Polymer Bulletin 13, 163-169 (1985)

Polymer Bulletin

Photoinitiation

Preparation of Low-Density Polyethylene Composites by UV Irradiation

Maria Isabel Felisberti, Ralf Giesse, and Marco-A. De Paoli*

Instituto de Química, Universidade Estadual de Campinas, C. Postal 6154,
13100 Campinas, SP, Brazil

SUMMARY

Composites of low-density polyethylene were prepared by the sorption of vinylic monomers and a photoinitiator into a polymer matrix, followed by UV irradiation. Gravimetric determinations showed that 2-4 % incorporation of the polymer in the host matrix is possible by this method. Transmission and reflectance infrared spectra measurements showed that the vinylic polymer is lodged in the bulk of the polymer film with no surfacial deposition.

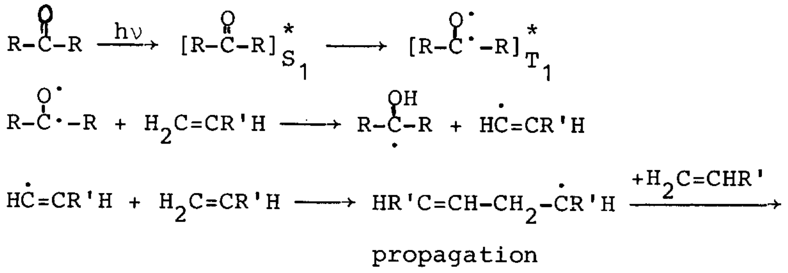
INTRODUCTION

There has been several atempts to use radiation to modify the physical properties of one of the most produced thermoplastics, low density polyethylene (LDPE). Irradiation of LDPE with high energy radiation was shown to produce oxidation, unsaturation and crosslinking formation (BIXLER et al., 1963). Also, attempts have been made to crosslink or graft different monomers in LDPE by means of photochemical reactions (OSTER et al., 1959). In general, long irradiation times in the presence of oxygen causes oxidation of the polymer unless additives are used. On the other hand, in the absence of oxygen crosslinking and chain branching are observed. More recently, the photografting of acrylic acid, methacrylic acid, acrylonitrile and methyl methacrylate onto the surface of LDPE has been studied (OGIWARA et al., 1982). In this work surfacial modification of LDPE was achieved with a high grafting degree.

The photoinitiated polymerization of vinylic monomers has also been intensely studied in recent years. As a general rule, carbonyl containing compounds are used as photoinitiators due to the relatively long lifetime of their triplet n-Π* excited states (LISSI and ENCINA, 1979). The relative rates of quenching by the monomers determinates the initiation efficiency of a given system (ENCINA et al., 1982). The general mechanism involves hydrogen abstraction by the triplet n-Π* excited ketone in the vinylic monomer, according to the following scheme:

---

* To whom offprint requests should be sent



$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{h\nu} [R-\overset{O}{\overset{\|}{C}}-R]^{*}_{S_1} \longrightarrow [R-\overset{O^{\bullet}}{\overset{|}{C}}{}^{\bullet}-R]^{*}_{T_1}$$

$$R-\overset{O^{\bullet}}{\overset{|}{C}}{}^{\bullet}-R + H_2C=CR'H \longrightarrow R-\overset{OH}{\underset{\bullet}{\overset{|}{C}}}-R + \dot{H}C=CR'H$$

$$\dot{H}C=CR'H + H_2C=CR'H \longrightarrow HR'C=CH-CH_2-\dot{C}R'H \xrightarrow{+H_2C=CHR'}$$

propagation

The usual way to make composites is either by the mechanical mixture of the molten polymer components or by mixture in a common solvent followed by solvent evaporation. Another way is by matrix polymerization, i.e. reaction proceeding via a new chain growth on macromolecules previously introduced into the system. Matrix polymerization is more interesting because it provides a method for obtaining composites which cannot be obtained by the conventional methods. A composite of polytetrafluorethylene (PTFE) and polyvinyl acetate (PVA) was obtained by the photochemical polymerization of VA previously sorbed in PTFE (DE PAOLI et al., 1979). The photoinitiated polymerization of methylmethacrylate (MMA) in a PMMA matrix (KOPIETZ et al., 1983 and 1984) has also been reported. In this case, the irradiation initially produces chain scissions with the subsequent growth of the chains by polymerization of the monomer present in the matrix. More recently, the condensation polymerization of urea and formaldehyde in water in the presence of a macromolecular matrix, polyacrylic acid, has been reported (PAPISOV et al., 1984). The products of this matrix polymerization are composites of polyacrylic acid and urea-formaldehyde. A composite has also been prepared by the electrochemical polymerization of pyrrole in poly-vinylchloride by coating a Pt electrode with this polymer (DE PAOLI et al., 1984). Also, the treatment of polyethylene with a Ziegler-Natta type catalyst yielded the polymerization of acetylene in its bulk (GALVIN and WNECK, 1982).

In this paper we report on the photoinitiated preparation of composites of LDPE with vinylic and acrylic monomers. The formation of the composite does not alter the surfacial properties of LDPE since the polymerization occurs exclusively in its bulk.

