

Modification of Polyethylene by Unsaturated Compounds

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SYNOPSIS

Polyethylene was reacted with maleic anhydride and *N*-phenylmaleimide in solution. The effect of modification on its physico-chemical properties, such as mechanical, oxygen gas transmission, water vapor transmission, and grease resistance properties, was studied.

INTRODUCTION

In food packaging, polyethylene (PE) is the most widely used polymer because of its many advantageous properties. However, it has also some major disadvantages, such as high oxygen transmission rate, poor grease resistance, and poor adhesion to other substrates. Because of these disadvantages, PE, especially the low density PE (LDPE), is rarely used alone and is mostly used in combination with other substrates, which invariably requires the use of adhesives. The disadvantages of PE are due to its totally nonpolar structure; structural modification of PE may be helpful in improving some of the properties of PE and may enhance the utility and decrease the need for lamination of PE to expensive substrates such as polyester and nylon. Structural modification may also help to bring down the package cost and thus the product cost.

Though there are reports on the modification of PE in the literature, they are mostly concerned with improving adhesion,¹⁻⁴ and information on modification for barrier properties is largely unavailable. In this article, we report the results of our studies on the chemical modification of PE resin with maleic anhydride (MA) and *N*-phenylmaleimide (NPM) and the effect of the modification on the oxygen transmission rate (OTR) and grease resistance. Though MA and NPM have been used for improving the adhesion properties of PE, this is the first study

to our knowledge to report the effect of such modification on gas and water vapor transmission and grease resistance characteristics.

MATERIALS AND METHODS

All solvents used in the experiments were purified by distillation before use. Benzoyl peroxide (BP) and maleic anhydride (MA) were recrystallized from ethyl alcohol and chloroform or benzene, respectively, before use. One grade of LDPE resin ($d = 0.923$ g/cc) (Indian Petrochemicals Corp., Ltd., Vadodara, India) was used as received or was used in purified form. The purified resin was made by dissolving in toluene and reprecipitating with acetone, followed by Soxhlet extraction for 16 h with acetone.

N-Phenylmaleimide (NPM)

NPM was made by slightly modifying Baumgarten's method.⁵ Instead of diethyl ether, chloroform was used at room temperature to prepare the maleanilic acid, followed by cyclodehydration in a toluene and dimethylformamide mixture with *p*-TsOH as catalyst. The product was recrystallized from toluene, yield 48%, m.p. 89–90°C.

Casting of Films

Simple glass molds (15 × 15 cm) were designed and fabricated for the casting of films. For this, glass strips 15–17 cm long, 1 cm wide, and 0.2 cm thick were fixed with Araldite on the four sides of a flat, defect-free, clean, glass plate (17 × 17 cm) to give

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an effective working area of 15 × 15 cm (6 in. × 6 in.). For making films, a hot toluene solution of the polymer (1% w/v) was poured into the glass mold, preheated to about 115–120°C, and covered with a plate to control the rate of solvent evaporation. After the complete evaporation of the solvent (about 2.5–3 h), the mold was quenched at ambient temperature. Films of excellent clarity and uniform thickness could be obtained. Such films were used for further measurements. Infrared spectra for polymers were measured on films with JASCO grating spectrometer.

Determination of Physico-Chemical Properties

All physico-chemical properties were determined on cast films. Tensile strength and elongation were determined as per ASTM D-882-83⁶ and are the average of 15 determinations. Water vapor transmission rate (WVTR) of the film was determined as per ASTM E-96-80.⁷ The OTR of the films was determined as per ASTM 1434-66⁸ and the results are the average of 3 determinations. Grease resistance⁹ for the films was done as follows. Pouches, 6 × 10 cm in size, were made and were filled with groundnut oil colored with 1% Sudan Red dye, sealed, and placed over a white sheet of paper at 40°C in an oven. The pouches were periodically checked for any oil seepage and when red spots appeared on the paper, the experiment was terminated. The time was noted and expressed in days. The results are presented in Table III.

