Photodegradable Polyethylene

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Synopsis

Polymer photodegradation can be achieved by introducing carbonyl groups which absorb radiations above the 300 mμ wavelength and thus are sensitized by solar or atmospheric radiations.

We introduced these groups in polyethylene by oximation of aliphatic chain with photoactivated NOCl and hydrolysis of the oxime.

Modified polymers show, during accelerated aging in Weather-O-Meter, a constant molecular weight decrease, which is directly proportional to the concentration of carbonyl groups.

INTRODUCTION

Solid waste disposal and litter are among the many problems that arise from the relationship between man and his environment. Plastic materials are particularly bad polluters due to their ever growing production and to their high degree of nondegradability.

Incineration, land fill, and recycling[1,2,3] are the most used methods for waste disposal; however, they are mostly confined to sufficiently big centers that can afford garbage collection and transportation. Recycling presents the great advantage of limiting the consumption of natural resources, but it has also the big problem of selection and separation of the wastes.

The use of plastic materials capable of transforming itself into products which can reenter the biologic life cycle appears as one of the best solutions to their disposal problem.
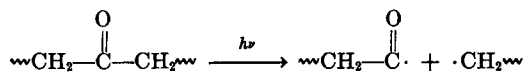
Concerning aliphatic chain polymers, most researchers agree on their high resistance to fungi and bacterial attack[4–7] unless they are previously submitted to strong breakdown of chain length.

This paper presents an original method to obtain a chemically modified polyethylene that, maintaining the same technical properties of the commercial product and after being normally employed, when exposed for a sufficiently long time to atmospheric agents submits to molecular weight decrease.
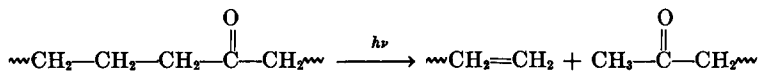
Many papers describe natural, thermal, and photochemical aging of polyethylene;[8–16] the degradation is always oxidative and proceeds via formation of hydroperoxides, which evolve to aldehydes and ketones.

What is known from the photochemistry of aliphatic ketones[17-21] shows that the photolysis follows the Norrish reactions:

Type 1

$$\text{wCH}_2\text{---C---CH}_2\text{w} \xrightarrow{h\nu} \text{wCH}_2\text{---C}\cdot + \cdot\text{CH}_2\text{w}$$

Type 2

$$\text{wCH}_2\text{---CH}_2\text{---CH}_2\text{---C---CH}_2\text{w} \xrightarrow{h\nu} \text{wCH}_2\text{=CH}_2 + \text{CH}_3\text{---C---CH}_2\text{w}$$

Guillet[22] showed in an ethylene–carbon monoxide copolymer that the principal photo-oxidative chain breakdown is of the second type.

Rice and Teller,[23] and Noyes and Davis[24] studied various mechanisms for the Norrish type 2 reaction of ketones and suggest a cyclic six-membered ring intermediate; it is characterized by the attachment of a hydrogen atom, in the γ-position with respect to the carbonyl group, to the oxygen atom:
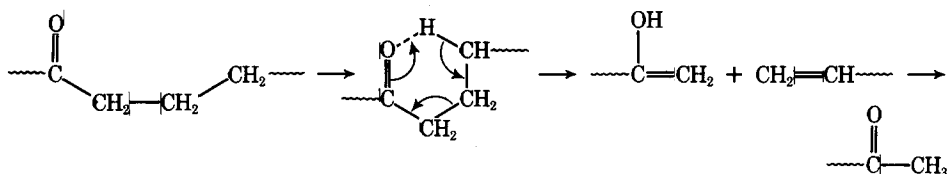

Polymer photodegradation can therefore be achieved by introducing carbonyl groups which absorb radiations above the 300-mμ wavelength and thus are sensitized by solar or atmospheric radiations but not by visible light.

Many industries[25] are developing or selling photodegradable plastics; and while they offer data on mechanical properties and degradability of their new products, little is known on the methods of introduction of the photosensible groups. This is obtained, however, either by mixing with an additive containing the groups or by copolymerization with a photosensible monomer.

CHEMISTRY AND MECHANISMS

We proceeded on the knowledge of the chemistry of oximation of saturated hydrocarbons with photoactivated NOCl. This reaction was discovered by Lynn[26,27] and is used in many processes, notably in the production of ε-caprolactam from cyclohexane.
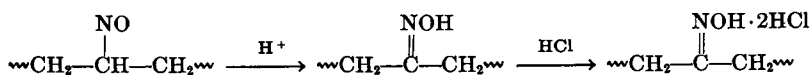
Radiation wavelengths up to 6400 Å cause scission of the NOCl molecule according to [28,29]

$$\text{NOCl} \xrightarrow{h\nu} \text{NO}\cdot + \text{Cl}\cdot$$
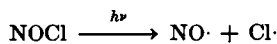
The photo-oximation reaction follows a nonchain radical mechanism:[30]

$$\text{Cl}\cdot + \text{RH} \rightarrow \text{R}\cdot + \text{HCl}$$
$$\text{R}\cdot + \text{NO}\cdot \rightarrow \text{RNO}$$
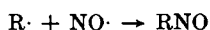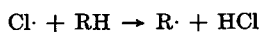
The presence of HCl causes the immediate nitroso derivative isomerization to oxime and the stabilization as hydrochloride:

$$\text{wCH}_2\text{---CH---CH}_2\text{w} \xrightarrow{\text{H}^+} \text{wCH}_2\text{---C---CH}_2\text{w} \xrightarrow{\text{HCl}} \text{wCH}_2\text{---C---CH}_2\text{w}$$