EXPERIMENTAL PART

Commercial low density polyethylene film samples of 0.50 mm thickness were used after being cleaned and dried. Acrylic acid (AA), vinyl acetate (VA), methyl methacrylate (MMA) and methyl acrylate (MA) furnished by Rhodia were distilled prior to use.

The composites were prepared by soaking the LDPE film in the liquid polymer containing 2% benzophenone (Aldrich, used as received) at room temperature for 48 hours. The saturation of the LDPE film with the monomer was followed by differential i.r. spectroscopy and gravimetry. After this the films were irradiated for 2 h at 10°C with a medium pressure mercury lamp in a water cooled Pyrex jacket. The principal lines of the emission spectrum of the jacketed lamp are 436, 405, 366 and 303 mm, that at 366 being the most intense.

The composites were characterized by differential i.r. spectrophotometry in a JASCO model A-220 spectrophotometer and by attenuated total reflectance (ATR) spectra using a JASCO ATR-6 attachment. UV-visible spectra were recorded by a Spectronic 2000 Baush-Lomb spectrophotometer.

RESULTS AND DISCUSSION

The sorption of gases, liquids or vapours in polymers is known to be favoured when the Hildebrand solubility parameters (δ) of the sorbent and the sorbate are similar. Before preparing the composites we determined the percent of monomer sorbed into the LDPE matrix (Q) by gravimetry. According to Table 1, Q increases as δ of the monomer approaches 8.1 (cal/cm^3)$^{1/2}$, which is the δ value determined for LDPE (GHOSH, 1971).

Table 1. Percent of monomer sorbed in LDPE (Q) and Hildebrand's solubility parameter (BRANDRUP and IMMERGUT, 1975).

Monomer	Q (%)	(cal/cm^3)$^{1/2}$
MMA	3.40	8.8
MA	2.32	8.9
VA	2.11	9.0
AA	1.69	12.0

The solution photopolymerization of vinylic monomers involves the absorption of light by the monomer and the formation of stable free-radicals. However, in our case a third factor is involved, desorption of the monomer from the LDPE matrix. In order to obtain a high degree of polymerization it is necessary to introduce a photoinitiator in such a way that the polymerization rate will be higher tham the desorption rate. To demonstrate this we irradiated samples of LDPE sorbed with the pure monomers and with monomers containing

2% benzophenone. According to the results shown in Table 2 there is a strong increase in the percent polymer incorporated in LDPE with the addition of the photo-initiator.

The data in Table 2 was obtained using the same sorption and irradiation times. Although MMA shows a high degree of sorption in LDPE, it is desorbed at a faster rate than when polymerized in the absence of a photoinitiator. We observed with MMA a higher percent of polymer incorporated into the matrix by adding benzophenone, showing that the production of the composite is solely due to the presence of the photoinitiator. For the other monomers the effect is less pronounced but the percent increase of incorporation showed that the polymerization rate increased in relation to the desorption rate.

Table 2. Percent of polymer incorporated in LDPE without (P) and with benzophenone (P_B) together with the percent increase of incorporation.

Monomer	P (%)	P_B (%)	Increase (%)
MMA	-	3.63	100
MA	1.55	1.78	69
VA	1.01	2.07	51
AA	0.91	1.69	46

The formation of the composites is particularly evidenced by the transmission infrared spectra of the LDPE films measured after the treatment with the monomer and after U.V. irradiation. In Figure 1 we show the differential spectrum of LDPE treated with VA before and after irradiation, together with the ATR spectrum of the LDPE/PVA composite after irradiation. In the first spectrum the expected absorptions of the monomer are observed evidencing its sorption by the LDPE matrix. After U.V. irradiation the C=C stretching band at 1640 cm^{-1} disappears as a consequence of the polymerization reaction. The ATR spectrum of the composite is identical to an ATR spectrum of pure LDPE. It is known that the radiation penetrates the film to an average depth of 10,000 Å in an ATR experiment. From our results we can conclude that the monomer polymerizes in the bulk of the matrix and not on its surface. The same features are observed for all other monomers studied. These results show that the surfacial properties of the composites obtained are unchanged in relation to pure LDPE, but bulk properties are expected to change.