Determination of Degree of Substitution

The extent of modification was determined by IR by measuring the absorbance of the C=O peak and comparing it with the C=O absorbance of the model compound.¹⁰ For this, a solution of known concentration of MA or NPM (model compound) in chloroform was prepared and the absorbance of the C=O peak (1700–1800 cm⁻¹) was measured in 0.1 mm liquid cell. The IR spectrum of the modified film of known thickness was determined. The degree of substitution (DS) (% w/w) was calculated from a slightly modified formula of Haslam and Willis¹¹

$$DS = \{A_p \times C_m\} / \{A_m \times t_p \times d_p \times 1000\}$$

where, A_p = Absorbance of the polymer film of thickness t_p (cm),

A_m = Absorbance of model compound (NPM or MA),

C_m = Concentration of the model compound (g/L) (MA or NPM), and

d_p = density of the polymer.

The results are shown in Tables I and II.

Reaction of LDPE with NPM or MA

In a 2-necked, 1-liter, round-bottom flask, fitted with a condenser and a mechanical stirrer, LDPE resin was dissolved in xylene or CCl₄ at refluxing temperature to obtain a 10% solution (w/v). After

Table I Preparation of Maleated PE (MPE)^a

Code	Feed (% w/w)		Solvent	Reaction Time (h)	Degree of Substitution (% w/w)
	MA	BP			
MPE-1 ^b	5	5	CCl ₄	6	0.67
MPE-2 ^c	5	5	CCl ₄	6	0.69
MPE-3	3	2	Xylene	1	0.27
MPE-4	3	2	Xylene	3	0.35
MPE-5	3	2	Xylene	5	0.40
MPE-6	3	2	Xylene	6	0.45
MPE-7	3	2	Xylene	8	0.45
MPE-8	3	2	Xylene	24	0.47
MPE-9	3.5	2	CCl ₄	5.5	0.42
MPE-10	5	2	CCl ₄	2	0.22
MPE-11	5	2	CCl ₄	3.5	0.55
MPE-12	10	2	CCl ₄	6	1.13
MPE-13	15	2	CCl ₄	6	1.67

^a PE = 100 parts; Solvent quantity = 1000 mL.

^b Purified PE.

^c Unpurified PE.

Table II PE Modified with NPM (NPE)^a

Code	NPM % (w/w) in Feed	Solvent	Degree of Substitution (% w/w)
NPE-1	1	Xylene	0.25
NPE-2	5	Xylene	0.27
NPE-3	10	Xylene	0.52
NPE-4	10	CCl ₄	0.97

^a PE = 100 parts; BP = 2 parts; Reaction time = 6 h; Solvent quantity = 1000 mL.

complete solution, a known amount of NPM or MA and BP were added and refluxed with stirring for an additional 6 h. Heating was stopped and the contents were transferred to a beaker and were allowed to cool to room temperature, during which time precipitation of PE occurred. Acetone (2–3 times) was slowly added with stirring and the contents were allowed to stand. The polymer was collected by filtration, and was washed with a fresh quantity of acetone (150 mL × 5). The product was reprecipitated 2 more times from xylene or CCl₄ solutions with acetone. The product was further subjected to Soxhlet extraction for 8 h with acetone and dried *in vacuo*. By this method, the polymer could be obtained as a fine powder.

RESULTS AND DISCUSSION

Useful properties of polymers can be attributed to their unique structural features. Structural features, such as the presence or absence of intermolecular attractions or rigidity in the molecule, seem to dictate the physico-chemical properties and the ultimate utility of the polymer. An understanding of the structure–property relationship is a powerful tool for designing polymers with special properties. As mentioned earlier, chemical modification of readily available polymers offers an attractive route to the improvement of some of the inherent characteristics, or to the creation of new ones.

The aim of the work reported in this article was to modify chemically LDPE in order to decrease OTR and to improve grease resistance without adversely affecting its excellent mechanical properties and moisture resistance.

