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OXIDATION OF LDPE IN PRESENCE OF AN AQUEOUS SOLUTION OF PHENYLTRIMETHYL AMMONIUM PERMANGANATE

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ABSTRACT

The oxidation of LDPE in an aqueous solution and at room temperature is desirable if the original morphology of the polymer must be maintained. We have used the phenyltrimethyl ammonium permanganate (Ph. TMAP), prepared in our laboratory, as an oxidizing agent.

The oxidation process leads to the formation of polar groups (C=O, OH, etc.) mainly carboxylate ions and quaternary ammonium hydroxides liberating MnO_2 as a by-product from the decomposition of the Ph. TMAP. The presence of the MnO_2 was confirmed by ESCA (XPS), IR, as well as by chemical tests.

The ESCA study shows an increase in the number of oxygen atoms absorbed as compared to the molar concentration of the oxidizing agent. The tensile shear strength increases linearly with the molar concentration of the Ph. TMAP.

A reaction mechanism of the LDPE oxidation at room temperature and in an aqueous solution of Ph. TMAP is proposed.

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INTRODUCTION

Usually, the oxidation of polyethylene leads to the formation of polar groups such as C = O (ketones, acids, esters) and R-OH (alcohols, hydroperoxides, etc.). These polar groups improve adhesion and mechanical properties of the polymer, as a result compatibility with fillers, pigments and other polar polymers are greatly enhanced [1].

Many processes exist to oxidize the polyethylene. It may be done in the molten phase [2-4], in solution [3, 5-7], in a mixture with a reactive solution [8-13], as an aqueous dispersion or as a foam [14-16], by a corona treatment [17], by a laser induced pulse technique [18] or by a hot aqueous oxidizing solution [19-22].

In this paper we will discuss the oxidation at room temperature of PE films and plaques in presence of an aqueous solution of phenyl trimethyl ammonium permanganate (Ph. TMAP). The Ph. TMAP was prepared in our laboratory and used, to the best of our knowledge, for the first time in such an application.

The choice of the oxidizer was governed by the possibility of having very rapid oxidation of LDPE and other saturated or non-saturated hydrocarbons at room temperature and in absence of an organic solvent. This has two benefits: as the treatment takes place at room temperature in the presence of inorganic solvents, the morphology of the polymer will not be affected and, due to the absence of organic solvents, it will be easier to eliminate the unreacted material at the surface simply by rinsing with water.

EXPERIMENTAL

Material

A film and sheeting grade LDPE (LF-0222B) used was obtained from Novacor Canada. It has a melt index of 2.2 and a density of 0.922 g/cm^3. The potassium permanganate and the phenyl trimethyl ammonium bromide (Ph. TMABr) were supplied by Sigma Chemical and used as received without further purification. The potassium permanganate however was finely ground before use. The solvents were of analytical grade.

Apparatus

The adhesive strength of the samples was measured using an Hounsfield horizontal tensio meter.

The samples were also characterized by NMR (Bruker W.H. spectrometer, 400,13 MHZ), by FTIR-(BOMEM DA3), by ESCA-(Escalab 3 MKII), IR-

(Perkin Elmer), by DSC-(Dupont model 910) and by X-ray diffraction (Philips PW 1130). An analytical mill, A-10 model of Jankel and Hunkel was used to grind the LDPE.

Preparation of the Oxidizing Agent

Phenyl Trimethyl Ammonium Permanganate (Ph. TMAP)

Initially, 0.432 g (1/500 mole) of phenyl trimethyl ammonium bromide is dissolved in 2 mL of deionized water, solution I. Solution II is prepared by dissolving 0.316 g (1/500 mole) of $KMnO_4$ in 6 mL of water. Solution II is added under constant stirring to solution I at room temperature. A purple precipitate of phenyl trimethyl ammonium permanganate (Ph. TMAP) forms immediately; after 1/2 hour the agitation is stopped and solution is allowed to settle for 1 hour and then cooled to 2°C. After rinsing the purple precipitate with 2 mL of cold water (≈ 2°C), it is dried under high vacuum for 36 hours at room temperature. The reaction yield was over 99%.

Properties of Ph. TMAP

Ph. TMAP is an explosive product in its dry state, and it must be handled with care. It must not be broken down physically with a hard metallic instrument. It is advised that this material should be used slightly moist, it is however generally more stable than TBAP [2]. When boiling an aqueous solution of Ph. TMAP at first, it turns yellow-green then after 30 minutes green-brown and after 45 minutes it becomes colorless, liberating dark brown particles which when reacted with H_2SO_4 give a colorless salt of Mn.

The purple solution of Ph TMAP diluted in warm MEK turns to brown purple after 30 minutes. In THF however it turns brown at room temperature. This indicates a more rapid oxidation in ethers than in Ketones.

From various solubility trials, (Table 1), it was found that the best film (for IR) was obtained in ethanol.

Preparation of Ldpe Thin Films

From PE Granule

The PE granules were pressed into films of 0.5 mm in thickness with a surface area of 10.925 cm^2. They were cut to the desired size for further testing according to ASTM D-1822. The samples were cleaned by washing with dry acetone for 76 hours in a soxhlet extraction apparatus under nitrogen atmosphere, dried, and kept in absence of air and light before further testing.

TABLE 1. Solubility Trials of Ph. TMAP

SOLUBLE	INSOLUBLE
Water	Benzene
MEK*	Toluene
Ethanol	Isopropanol
Methanol	Dioxane
50% v/v Ethanol	Cyclohexanol
50% v/v Benzene	
THF (slightly when cold)	Cyclohexane
THF + benzene (slightly soluble when warm)	Hexadecanol
Monochlorobenzene (slightly when warm)	Monochlorobenzene
	Biphenyl
	p-toluene sulphonic acid**

* Partially soluble when warm

** When mixed with an aqueous of Ph. TMAP, it gave a white crystalline precipitate.

From Ground PE Granules

The granules of PE were ground in presence of liquid nitrogen in a micro-mill. It gave a powder of PE mixed with metal contaminations. The rest of the procedure is similar to the one described in the previous paragraph.

Oxidation Reaction

The prepared PE samples were dropped in 12.5 mL test tubes containing a 12.5 mL purple solution of Ph. TMAP. The concentration of Ph. TMAP in the test-tubes ranged between 0.78→ 2.34 moles/100 mL, great care was taken in eliminating the oxygen from the solution.