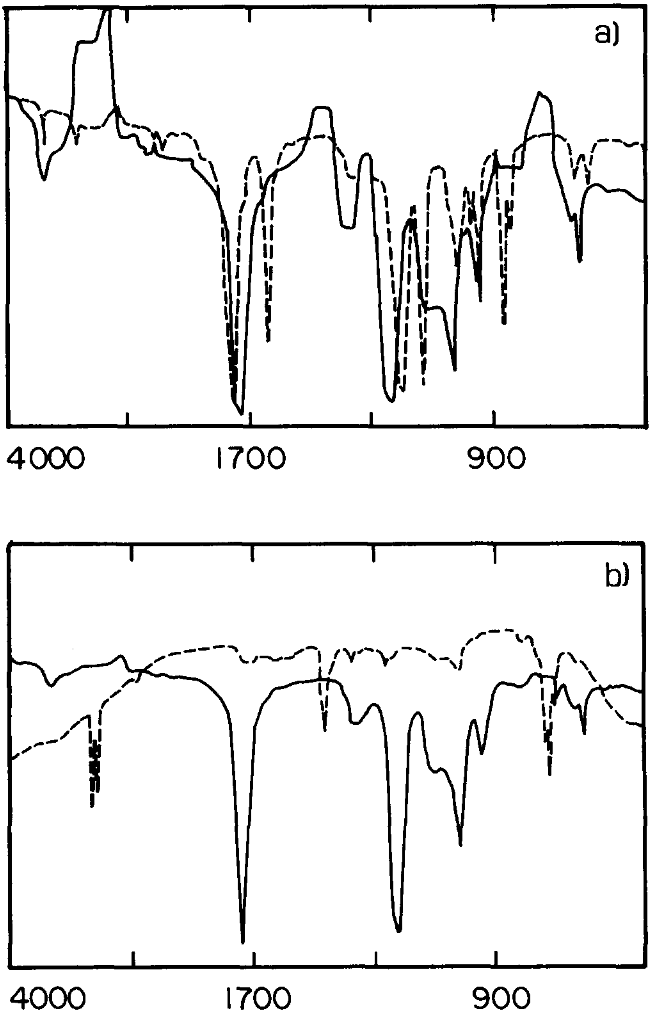


Figure 1. a) Infrared differential spectra of LDPE treated with VA prior (broken line) and after UV irradiation (full line). b) ATR spectrum of the composite (broken line).

In Figure 2 we show the differential absorbance U.V. spectra of the composites together with the spectrum of LDPE. The absorptions are typical for polyesters or polycarboxylic acids.

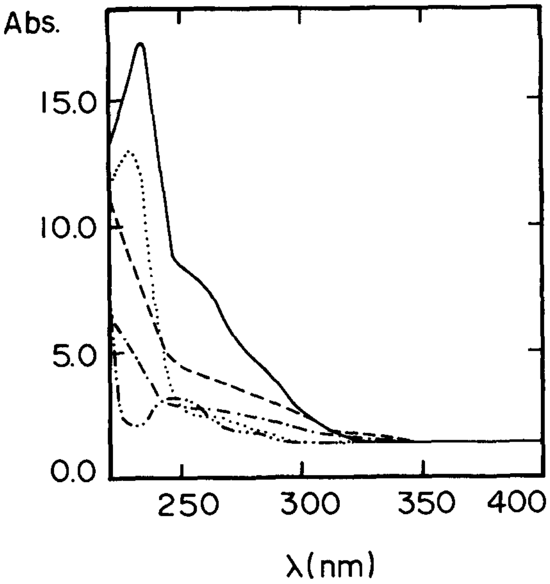


Figure 2. UV differential spectra of the composites: (——) LDPE/PMA, (...) LDPE/PVA, (---) LDPE, (-.-.-) LDPE/PMMA and (-..-..) LDPE/PAA.

In conclusion we have shown that it is possible to prepare composites from films of LDPE by the photoinitiated polymerization of a vinylic monomer in its bulk. Work is in progress to study the effect of the composition on the permeability of gases and vapours in the films.

Acknowledgements. Financial support from CNPq and FAPESP is acknowledged, RG and MIF acknowledge fellowships from FAPESP.

REFERENCES

BIXLER, H.J., MICHAELS, A.S. and SALAME, M., J. Polym. Sci, A1 (1963) 895.

BRANDRUP, J. and IMMERGUT, E.H. eds., Polymer Handbook, New York, John Wiley, 1975.

DE PAOLI, M.A., TAMASHIRO, I.T. and GALEMBECK, F., J. Polym. Sci., Polym. Let. Ed., 17 (1971) 391.

DE PAOLI, M.A., WALTMAN, R.J., DIAZ, A.R. and BARGON, J., JCS Chem. Commun. (1984) 1015.

ENCINA, M.V., LISSI, E.A., KOCH, V. and ELORZA, E., J. Polym. Sci., Polym. Chem. Ed., 20 (1982) 73.

GALVIN, M.E. and WNECK, G.E., Polym. Commun. 23 (1982) 795.

GHOSH, S.K., Makromol. Chem., 143 (1971) 161.

KOPIETZ, M., LECHNER, M.D. and STEINMEIER, D.G., Makromol. Chem., Rapid Commun., 4 (1983) 113.

KOPIETZ, M., LECHNER, M.D. and STEINMEIER, D.G., Eur. Polym. J., 20 (1984) 667.

LISSI, E.A. and ENCINA, M.V., J. Polym. Sci., Polym. Chem. Ed., 17 (1979) 2791.

OGIWARA, Y., TAKUMI, M. and KUBOTA, H., J. Appl. Polym. Sci., 27 (1982) 3743.

OSTER, G., OSTER, G.K. and MOROSON, H., J. Polym. Sci., 34 (1959) 671.

PAPISOV, I.M., KUSOVLEVA, O.E., MARKOV, S.V. and LITMANOVICH, A.A., Eur. Polym. J., 20 (1984) 195.

Accepted February 1, 1985