There have already been attempts to surface modify PE films by treatment with oleum,¹² chromic acid,¹³ SO₃,¹⁴ etc. There are reports on the modification of PE by irradiation followed by reactions with functional compounds. Similarly, PE resins are

modified by reacting with carbonyl functional unsaturated compounds.^{1–3} The treatment of PE film with oleum and SO₃¹⁴ is done to decrease the OTR. Most of the studies on PE resins seem to be mostly concerned with the improvement of impact strength¹⁵ and adhesion properties.^{1–4} In this work, the goal was to improve the barrier properties and grease resistance by employing LDPE granules in solution by reaction with unsaturated functional compounds. The compounds employed were MA and NPM. The LDPE granules were reacted with varying amounts of the compounds. Solvents, such as *n*-heptane, toluene, xylene, and CCl₄, were used as media for reaction. Among the solvents used, CCl₄ was found to be the best, followed by xylene, in modifying the polymer. The *n*-heptane and toluene solvents were found to be ineffective for modification reactions. Hence, in our work, we have employed xylene and CCl₄ as solvents.

The preliminary work involved reacting LDPE with MA in the presence of BP (initiator). The reaction was carried out for various intervals of time, namely 1, 3, 5, 6, 8, and 24 h. The extent of modification increased with time up to 6 h and, after that, it was almost constant. Therefore, in our further experiments with NPM, we fixed the reaction time at 6 h. Accordingly, LDPE was reacted with varying amounts (1%, 5%, and 10%) of NPM in the presence of 2% BP for 6 h.

Both purified and unpurified LDPE resin were used for the reaction to see the effect of purification (for example, MPE-1: purified resin, and MPE-2: unpurified resin). It was found that the commercially available, virgin LDPE could be chemically modified with equal effectiveness. Hence, in our work, we have used commercially available LDPE resin.

The IR spectra of PE modified with NPM and MA are shown in Figures 1 and 2, respectively.

The presence of the bands at 1710, 1778, and at 1170 cm⁻¹ in the IR spectrum of the NPEs (i.e., modified with NPM) and the bands at 1785, 1860, and 1070 cm⁻¹ in the IR spectrum of MPEs (i.e., modified with MA) confirm the chemical modification of LDPE with NPM or MA. The absence of the peak at 1596 cm⁻¹ or the one at 1600 cm⁻¹ in the IR spectrum of NPEs or MPEs, respectively, indicates that NPM or MA is covalently linked to the backbone through its C=C bond forming *N*-phenylsuccinimide (NPS) or succinic anhydride (SA) group on PE.

Some important peaks in the IR spectra of MA and NPM are: 1778 and 1713 cm⁻¹ (NPM)¹⁶ or 1850 and 1784 cm⁻¹ (MA),¹⁷ due to stretching vibrations of the C=O; 3100 cm⁻¹ (NPM) or 3130 cm⁻¹ (MA),

