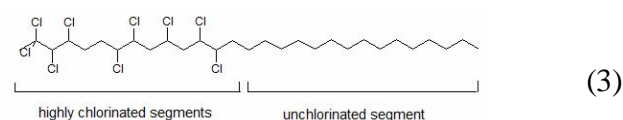
Many CPE with various physical and chemical properties could be achieve due to the variation of the distri-

bution of chlorine along the polymer chain, as a result of the change in morphology of the polyethylene during chlorination. The various types of products which may be obtained may be represented schematically as follows^[2]:

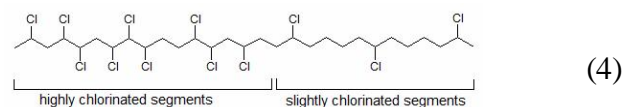
Chlorination in suspension phase above the melting point of the PE results, chlorine distribution at randomly and fairly homogenous through the entire chain.



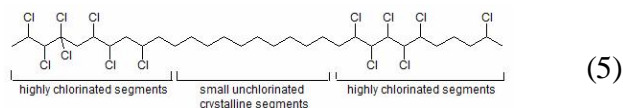
Chlorination in suspension below the melting point of PE results nonhomogenous product.



Chlorination in suspension below the melting point of PE, followed by chlorination above the melting point. This process results both highly and slightly CPE segments.



Chlorination initially above the melting point to reduce the crystallinity followed by chlorination below the melting point; especially applicable to linear polyethylene polymers and copolymers of higher densities^[2].



Materials and equipment

HDPE (with density of 0.994 g/cm³) was prepared as powder from Iranian Petrochemical Company. Chlorine gas with a purity of 99.5% was used.

The Fourier Transfer Infrared (FTIR) spectrophotometer, Equinox 55 has been used for chemical analyzing of the CPE product. An elemental analyzing method, European Standard EN ISO 1158 (DIN EN ISO 1158) was applied for determining the chlorine content of products. This procedure will be explained in the next section. a standard screen set was used for screening analysis of row material and product.

An experimental setup was made for performing of

PE photo chlorination. This setup comprises; a 12 liter cylindrical reactor equipped with some other accessories (such as a chlorine gas bubbler, a UV cell with a 500 Watt UV lamp and a pressure and temperature gage), a variable speed (0-60rpm) mechanical mixer, a gas flow meter and a trap for chlorine gas. A schematic diagram of the setup is shown in Figure 1.

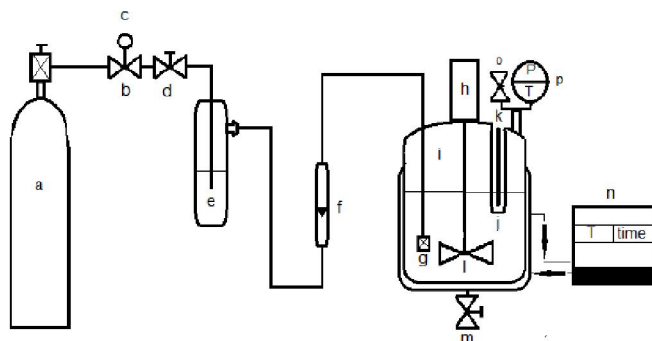


Figure 1 : Schematic diagram of the setup: (a) chlorine gas cylinder, (b) pressure reducing valve, (c) pressure gauge, (d) needle valve, (e) trap, (f) gas flow meter, (g) gas Bubbler, (h) mechanical mixer, (i) reactor, (j) UV cell, (k) UV lamp, (l) impeller, (m) outlet valve, (n) hot oil circulator, (o) safety valve and (p) pressure and temperature gage.