By hydrolysis of the oxime, the carbonyl group is obtained:

$$\text{wCH}_2\underset{\text{NOH}}{\overset{\text{NOH}}{-\text{C}-}}\text{CH}_2\text{w} \underset{\underset{(-)\ddot{\text{N}}\text{OH}}{\text{H}^+}}{\overset{\text{H}_2\text{O}}{\longrightarrow}} -\underset{(-)\ddot{\text{N}}\text{OH}}{\overset{(+)\text{OH}_2}{\text{C}-}} \rightarrow -\underset{\text{NH}_2\text{O}}{\overset{\text{OH}}{\text{C}-}} \rightarrow -\underset{(+)}{\overset{\text{OH}}{\text{C}-}} \rightarrow -\overset{\text{O}}{\text{C}-} + \text{NH}_2\text{OH}$$
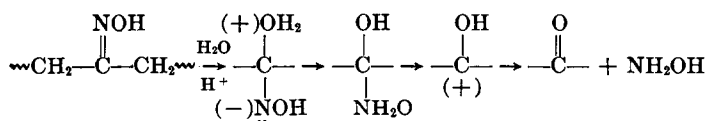
EXPERIMENTAL

The reaction vessel for the photo-oximation is a rotating 5-liter glass flask containing on its axis a cooling jacket (tap water is used) that carries an ultraviolet radiation lamp (Philips HPV 125 W).

The cooling jacket is made of Pyrex glass, transparent to the necessary radiation wavelengths (above 400 mμ).

NOCl is prepared by bubbling gaseous HCl in NOHSO$_4$ and fractional distillation of the product.

The polymer, high-density polyethylene, has been made for this work without additives, antioxidants, or lubricants, in order to avoid interference during the study of photodegradation.

A TiCl$_3$ with polyimino alanate derivatives as catalyst was employed, and molecular weight was controlled with H$_2$: density 0.9622 g/cm^3; *MFI*, 1.30 g/10 min; mp 134°C; ashes, 0.025%; CH$_3$, 0.55%; crystallinity RX, 92%; crystallinity DTA, 72%.

Vinyl and vinylidene double bonds are present in subanalytic quantities.

The procedure for carrying out the reaction is as follows: the polymer is introduced into the vessel; alternatively, N$_2$ is fluxed and vacuum pulled; then NOCl and HCl are introduced in a 1:5 ratio. The rotation of the vessel assures a good polymer mixture, and then the lamp is lighted. When the reaction is over, the excess of NOCl is removed by a flux of N$_2$.

The hydrolysis reaction is carried out by heating to reflux for a few hours in a H$_2$O–EtOH–HCl conc. mixture in a 7:2:1 ratio. After drying, the polymer is aged in an Atlas Model 600/DMC-WR Weather-O-Meter.

The polymer behavior during aging is studied by the following techniques: (a) infrared spectrography with Perkin-Elmer Model 221; (b) *MFI* (melt flow index) ASTM D 1238-65 T; (c) tensile properties D 638-68; (d) intrinsic viscosity [η].

RESULTS AND DISCUSSION

In a first series of experiments, we found that for a reaction time inferior to 15 min, the modified polymer did not change its physical characteristics.

MFI essays and tensile properties data on unreacted polymer and polymer reacted for 1, 2, and 20 min are shown in Table I. The low *MFI* value of the 20-min product is due to the high quantity of carbonyl groups that undergo thermal degradation during the *MFI* measurement (190°C), forming radicals that give crosslinking.

For the polymer aging, the Weather-O-Meter was set to the following cycle: maximum light without water sprinkling, two arc lamps, humidity 50%, temperature 63°C on black panel. The polymer was molded under 45 × 55 × 1 mm plates.

TABLE I
MFI Assays and Tensile Properties on Unreacted and Reacted
1 min, 2 min and 20 min polymers

Reaction time, min	MFI	Tensile strength	Tensile yield	% El
0	1.32	536	476	1077
1	1.30	523	491	1087
2	1.27	519	533	1117
20	0.87	516	465	1030

TABLE II
Tensile Strength of Unreacted and Reacted 1 min and 2 min Polymers at Different Aging
Times

Reaction time, min	W-O-M,[a] hr	Tensile strength	Tensile yield	% El	W-O-M, hr	Tensile strength	Tensile yield	% El
0	100	529	314	1035	200	526	291	1144
1	100	—	530	—	200	—	421	—
2	100	—	480	—	200	—	368	—
0	400	—	311	—	600	—	291	—
1	400	—	160	—	600	—	144	—
2	400	—	186	—	600	—	167	

[a] Weather-O-Meter.