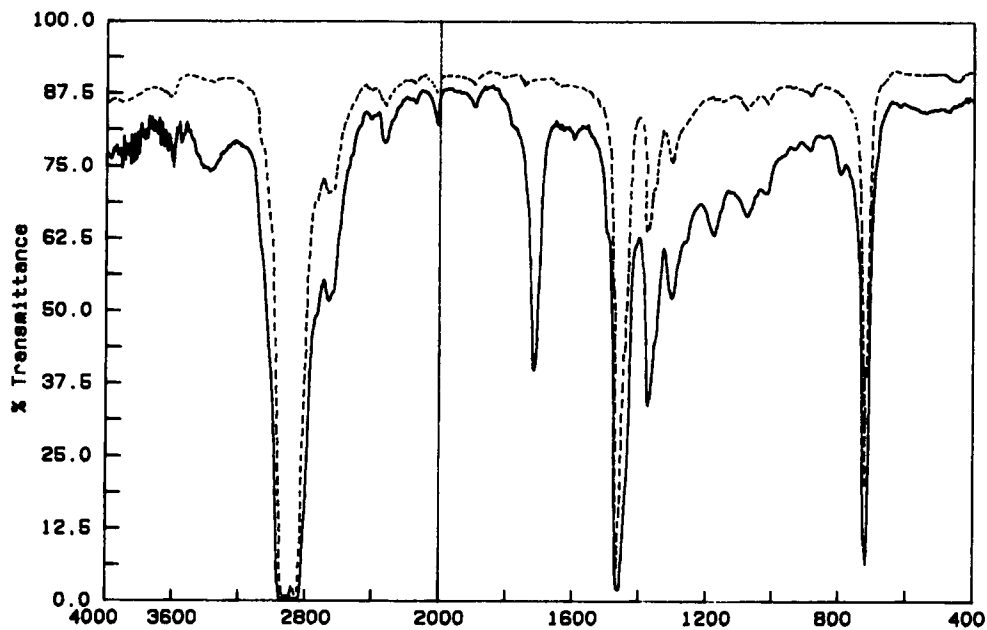


Figure 1 IR spectra of PEs modified by *N*-phenylmaleimide: (—) Modified PE; (-----) Virgin PE.

due to the stretching vibration of $-C=C-H$; and 1596 cm^{-1} (NPM) or 1600 cm^{-1} (MA), due to the stretching vibration of $-C=C$ in conjugation with $C=O$; 1164 and 1150 cm^{-1} are due to $C-N-C$ stretching vibrations in the IR spectrum of NPM,¹⁵ and the band at 1060 cm^{-1} is typical of 5-membered anhydrides.¹⁶

As far as the structure of modified PE is concerned, there are two possibilities. Either the NPM or MA may react with PE as single unit by forming NPS or SA derivative, or they may form graft copolymers of short branches with PE.

It is known that MA can homopolymerize only under very vigorous conditions.¹⁷ The reactivity of

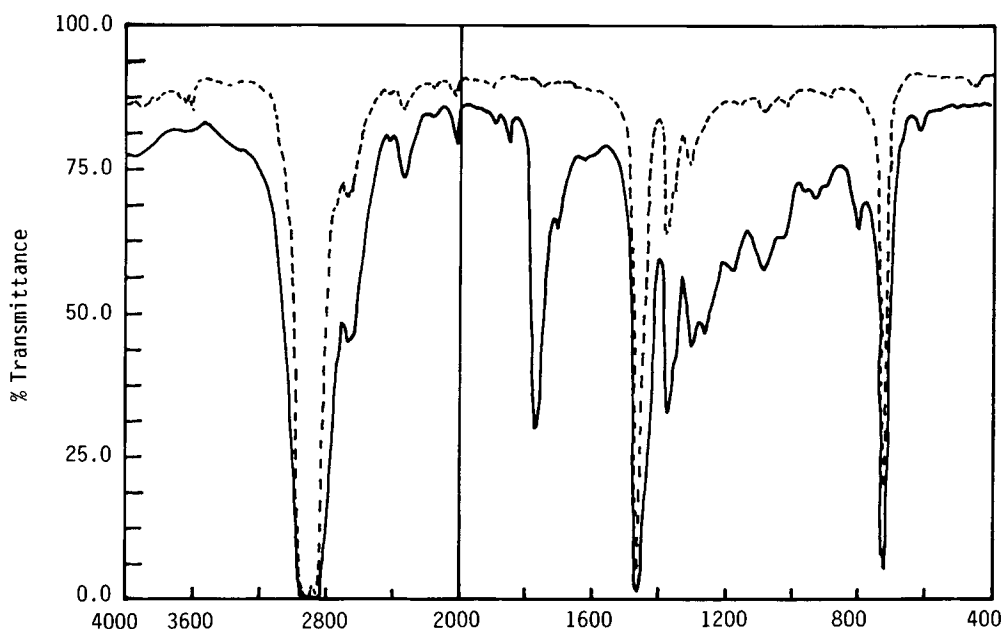
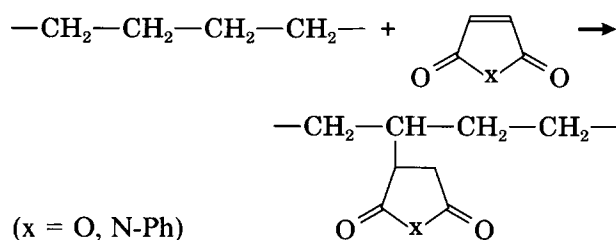


Figure 2 IR spectra of PEs modified by Maleic anhydride: (—) Modified PE; (-----) Virgin PE.