Experiment procedure

Chlorination of polyethylene was performed in an aqueous slurry phase in a closed, agitated vessel or reactor. 1 kg of polyethylene was slurred in 8 lit of water. 2 milliliter nonylphenol surfactant (for decreasing of surface tension) and 45 g of talc (for inhibiting from agglomeration) were added to the slurry. The temperature of slurry was increased to about 95 °C and in this conditions the reaction was started by injection of chlorine gas at a rate of 0.5 lit/min under UV light radiation, after 15 minutes the pressure of reactor was increased to 2.8 bar and reaction was continued for 5 minutes at this pressure. After the chlorination was completed, the content of slurry was transferred to another agitated vessel to neutralize remained HCl, in which the slurry was rinsed and washed in a caustic batch at 80 °C. Polymer was dried at approximately 40 °C. This product namely CPE-1 was sieved into different fraction based on their size distribution^[22]. The different fractions were analyzed for determining their chlorine contents according to DIN EN ISO 1158 method^[23].

Similar experiments were carried out at the same procedure (at same 2.8 bar pressure) but the times of reactions were 30 and 80 minutes respectively. These

two products, namely CPE-2 and CPE-3 were sieved into different fractions and separated based on their size distributions and the degree of chlorination was determined by the method of DIN EN ISO 1158.

Analyzing procedure

The oxygen flask combustion method could be applied for the determination of halogens or sulfur produced after the combusting of the desired organic compounds in a flask filled with oxygen these compounds may have chlorine, bromine, iodine, fluorine or sulfur groups^[24].

Base of DIN EN ISO 1158 method is similar oxygen flask combustion method.

About 50 to 70 mg, with the 0.01 mg accuracy, from the CPE sample were weighed and placed on a filter paper cut as shown in (Figure 2a). It was clamped in the platinum spiral with the paper tail protruding (Figure 2b).

About 15 ml of water, 4 ml of potassium hydroxide solution (100g/l) and 1 ml of hydrogen peroxide solution (300g/l) were introduced into the flask (Figure 2b). Oxygen was passed through a glass tube at 250 ml/min for 5 min to displace the air in the flask^[23].

The tail of filter paper was ignited with a gas flame. The stopper carrying the platinum wire was quickly inserted and let the filter paper burns. When combustion was finished, the flask was turned upright. The flask was shaken and cooled under a stream of cold water in order to the absorption of produced hydrochloric acid rapidly and completely.

After 30 min the content of flask was transferred to a 250 ml Erlenmeyer and the flask was rinsed and transferred to Erlenmeyer so that its final volume became about 40 ml. About 1 g of sodium nitrate and 2.5 ml of nitric acid solution (2 N) were added to the Erlenmeyer. The solution was boiled for 5 min^[23]. After cooling, 1 ml potassium chromate solution (50g/l) was introduced to the solution and was titrated by silver nitrate solution (0.1 N). The chlorine content of solution was calculated by following equations.

$$X_{Cl} = 3.5453 \times \frac{0.1 \times (V_1 - V_2)}{m} \quad (6)$$

In which:

X_{Cl} is the chlorine content of CPE

V_1 is the volume of silver nitrate solution used for

Full Paper

the determination (in milliliter)

V_2 is the volume of silver nitrate solution used for the blank test (in milliliter). For pure materials and still equipment V_2 usually is zero.

m is the mass of CPE sample (in grams).

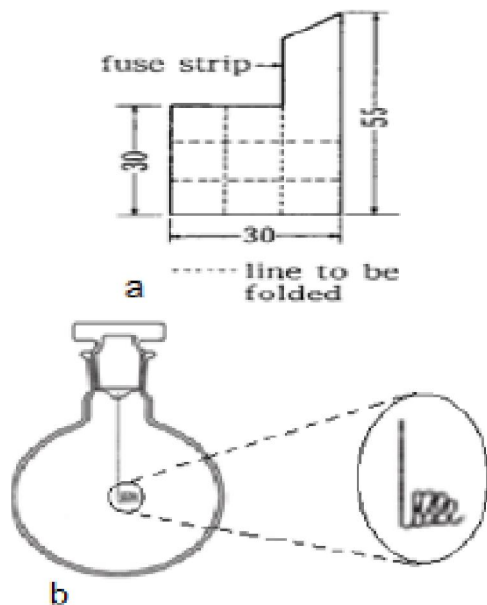


Figure 2 : a) Filter paper cut, b) platinum spiral in oxygen flask

RESULTS AND DISCUSSION

Progress of reaction

The chlorine content of CPE-1, CPE-2 and CPE-3 according to the DIN EN ISO 1158 were determined about 6.5, 12 and 34 in weigh percent respectively. Figure 3 shows the reaction time for three productions of CPE-1, CPE-2 and CPE-3 versus their reaction times respectively.