The test tubes were kept protected from oxygen and air during the reaction.

The reaction is considered complete when the purple color of the aqueous solution disappears and a brown precipitate is formed. Although Ph. TMAP has a greater efficacy, it took about 120 hours at room temperature before the solution is completely colorless.

At the end of the reaction the PE films samples were extracted and washed with demineralized water and kept in water for 24 hours after which they were dried with alpha-cellulose paper and then under vacuum, these samples were analyzed by IR and ESCA.

One sample was treated with sulphuric acid until it is colorless, it was rinsed with deionized water and kept in water for 48 hours, rinsed and dried with alpha-cellulose paper and finally under high vacuum at room temperature. The sample was used for the IR studies.

After filtration, the solution containing the brown precipitate was vacuum dried at 50°C. The viscous material was analyzed by IR. A complete sequence in the treatment of the LDPE film is given in Figure 1.

ESCA Analysis

The ESCA analysis of the oxidized surfaces shows an increase of absorbance of oxygen, manganese and nitrogen when increasing the molar concentration of Ph. TMAP (Table 2). These results are obtained by considering the number of oxygen atoms (or reactive oxygen) as compared to the molar concentration of Ph. TMAP (Figure 2).

By chemical analysis and XPS, the final product of the decomposition of Ph. TMAP was found to be MnO_2. The major part of the MnO_2 is precipitated with other insoluble material from the aqueous solution, it contains nitrogen as indicated by the ESCA analysis results given in Table 3.

By determining the amount of MnO_2 at the surface one can determine the percent of oxygen which participated in the various reactions (Table 2). Variations of the ratio of the number of oxygen atoms absorbed per carbon $(O/C)^*$ vs the molar concentration of Ph. TMAP or the variation of the ratio between oxygen and carbon (O/C) shows the progressive oxidation reaction against the liberation of reactive oxygen from Ph. TMAP (Figure 2).

The existence of nitrogen at the surface of the films may be attributed to the presence of quaternary ammonium carboxylate ions. This is confirmed by the IR spectra as the number of these groups correspond to the nitrogen atoms in oxidized polyethylene (Table 2).

In all cases, the reactions with PE or heating the different solutions of Ph. TMAP, it gave a brown precipitate, the solution becomes colorless, i.e. no green color from K_2MnO_4. The solid precipitate resulting from the decomposition being MnO_2.

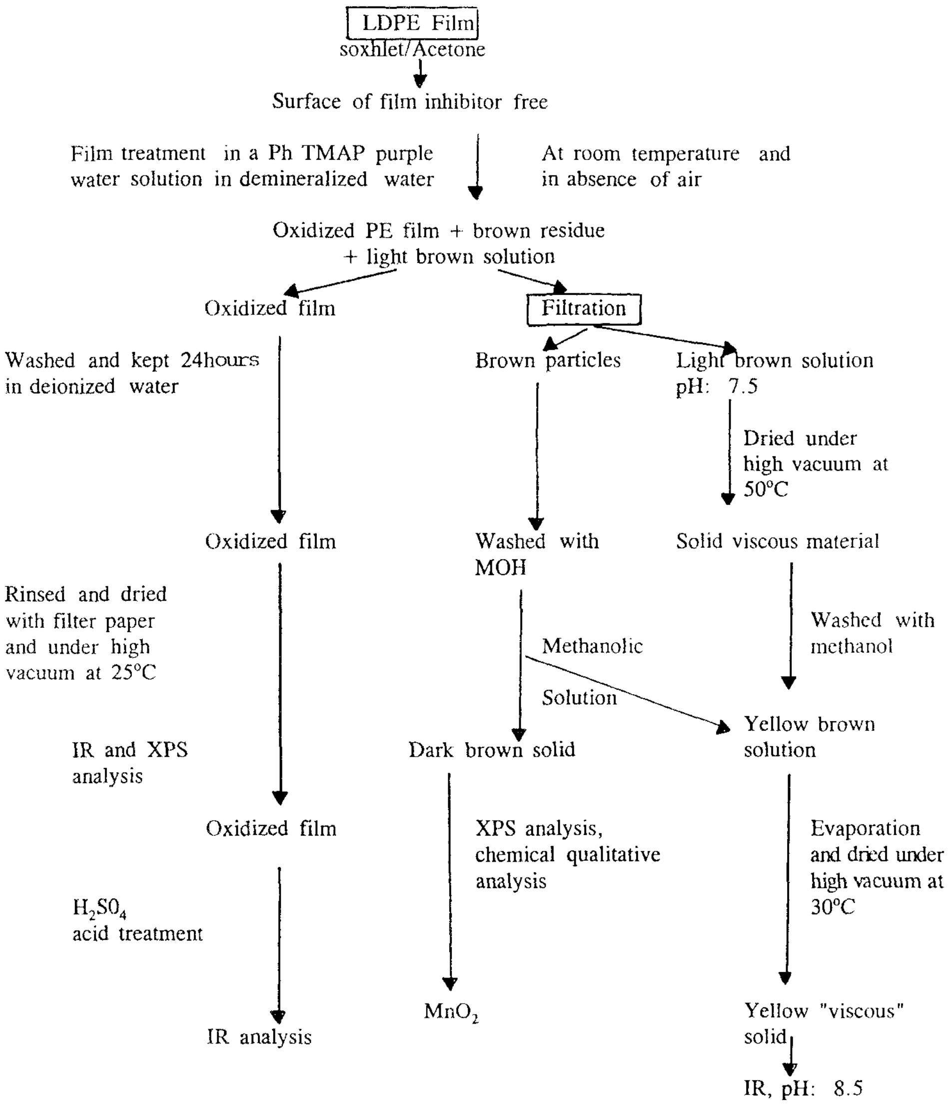


Figure 1. Treatment sequence of LDPE films

The brown precipitate reacts with diluted sulphuric acid and gives a colorless solution (Mn^{++} ions) whereas it is stable in a basic medium.

From the ESCA measurements, before washing with methanol, the percent of atoms of Mn in the residue, is 14.0 and for oxygen it is 39.6 which corresponds respectively to 35.6% and 29.3% in weight (Table 3). This indicates the existence of Mn derivatives which contains a higher level of oxygen corresponding to MnO_2.