NPM may also be thought to be similar to that of MA, considering the environment around the C=C double bond. Moreover, such vigorous conditions are not employed in this work; therefore, the chances for the formation of a graft copolymer of NPM or MA may be remote. The absence of peak at 3300 cm^{-1} or at 3130 cm^{-1} [present in the IR spectrum of poly(NPM) or poly(MA) respectively] in the IR spectrum of NPE or MPE also seems to support the assumption that long branches of NPM or MA are formed with difficulty on PE backbone. Therefore, it may be assumed that the NPM or MA is attached to the PE chain as a single unit to give corresponding NPS or SA derivatives. Thus, the assumed structure of modified PE may be as follows:



This was also confirmed by separately reacting NPM (0.029 mol) or MA (0.5 mol) with BP (0.0047 mol) in xylene for 6 h in the absence of LDPE. No acetone-insoluble compound was found, indicating that the NPM or MA do not form corresponding homopolymers under the conditions employed in the present experiments; thus the modified PE is free from impurities from poly(NPM) or poly(MA).

The NPM or MA content in the polymer increased with its increasing amount in the feed. Thus the NPM content in the polymer was 0.25% (NPE-1), 0.27% (NPE-2), 0.52% (NPE-3), and 0.97%

(NPE-4) (w/w) for the feed NPM amount of 1%, 5%, 10%, and 10% (w/w), respectively. The CCl_4 was more effective for modification in the case of NPEs. Similarly, the MA content in the polymer ranged from 0.27% (MPE-3) to 0.47% (MPE-8) for one grade of PE when xylene was used as the solvent, and the MA content ranged from 0.22% (MPE-10) to 1.67% (MPE-12) when CCl_4 was employed as solvent. No definite conclusion can be drawn on solvent effect in the case of MPEs. The MA content in purified (MPE-1) and unpurified PE (MPE-2) was 0.67% and 0.65%, respectively.

Physico-chemical properties of the modified materials, such as tensile strength, elongation, grease resistance, WVTR, and OTR measured in comparison with the unmodified film are, shown in Table III.

The tensile strength and elongation for MPE and NPE do not seem to be affected by modification and were comparable with that of the unmodified PE. The WVTR values were also not significantly different from that of the unmodified PE. Thus, if the WVTR for PE modified with NPM in xylene was $21 \pm 1\text{ g/m}^2$, the one for PE modified with NPM in CCl_4 (NPE-4) was 18 g/m^2 . The WVTR for MPE-11 was 20 g/m^2 when compared with the WVTR for unmodified PE, which was 20 g/m^2 under same conditions. It appears from the results that the slight polarity conferred on PE does not affect the properties of PE adversely.

However, the effect of modification was significant in increasing the grease resistance and decreasing the OTR. The grease resistance for NPE was 12–18 days and that for MPE was 21 days as compared with 9 days for the unmodified PE at 40°C . Also, the grease resistance of NPE increased with the increasing NPM content in the polymer.

Table III Physico-chemical Properties of Modified PE

Code	Tensile Strength (MPa)	Elongation (%)	WVTR ^a	OTR ^b	Grease Resistance (days)
MPE-11	8.0	> 600	20	10,500	21
NPE-1	7.9	> 600	20 + 1	10,500	12
NPE-2	8.6	> 600	21 + 1	9630	14
NPE-3	7.9	> 600	22	9380	15
NPE-4	7.2	> 400	18	8700	18
VPE ^c	7.4	> 600	19	14,000	9

^a $\text{g}/(\text{m}^2 \cdot 24\text{ h})$ at 38°C and 90% RH gradient for film thickness of 0.0025 cm.