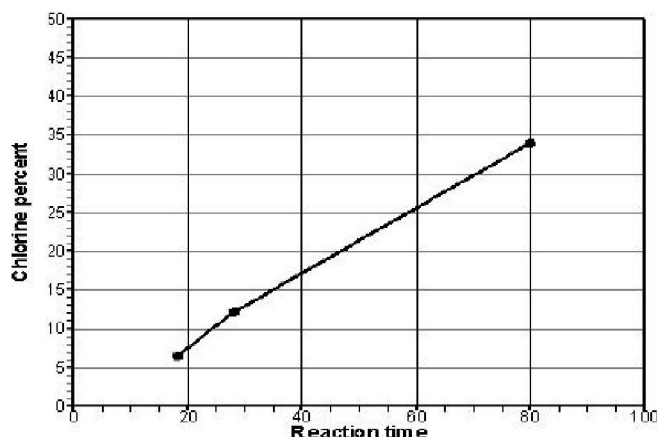


Figure 3 : the chlorine content of products vs. time (minute)

As it could be observed the progress of reaction increases linearly by increasing the time of reaction of chlorination in this rang. This procedure is acceptable and shows that the chlorination reaction was carried out successfully. This Figure is useful for the future kinetic reaction studies.

Screening analysis

For differential screening analyzing of initial PE and produced CPEs, 6 sieves with different (mesh) sizes including 100, 150, 300, 500, 1015 and 2000 were used. The screening analyzing was done for Polyethylene, CPE-1, CPE-2, and CPE-3. The results are shown in TABLE 1.

TABLE 1 : Differential screening analysis

Size distribution (μm)	Weight of polyethylene and products (g)			
	PE	CPE-1	CPE-2	CPE-3
2000	104	110	115	136.5
1015	383	407	427.5	510
500	276	294	310	370
300	90	96	101	121.5
150	105	112.5	118	142.5
100	42	45.5	47.5	57.5
Total Summation	1000	1065	1119	1338

According to the TABLE 1, the weights of extremely small or large particles are lighter than mean ones. For example, the weight of Particles of PE having 100 micron diameters is about 42 gram whereas those have 2000 micron diameter weight 104 gram.

Moreover, the TABLE shows the increasing weight of CPE-1, CPE-2 and CPE-3 in comparison to PE. The weight of products increases at the result of the reaction of chlorination.

For example in production of CPE-2 process, the total amount of output product from reactor was 1119 gram per 1000 gram PE, the extra 119 gram is the weight of chlorine added to PE chain and resulted to weight increase.

However, TABLE 2 explains the amount of increasing weight per produced CPE in comparison to initial PE for a given diameter of particles.

For instance, there was a 31.5 gram weight interval in CPE-3 particles that have 300 micron diameter comparing to initial PE that have the same particle size. Also, the 24 gram weight increment in CPE-1 particles was

reported for 1015 micron diameter particles in comparison to initial PE particles with the same size. Consequently, the percentage of chlorine used per given particle size can be calculated with the distribution (division) of the weight difference between a given CPE and initial PE per the mass amount of initial PE. TABLE 3 indicates the percentage of chlorine per produced CPEs with different sizes.

TABLE 2 : Increment of chlorine content

Size distribution (μm)	Weight difference between products and polyethylene (g)		
	$m_{\text{CPE-1}}-m_{\text{PE}}$	$m_{\text{CPE-2}}-m_{\text{PE}}$	$m_{\text{CPE-3}}-m_{\text{PE}}$
2000	6	11	32.5
1015	24	44.5	127
500	18	34	94
300	6	11	31.5
150	7.5	13	37.5
100	3.5	5.5	15.5

TABLE 3 : chlorine percent with size distribution

Size distribution (μm)	Percent of chlorine for different particle size		
	CPE-1	CPE-2	CPE-3
2000	5.76	10.57	31.25
1015	6.26	11.61	33.16
500	6.52	12.31	34.05
300	6.66	12.22	35
150	7.14	12.38	35.71
100	8.33	13.1	36.9

Remarkable results can be obtained by regarding of the TABLE:

1- Depending to particle size different percentages of chlorine were reported for the different particle sizes.