TABLE 2. ESCA Analysis of Oxidized PE

Molar concentration of Ph TMAP x 10^4	O_{1s}	N_{1s}	C_{1s}	Mn_{2p}	F_{1s}	Ca_{2p}	K	S_{2p}	Si_p	MnO_2 % (w/w)	Ratio of number of oxygen atoms to the number of carbon atoms x 10^2	Ration of number of atoms
0.780	7.3		90.6	2.1						13.85	8.0	3.4
0.780	11.3		85.6	2.7	0.4					17.22	13.2	6.6
1.171	15.6	4.4	75.0	3.4	1.1	0.7				20.44	20.80	11.7
1.171	24.5	3.0	64.8	4.5	0.4	1.3		0.5	1.1	25.00	37.80	0.23
1.562	19.3	*	41.0	4.7	22.7	1.7	10.6			20.69	47.00	24.0
1.562	20.1	1.4	52.7	4.4	20.3	1.0				29.0	38.00	21.0

* The N_{1s} exist but was not measured. It will however influence the results.

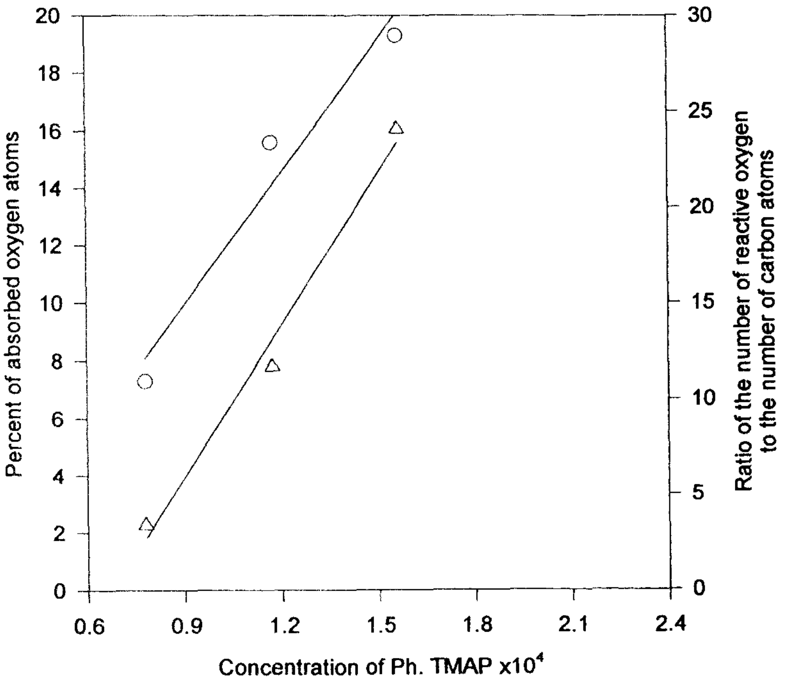


Figure 2. Effect of the concentration of Ph. TMAP

O % of absorbed oxygen atoms on the surface of LDPE as measured by ESCA vs the concentration of Ph. TMAP

Δ Ratio of the number of reactive oxygen to the number of carbon atoms vs the concentration of Ph. TMAP

TABLE 3. ESCA Analysis of the Residue after Oxidation of PE Film

Percentage of the number of atom element in the residue							
	Mn_{2p}	O_{1s}	C_{1s}	N_{1s}	F_{1s}	K_{2s}	Al_{2p}
- Precipitated product before washing	14.0	39.6	35.5	2.3	1.0	6.2	1.4
- Precipitated product after washing with MeOH	14.7	45.8	27.0	0	3.7	6.7	2.0