^b $\text{cc}/(\text{m}^2 \cdot 24\text{ h} \cdot 1\text{ atm.})$ at 27°C for film thickness of 0.0025 cm.

^c Virgin polyethylene.

As can be seen in Table III, there is a significant improvement in gas barrier properties (i.e., a decrease in OTR). The OTR for MPE-11 was reduced by 25% while the OTR for NPE decreased with increasing NPM content in the polymer. The minimum reduction in OTR was 25% at an NPM content of 0.25% (NPE-1), and the maximum reduction in OTR was about 37% at an NPM content of 0.97%. Thus it can be seen that, though the degree of substitution is as low as 0.97%, the modification is effective in bringing about the necessary improvement in the barrier properties.

Regarding the effect on heat sealing characteristics by modification, MPE and NPE need relatively higher temperatures for heat sealing (450°F, 2 s, 30 psi) as compared to the heat sealing temperature of virgin PE (350°F, 0.5 s, 20 psi). This increase may be due to partial rigidity in the structure because of conferred polarity. Further studies are necessary in this area.

CONCLUSION

LDPE can be effectively modified with NPM or MA even at low degrees of substitution (0.97% or 0.55%, respectively). Though this level of substitution is too low to affect adversely the other essential characteristics of the LDPE, it is, however, sufficient to bring about significant reduction in OTR and some improvement in grease resistance.

REFERENCES

1. S. Urawa, K. Nagato, and N. Yamaguchi, *Jpn. Kokai Tokkyo Koho*, JP 61-276808 (86-276808) (1986); *CA*, **107**, 40613m (1987).
2. C. Bergstrom and T. Palmgre, *Eur. Pat. Appl. EP*, **247**, 877 (1987); *CA*, **108**, 151503r (1988).
3. S. Urawa, K. Nagano, and N. Yamaguchi, *Jpn. Kokai Tokkyo Koho*, JP 62-57442 (87-57442) (1987); *CA*, **107**, 24508a (1987).
4. T. Okano, K. Hayasi, Y. Sakurazawa, and S. Suga, *Jpn. Kokai Tokkyo Koho*, JP 62-10107 (87-10107) (1987); *CA*, **107**, 59731v (1987).
5. H.E. Baumgarten, *Organic Synthesis*, **5**, 944 (1973).
6. ASTM Standard D882-1983, 1983 Book of ASTM Standards.
7. ASTM Standard E96-1980, 1986 Book of ASTM Standards.
8. ASTM Standard D1434-1966, 1966 Book of ASTM Standards, Part 27.
9. B. Raj, A. R. Indiramma, and N. Balasubramanyam, *Symposium on Recent development in Food Packaging*, Mysore (India), Jan. 17-18, 1985.
10. *Standard Method of Chemical Analysis*, 6th Ed., Vol. 3, Part B, F. J. Welcher, Ed., Van Nostrand, NJ, 1966, pp. 1170, 1612.
11. *Identification and Analysis of Plastics*, J. Haslam and H. A. Willis, Eds., Iliffe, London, 1967, p. 164.
12. B. Raj and R. A. N. Murthy, Unpublished work.
13. V. P. Pilnikov, L. N. Maskaeva, G. A. Kitaev, and V. A. Lisovaya, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*, **19**(7), 1093 (1976); *CA*, **85**, 144190q (1976).
14. N. D. Pintauro, In *Food Packaging*, Food Technology Review No. 47, Noyes Data Corporation, NJ, 1978, p. 220.
15. T. Abe and K. Kudo, *Jpn. Kokai*, **76**, 96872 (1975); *CA*, **85**, 161444t (1976).
16. I. M. B. Rienda and J. G. Ramos, *J. Polym. Sci. Symp.*, **42**, 1249 (1973).
17. S. G. Joshi and A. A. Natu, *Die Angew. Makromol. Chemie.*, **140**, 99 (1986).

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