For example, CPE-1 particles with 2000 micron size diameter were chlorinated up to 5.76% whereas particles with 100 micron diameter size were chlorinated up to 8.33%.

2- A comparison between two TABLES (2 and 3) resulted in the fact that there is more weight difference between CPE and PE in the average particle size since there is more number of particles in such a size. However it didn't imply to more chlorination ratio of average particles in comparison to small particles. For example TABLE 2 shows that weight increment in CPE-2 is equal to 44.5 gram for the particles of 1015 micron

whereas this amount was 13 gram for size of 150 micron. However, a comparison between the related (homologous) Figures of these two TABLES (2 and 3) indicates that the chlorine percentage of CPE-2 in 100 micron diameter is equal to 13.1 whereas it is 11.61% for the CPE-2 in 1015 micron diameter.

3-The chlorine percentage of products is very similar (close) to chlorine percentage of particles of 500 micron diameter.

4-Particles with smaller size have a light weight but more chlorine percentage. In other words, chlorine is added easier on the particle that has the less size. As a result, there is a reverse relationship between the two factors of the particle size and the percentage of chlorine.

5- For CPE-1 with 6.5% total chlorine content, the chlorine percentage of each size was obtained by DIN method after screening and was compared with the data of TABLE 3 which is based on dimension analyze method. The comparison has been shown in TABLE 4.

TABLE 4 : Comparison chlorine percent of DIN EN ISO 1158 and size distribution methods for CPE-1

Size distribution of CPE-1 (μm)	DIN EN ISO 1158 method	% cl with size distribution method
2000	5	5.76
1015	6	6.26
500	6.5	6.52
300	6.5	6.66

The results show the similarity of the two methods for determination of chlorine percentage.

FTIR Spectra

For taking FTIR spectra the samples were prepared as powder with a diameter of about 100 μm .

Figure 3 and Figure 7 show the infrared spectra of the original polyethylene and polyvinyl chloride respectively.

The infrared spectra of the several chlorinated polyethylene are represented in Figure 4, 5 and 6.

The CCl-stretching mode is usually appears in the region of 500-700 cm^{-1} [18]. In Figure 4 the peak appeared at 601 cm^{-1} , in Figure 5 at 595 cm^{-1} and in Figure 6 at 570 cm^{-1} . The infrared spectra of the chlorinated polyethylenes are more closely analogous to those

Full Paper

of polyvinyl chloride.

The CH_2 -rocking mode of polyethylene is found at about 720 cm^{-1} . In the spectrum of CPE-1 which contains about 6.5% chlorine, this band disappears quickly as the chlorination reaction^[1].

The carbon-carbon skeletal mode generally appears in the region from 800 to 1100 cm^{-1} this region. The C-C skeletal mode of polyethylene appears weakly, but a few new bands which are not observed in the spectrum of polyethylene appear now in the spectra of the chlorinated polyethylenes this phenomenon is due to existence dipole moment of CCl at their vicinity. Two such bands, namely, those at about 920 and 1060 cm^{-1} , become stronger as the chlorination proceeds. Polyvinyl chloride has also two carbon-carbon skeletal modes at 960 and 1090 cm^{-1} . The bands at about 880 and 1066 cm^{-1} in the spectrum of CPE-1, 917 and 1058 cm^{-1} in the spectrum of CPE-2, 920 and 1060 cm^{-1} in the spectrum CPE-3 resembles those at 960 and 1090 cm^{-1} in the spectrum of polyvinyl chloride in their frequencies and their shapes^[1, 18].

The CH-deforming bands usually appears in the region of 1100 to 1300 cm^{-1} , a weak band appearing at about 1195 cm^{-1} in the spectra of the chlorinated polyethylenes could not be found in the spectrum of the original polyethylene. This band probably corresponds to the weak band at 1196 cm^{-1} in the polyvinyl chloride^[18].