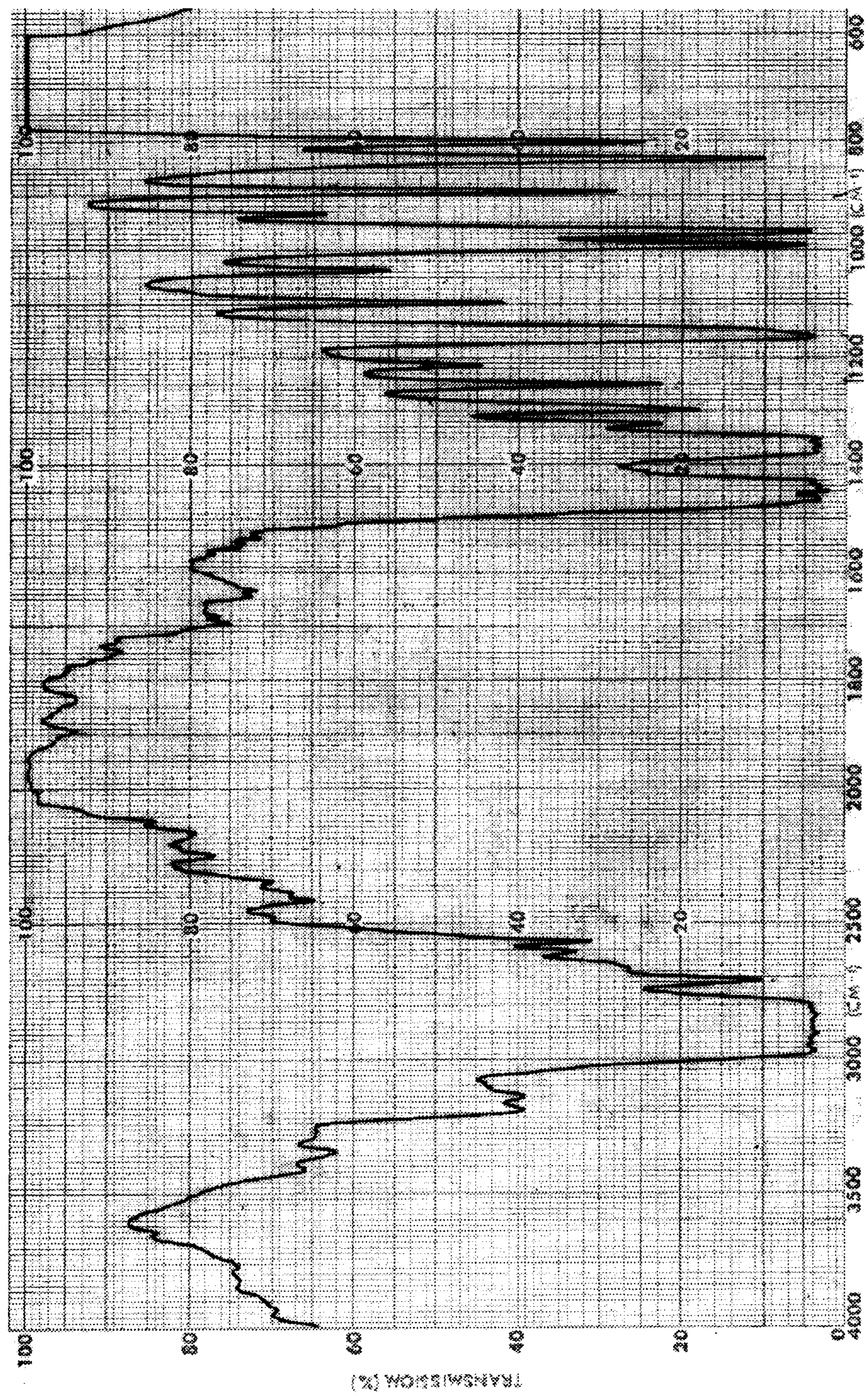


Figure 3. Infrared red spectra of an inhibitor free LDPE film

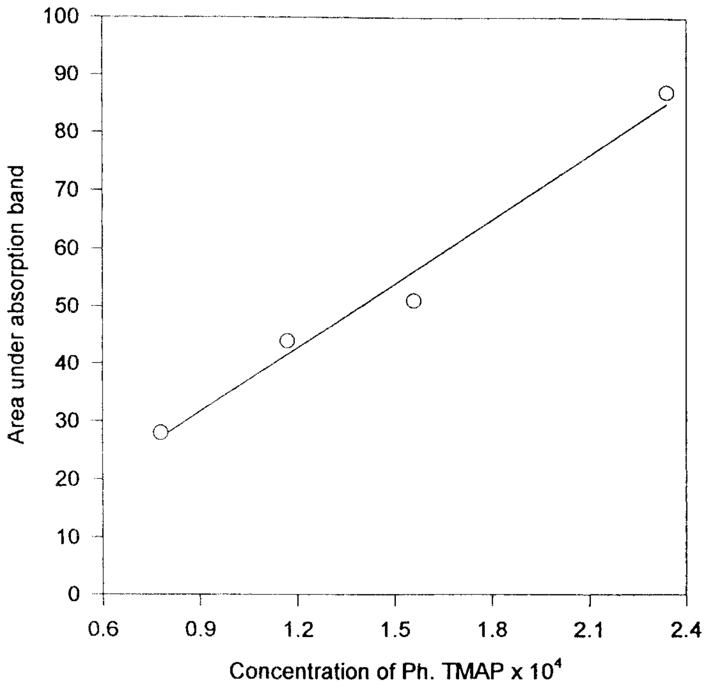


Figure 4. Area under the IR absorption band (1745-1590 cm^{-1}) vs the molar concentration of Ph. TMAP

When the residue is washed with methanol the percent of oxygen atoms increases considerably with a decrease in the number of carbon atoms. The number 2.3 representing the number of nitrogen atoms that has disappeared (Table 3) indicates the elimination of hydrocarbons containing nitrogen atoms.

Initially the Ph. TMAP solution has a pH of 7.4, at the end of the reaction it reaches a pH of 8.5 -9 which suggests the existence of a basic nitrogen product soluble in methanol. These results confirms the ESCA findings.

Spectroscopic Analysis And Reaction Mechanism

The various Ph. TMAP solutions were tested on the inhibitor free surface of LDPE. The qualitative analysis by IR showed absorption bands of quaternary ammonium carboxylate ions at 1700-1590 cm^{-1}, ketonic carbonyl groups at 1721 cm^{-1} and a certain amount of ester groups at 1745-1740 cm^{-1} (Figure 3).

We found that the higher the concentration of the oxidizing agent the greater the surfaces of the absorption band between 1745-1590 cm^{-1}. We also found that