TABLE III
MFI Variation During Measurement at 190°C

Reaction time, min	W-O-M, hr	MFI	W-O-M, hr	MFI	W-O-M, hr	MFI
0	0	1.32	100	0.35	200	0.060
		1.29		0.33		0.059
		1.36		0.33		0.057
1	0	1.35	100	0.45	200	0.47
		1.26		0.37		0.38
		1.30		0.30		0.26
2	0	1.24	100	0.52	200	0.61
		1.31		0.40		0.52
		1.26		0.33		0.40

Table II gives the results of tensile strength essays of unreacted and reacted 1- and 2-min polymers after different aging times. We have used samples of low carbonyl content to study more thoroughly the aging process. These results show that the modified polymer loses its elongation properties after 100 hr while the nonreacted polymer retains its elastic properties for longer times.

Molecular weight could not be determined by MFI because of crosslinking of the aged modified polymer during the measurement at 190°C.

Table III shows MFI change for three consecutive measurements of the same sample. We therefore used the intrinsic viscosity measure ($[\eta]$) at 135°C in decalin.

Figure 1 shows the $[\eta]$ variations of the unreacted and 1- and 2- min polymers. The unreacted polymer after 200 hr of aging is so crosslinked that viscosity is not
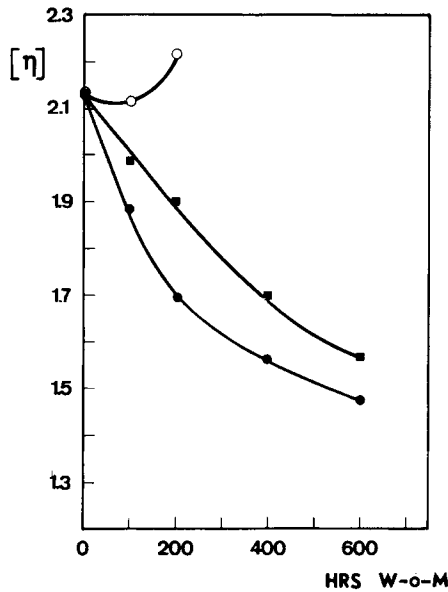
Fig. 1. Intrinsic viscosity ($[\eta]$) variations as a function of time of aging: (O) 0 min; (■) 1 min; (●) 2 min.

measurable; the modified polymers instead show a constant molecular weight decrease. This means that aging proceeds without crosslinking, which is very important in the eventuality of attack by microorganisms, also favored by the presence of hydrophylic functional groups.

The aging process was also studied by IR spectroscopy. Chain breaking according to Norrish type 2 reaction gives[31-35] terminal vinyl groups which react with singlet O_2 molecules formed by quenching of n—π^* carbonyl triplets to form hydroperoxides:
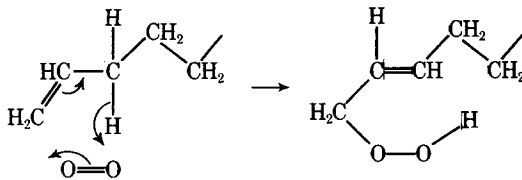
These lead to formation of carbonyl groups, which we measured by IR spectroscopy.

Figure 2 shows the absorption ratio of the carbonyl band at 1720 cm^{-1} and the 4420 cm^{-1} reference band at different aging times of the unreacted and 1- and 2-min polymers. Before aging the polymers do not have a sufficient percentage of carbonyl groups for IR detection. The increase in carbonyl groups agrees with the theory of vinyl-terminal oxidation during aging.

CONCLUSIONS

Our method for the preparation of photodegradable polymers has undoubtable advantages over the copolymerization or additive methods: it does not modify
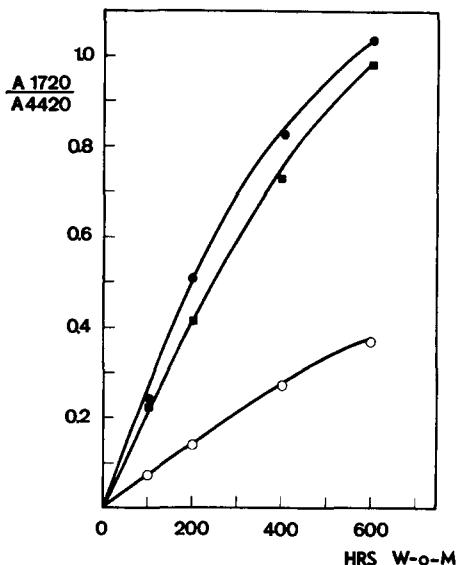
Fig. 2. Carbonyl adsorption variations as a function of time of aging: (O) θ min; (■) 1 min; (●) 2 min.

polymerization techniques and the carbonyl groups are chemically bonded to the polymeric matrix.

Additional costs are of minor importance and the simplicity of the reaction confers application versatility.

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