The CH-deformation mode appears strongly at 1255 cm^{-1} in the spectrum of polyvinyl chloride. A similar strong band appeared at about 1270 cm^{-1} in the spectra of the chlorinated polyethylene. The band is not so strong in the spectrum of CPE-1 and CPE-2, but it becomes strong as the chlorine content of the CPE-3 rises above 34%, this phenomenon is due to the CCl -stretching at their vicinity.

Generally, the infrared spectra of the chlorinated polyethylenes strongly resemble those of polyvinyl chloride in the region of 1100 to 1300 cm^{-1} . This observation suggests that polyethylene is chlorinated in the form of $-\text{CHCl}-$ and that hardly any $-\text{CCl}_2-$ units are formed.

The CH_3 deformation mode appears at about 1380 cm^{-1} in the spectrum of the original polyethylene. In the spectra of the chlorinated polyethylene this band becomes weaker as the chlorine content increases, but it

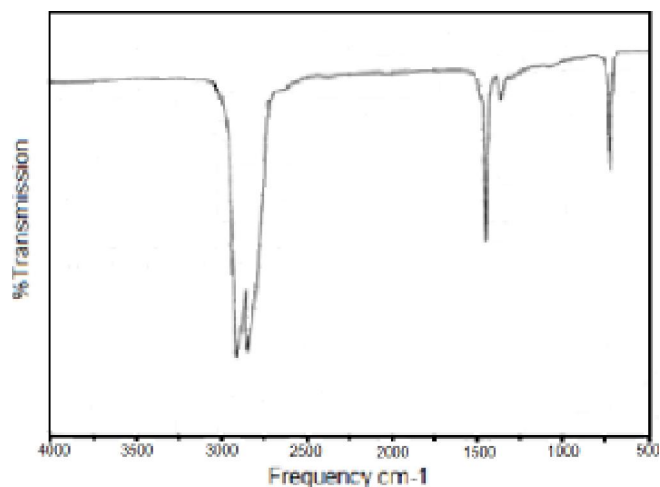


Figure 4 : FTIR spectrum for polyethylene^[1]