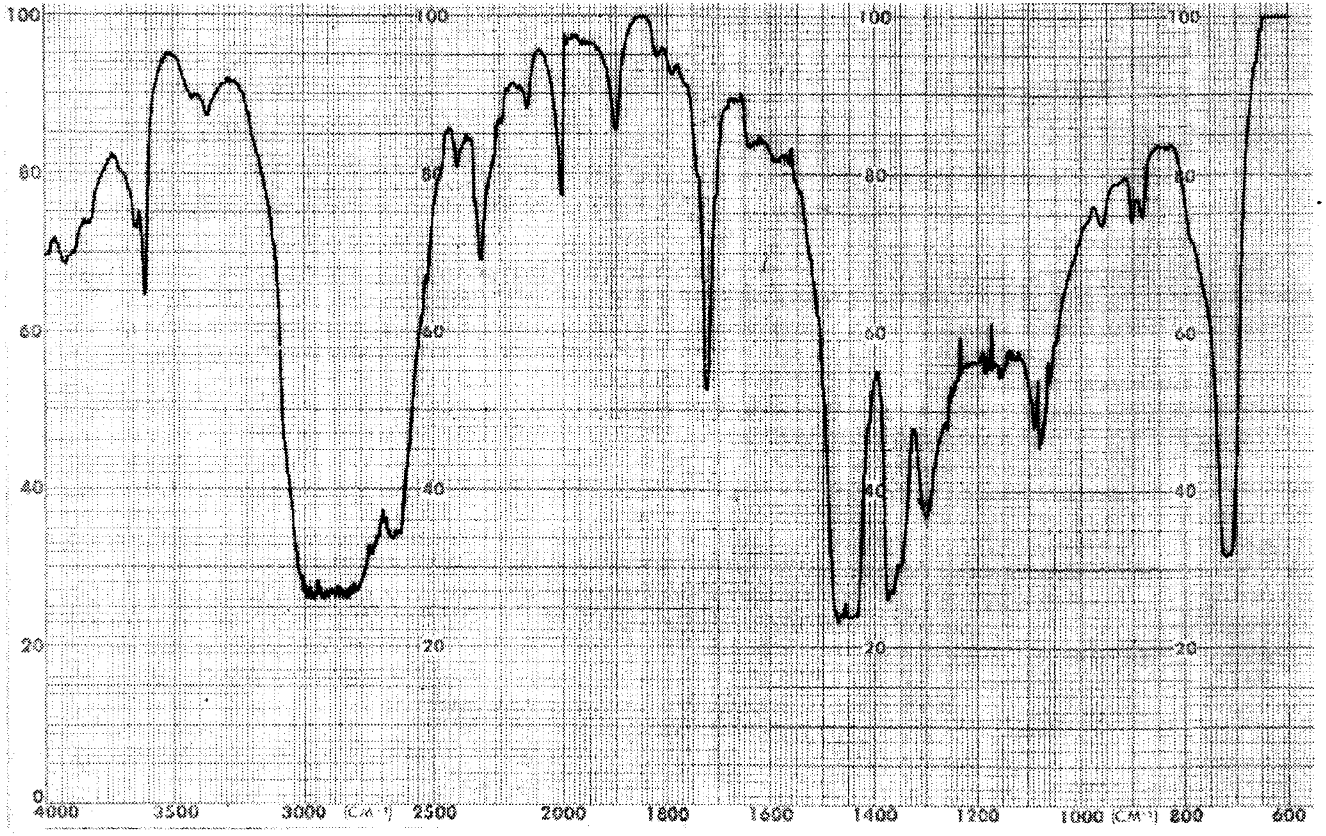


Figure 5. Infrared red spectra of LDPE film after treatment for 48 hours with Ph. TMAP

there is a direct relationship between the concentration of Ph. TMAP and the surface of the absorption band (Figure 4).

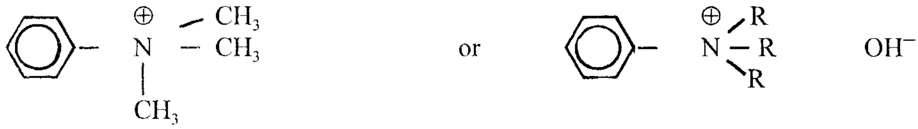
The absorptions bands at 3410 and 3340 cm^{-1} indicates an association with polymeric OH groups.

It seems that at the beginning of the oxidation reaction, ketonic groups, (1721 cm^{-1}) and alcoholic groups (3605, 3625, 3370 cm^{-1}) are formed (Figure 5) and it is the quaternary carboxylate ammonium group which replaces gradually the ketonic group (Figures 5 and 6).

According to the IR spectra (Figure 7) of the viscous residue obtained after the oxidation treatment, the solution being evaporated and dried under high vacuum at 40 °C, weak absorptions bands appear at 730 cm^{-1}, 690 cm^{-1}, 610 cm^{-1}, 1060-1030 cm^{-1}, 1250 cm^{-1}, 1120 cm^{-1} and 3100-300 cm^{-1} belonging to monosubstituted benzene or phenyl groups.

The absorption bands between 3600 - 3120 cm^{-1} are from the ammonium ions, the phenyl groups as well as from the associated acidic OH groups. At 1150-1100 cm^{-1} one notices the C-N aliphatic, the N-CH_3 at 2880 cm^{-1} and N-  at 1395-85 cm^{-1} groups.

In the region between 1650-1550 cm^{-1} one can also notice the alkyl-aryl quaternary ammonium groups, we can then suppose the existence of ammonium ions of the following types:



The existence of nitrogen has been confirmed by XPS (Tables 2-3). The increase of pH of the aqueous solution of Ph. TMAP from 7.4 to 8.5 after treatment and the quantity of excess oxygen, determined from the consumption of O to the MnO_2 state as shown by ESCA, the number of atoms of O being found as 39.6 and for Mn: 14, shows that there are other oxygenated products already formed which are probably hydroxyl or carboxylate intermediates of quaternary ammonium ions.

It is interesting to note that the oxidized films after treatment with diluted H_2SO_4 and with NaOH, for 48 hours at 30°C, shows no change in the absorption band in the region if 1750-1600 cm^{-1} (Figure 8). Generally, the quaternary ammonium salts (Q^+) do not dissociate into an amine and its corresponding acid in a basic medium [23]. As Ph. TBAP is a strong oxidant, the negative ions of MnO_4^-, as in the case of $KMnO_4$ decomposes into MnO_2 and in the aqueous medium it is the OH ions which replace MnO_4^- giving quaternary ammonium

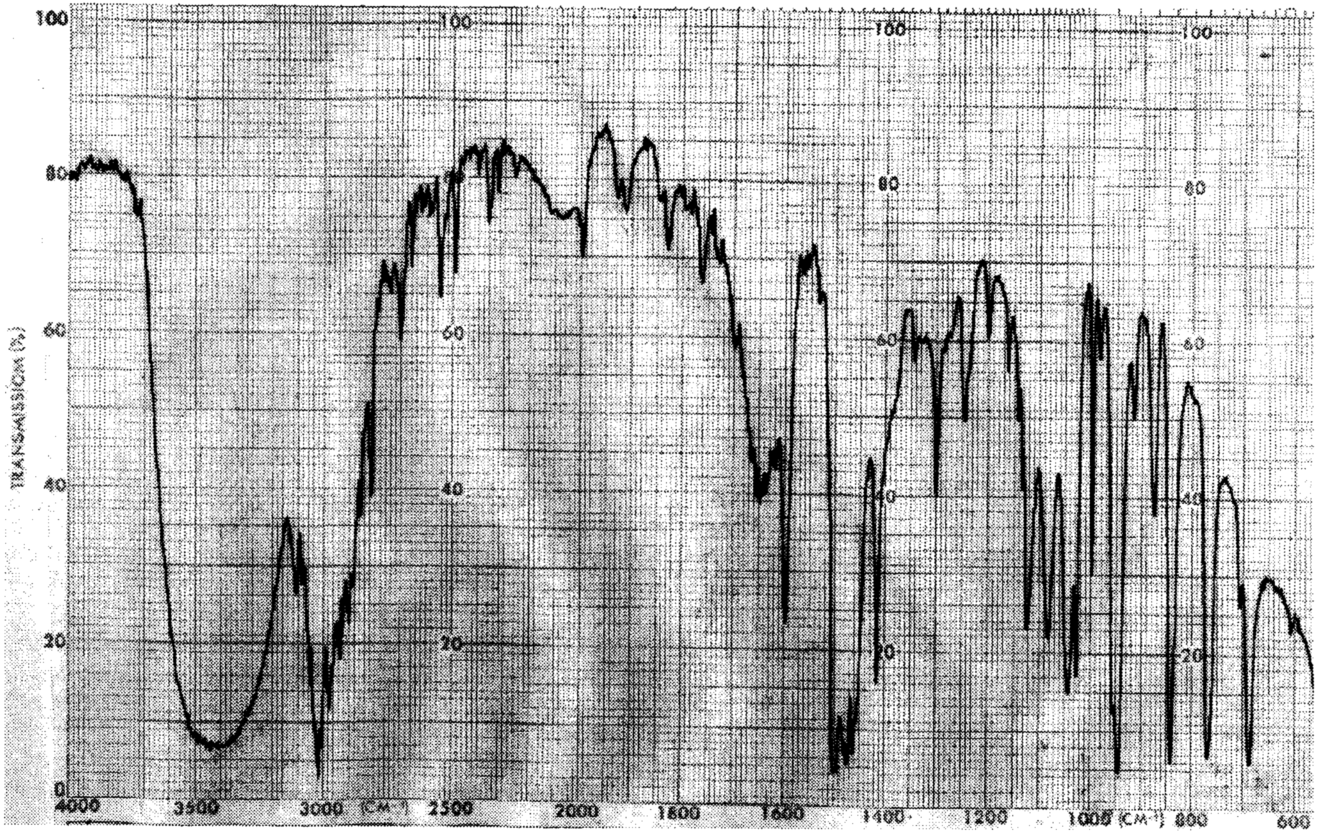


Figure 6. Infrared red spectra of phenyl trimethyl ammonium bromide (Ph. TMABr)

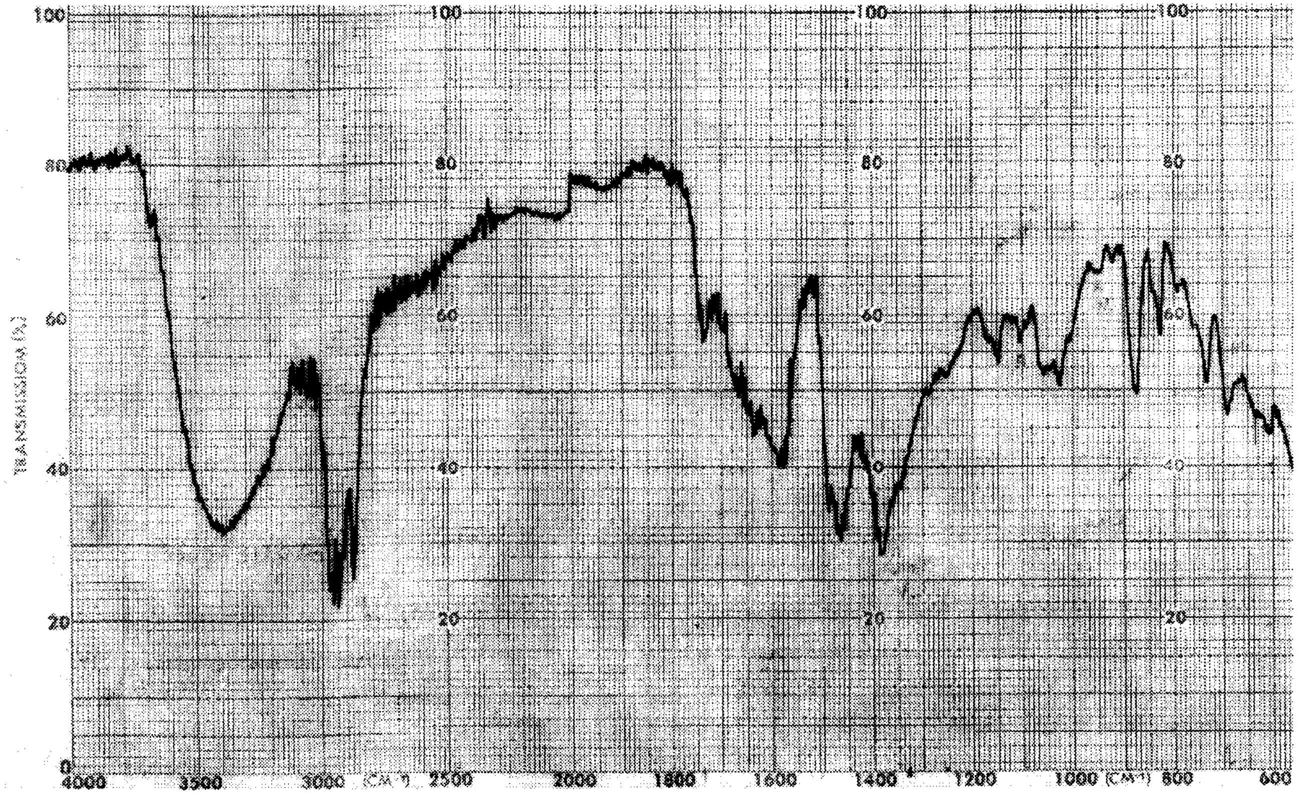


Figure 7. Infrared red spectra of viscous residue obtained after oxidation treatment