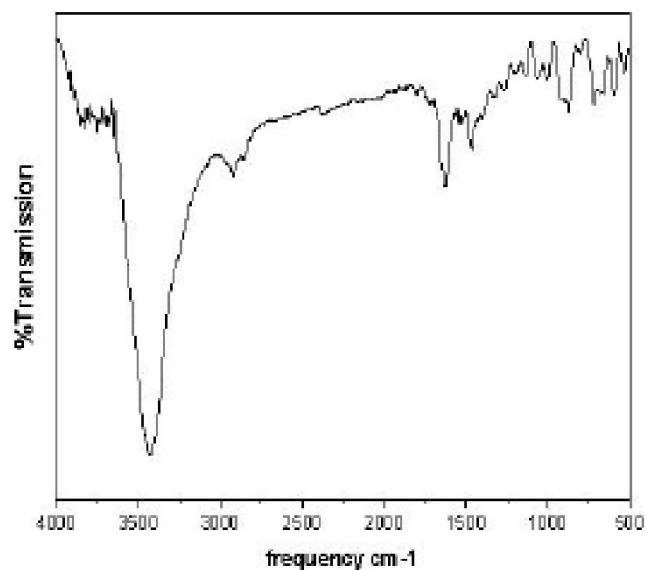


Figure 5 : FTIR spectrum for CPE-1

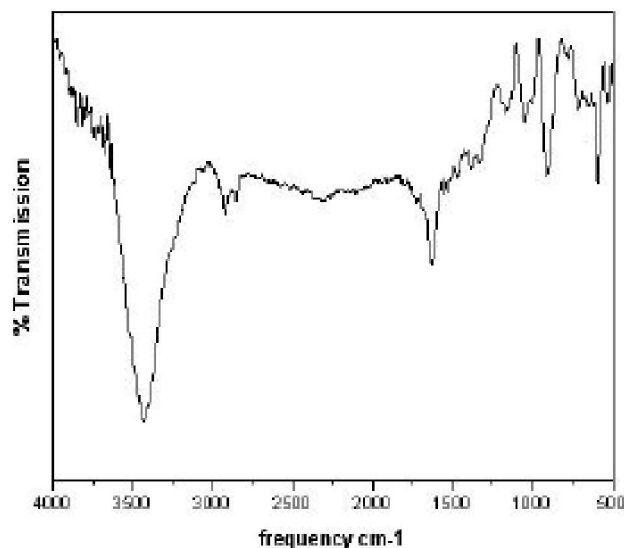


Figure 6 : FTIR spectrum for CPE-2

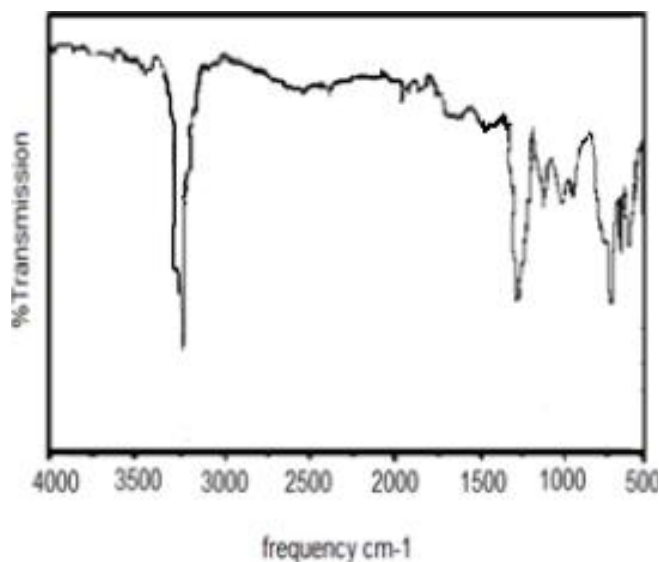


Figure 7 : FTIR spectrum for CPE-3

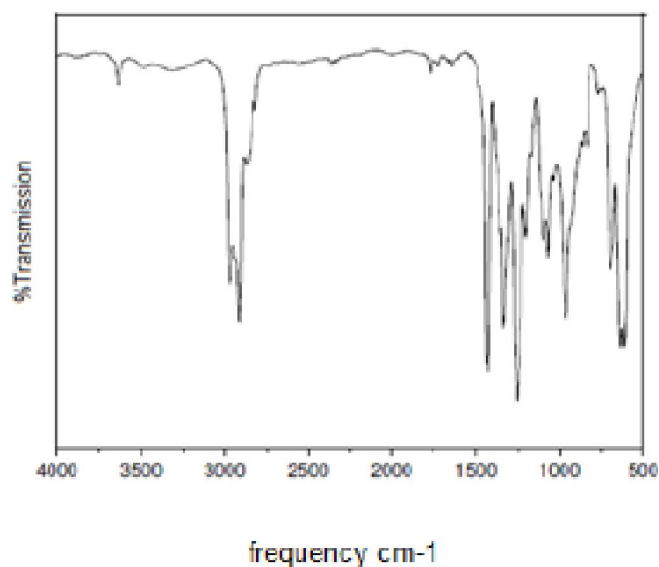


Figure 8 : FTIR spectrum for PVC^[25]

is still present in the spectra of the products containing more chlorine than polyvinyl chloride, that is, methyl groups are still found in the molecule^[18].

The CH₂-bending mode appears at about 1470 cm⁻¹ in the spectrum of polyethylene, at about 1428 cm⁻¹ in the spectrum of polyvinyl chloride. Thus the CH₂-bending mode shifts to lower frequency as the CH₂-CH₂ unit is changed to the CH₂-CHCl and to the CH₂-CCl₂ units^[18].

CONCLUSIONS

In this article radical chlorination of polyethylene in suspension phase under pressure and UV irradiation

has been considered. The differential screening analyzing show those particles having smaller size have a light weight and more chlorine percentage. The FTIR spectra of CPE's samples show that as reaction proceeds, the CCl-stretching and bending modes and C-C vibrations create a broad peak. Also it is observed that the peak corresponding to CH₂-stretching mode become wider due to the induction effect of chlorine atoms added to the polymeric structure.