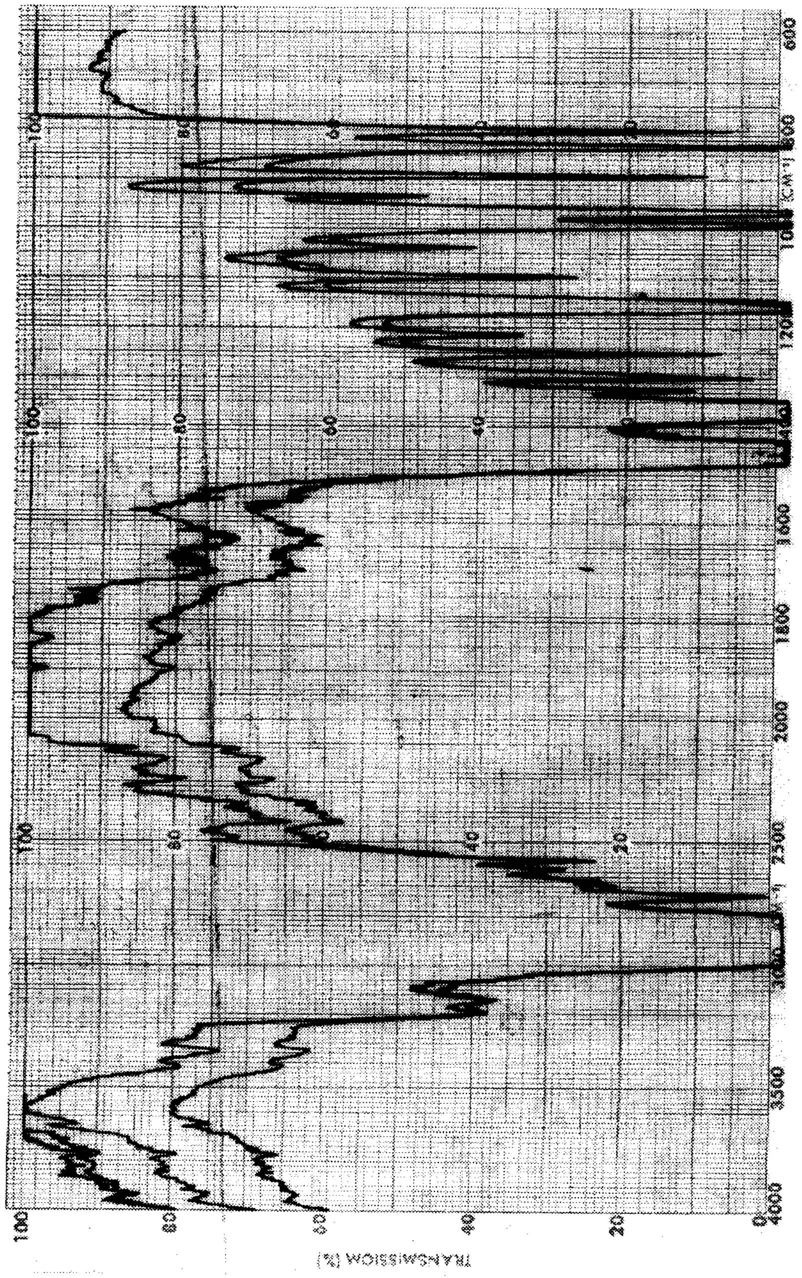


Figure 8. Infrared red spectra of oxidized film

1. not treated
2. after acid treatment

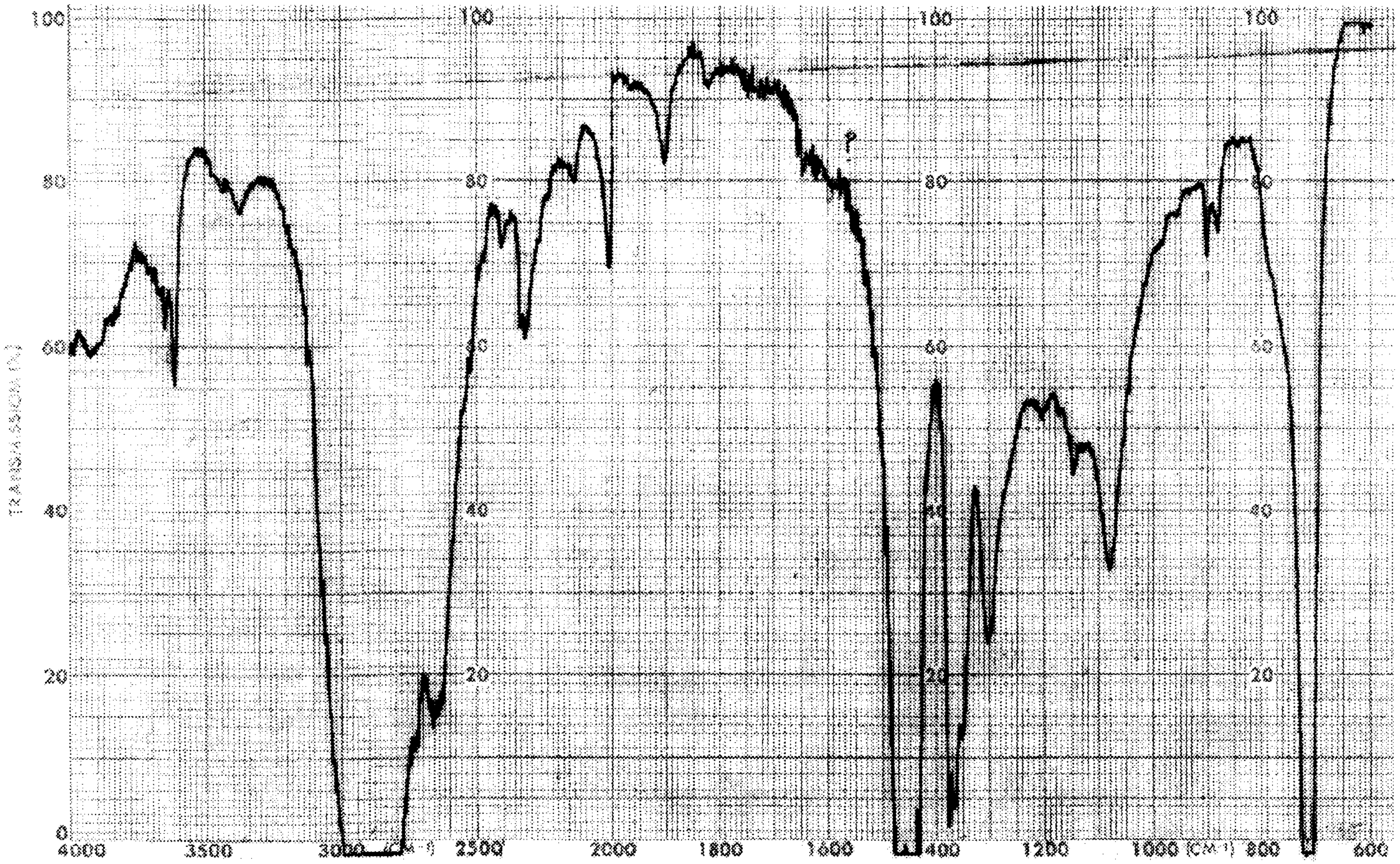
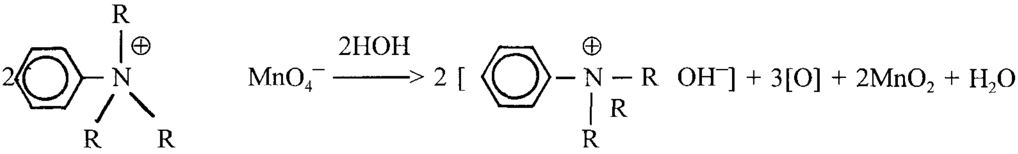


Figure 9. Infrared red spectra of LDPE powder after oxidation by Ph. TMAP

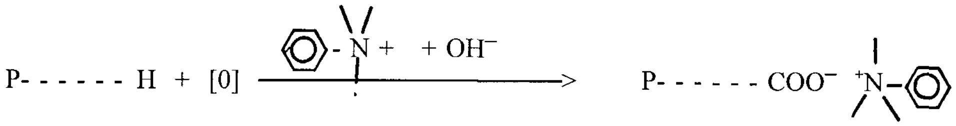
TABLE 4.