REFERENCES

- [1] A.Moradi, A.Ramazani, M.shahrokhi; J.Polm., **37(9)**, 661-668 (2005).
- [2] J.Kroschwite, H.F.March, N.M.Gaylord; Encyclopedia of Polymer Science and Technology, 431-436, in N.L.Zutty, J.A.Faucher, S.Bonotto. 'Ethylene Polymers', John Wiley and Son's, (1985).
- [3] W.Nishimato, K.B.Sinclair; Chlorinated Polyethylene, 1-70, Stanford Research Institute (SRI International), (1984).
- [4] J.C.Salamone; Polymeric Material Encyclopedia, 1235-1262, 'Chlorinated and Chlorosulfonated Polyethylene', CRC Press, (1996).
- [5] N.Ito, K.Okayama, T.Karasuda, Y.Migagawa; 'Process for the Preparation of Chlorinated Polyolefins and Chlorosulfonated Polyolefin', US. Patent 5378766, (1995).
- [6] T.Nakagawa, M.Narui, Y.Sakanaka; 'Method of Making Chlorosulfonated Polyethylene', US. Patent 4871815, (1989).
- [7] M.Narui; 'Method of Chlorination or Chlorination and Chlorosulfonation', JP. Patent 63172702, (1988).
- [8] Y.Ishida, K.Okayama; 'Process for Producing Chlorinated Polyolefin', US. Patent 5290879, (1994).
- [9] D.J.Ryan; 'Chlorination and Chlorosulfonation of Polyethylene in Mixed Solvent', US. Patent 4145491, (1979).
- [10] E.G.Brugel; 'Process for Chlorination and Chlorosulfonation of Olefins Polymers in Suspensions of Perfluorinated Liquids', US. Patent 5242987, (1993).
- [11] C.Bish, E.G.Brugle, R.F.Eniss; 'Process for Preparation and Chlorosulfonation of Olefin Polymer Having Low Level of Residual Monoflorobenzene Reaction Solvent and Its Chlorinated Byproducts', US Patent H1, 582, (1996).

Full Paper

- [12] Y.Ishida, K.Okayama; 'Process for Producing Chlorinated Polyethylene in Presences of Olefin', US Patent 5212254, (1993).
- [13] R.R.Blanchard; 'Chlorosulfonation of Chlorinated Polyethylene', US Patent 4584351, (1986).
- [14] R.Zhao, Sh.Cheng, Y.Shun, Y.Huang; J.Appl.Polm.Sci., **81**, 3582-3588 (2001).
- [15] E.M.Cross, T.J.McCarthy; J.Macromolecules., **25**, 2603-2607 (1992).
- [16] V.Tricoli, N.Cerretta; J.Electrochemistry Communication., **4**, 272-276 (2002).
- [17] A.J.Varma, P.Kondapalli, S.V.Deshpande, S.P.Kokane; J.Polm.Degr.Stab., **63**, 5-9 (1999).
- [18] K.Nambu; J.Appl.Polym.Sci., **4**, 69-73 (1960).
- [19] B.Bikson, J.G.Joseph, D.Vosfi; J.Polm., **22**, 641-645 (1981).
- [20] M.A.Smook, E.T.Pieski, C.F.Hammer; J.Ind.Eng. Chem., **45(12)**, 2731-2737 (1953).
- [21] B.Magloire, B.Philippe, V.Georges; J.Polm., **7**, 287-299 (1975).
- [22] G.Johnson, W.Michie; 'Chlorinated Polyethylene, Method of Producing The Same, and Articles Made There From', Wo. Patent 140169 A1, (2009).
- [23] <http://211.67.52.20:8088/xitong/BZ%5C8001901.pdf>, "European standard, plastics -vinyl chloride homopolymers and copolymers "determination of chlorine content" EN ISO 1158.
- [24] W.Schoniger; J.Pergamon Press., **40**, 93-95 (1958).
- [25] M.saleem khan, R.aman qazi; J.Pur.App.Chem., **25120**, 41-45 (2008).