Molar concentration of Ph. TMAP in water x 10^4	Temperature °C	Time (hours)	Time (days)
0.78	40, 55, 70	6, 12	2, 10, 60, 180
1.17	" " "	" "	" " " "
1.56	" " "	" "	" " " "

hydroxyl ions:



The hydroxyl groups may be titrated with acids which gives a white precipitate in presence of Barium salt. It is probable then that there is a reaction between the carboxylic acid group originating from the oxidation by the native oxygen and the hydroxyl ions already formed as shown.



This mechanism is in agreement with the results obtained by IR (carboxylic ions), the basic pH of the solution after treatment, the XPS measurements (the existence of nitrogen at the surface of the films and in the residue, the excess of oxygen, the existence of MnO_2), the determination of MnO_2 by physical-chemical methods and the stability of ammonium R^+ ions in both basic and acid mediums.

LDPE and the Impurities from the Micro-Mill

LDPE granules were ground in a micro-mill in presence of liquid nitrogen, the powder had a light grey color. This due to impurities originating from the micro mill.

The powder was washed in a soxhlet at 30°C for 72 hours with acetone and dried under high vacuum.

TABLE 5. Atomic Absorption and Neutronic Activation Analysis of the Metallic Residue

Elements	Cr	As	Sb	W	Fe	Cu	La	U	Si	V	Ni	Mn
ppm	45	0.04	0.003	0.21	22.3	0.54	0.02	0.03	750	<1	20	50

The IR analysis of these films show that the LDPE do not participate in the oxidation reaction which forms CO groups and carboxylate quaternary ammonium in presence of the oxidizing agent Ph. TMAP in water even after 5 months of contact (Figure 9 and Table 4).

This may be interpretated as that the micro mill residues act an inhibitor to the oxidation reaction.

The metallic impurities were analyzed by atoms absorption and by neutronic activation (Table 5).

Some of the elements such as Si, U, Ni and Mn were determined by atomic absorption and the others by neutronic activation. These residues constituted 0.11% in weight of the polymer.

Certain metals such as Ca, Fe, Pb, Mg, Cu, Sn, Mn, Si, Ti and Al accelerate the oxidation of PE [24] the same is true for salts of Co [25-26], Cr, Mo and for Bi [27]. Chelates of Ni are used however as stabilizer for olefins [28]. No reports on the effects of the following elements As, Sb, W, La, U, V, Mo and Ni could be found in the literature.

Experience has shown that the metals or theirs alloys do not participate in the degradation reaction of Ph. TMAP as they play the same role as in the case of the PE film obtained from granules i.e. formation of MnO_2 and discoloration of the solution. In spite of the degradation of Ph. TMAP and formation of native O there is no gas formed. This might be interpretated as that certain elements absorbs the native oxygen or degrade the oxygen groups formed during the reaction. Further work will be required in order to establish which metal or alloy is an inhibitor.

Mechanical Properties

The tensile shear strength of various oxidized polyethylene films was tested according to a method describe elsewhere [21] and to ASTM D-618 as function of the concentration of oxidizing agent (Figure 10). One can notice a direct relation between the tensile strength and the concentration of the oxidizing agent in the solution.

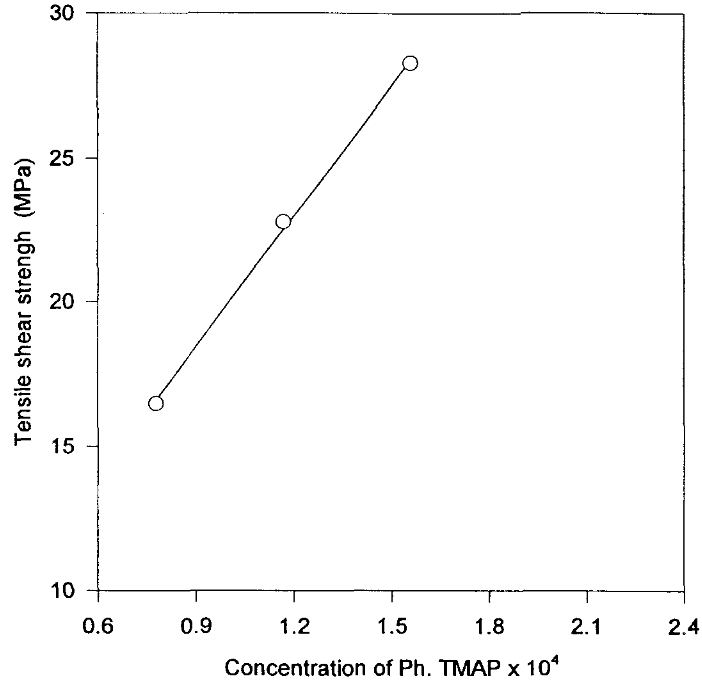


Figure 10. Tensile shear strength (MPa) vs concentration of Ph. TMAP

CONCLUSION

A simple, rapid and economic method to oxidize polyolefins was developed. The oxidation is carried out in aqueous medium at room temperature.

Due to the absence of organic solvent and due to the low temperature reaction conditions, the original morphology of the film should not be affected.

IR and ESCA analysis and physical-chemical treatments lead us to suggest a reaction mechanism and a rapid, precise and quantitative measurement of the oxidation.

The formation of oxygenated polar groups and more particularly quaternary ammonium carboxylate groups on the film surface should increase the adhesion properties and the hydrosolubility of the films.

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