

Dynamic Mechanical Properties of Methacrylic-Acid-Grafted Polyethylene Films

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Synopsis

A dynamical mechanical relaxation study has been made of low density polyethylene films to which methacrylic acid has been grafted by γ irradiation. The grafted films retain the original degree of crystallinity and show only slight changes in melting points and melt viscosities. This indicates that the grafted methacrylic acid side chains are long, few in number, and completely phase separated from the polyethylene matrix. Three dispersion regions are observed in plots of the loss modulus, E'' vs. temperature at constant frequency and these are labeled γ , β , α' , in order of increasing temperature. The α' peak, above 215°C, was assigned to microbrownian segmental motions accompanying the T_g of polymethacrylic acid. The β peak, at -20°C, was assigned to motions accompanying the T_g of branched polyethylene, and the γ peak, at -120°C, was assigned to local motions of a few CH_2 sequences in polyethylene.

INTRODUCTION

Acrylic- or methacrylic-acid-grafted polyethylene films have been used as separating membranes for alkaline batteries and as ion exchange membranes.¹ The differences in properties between such grafted polyethylene films and ethylene-acrylic or methacrylic acid copolymers have been studied extensively.² Among the most striking differences are the retention of the original degree of crystallinity and only slight changes in melting points and melt viscosities as a function of grafting whereas the copolymers show great differences in these parameters. This indicates that the grafted side chains are long, few in number, and completely phase separated from the polyethylene matrix.

We measured dynamic mechanical properties of methacrylic-acid-grafted low-density polyethylene, and observed two clearly separated peaks in the loss modulus E'' , one arising from the polyethylene phase and the other from the grafted methacrylic acid phase. It was reported in a previous paper² that separated loss peaks could not be observed in acrylic-acid-grafted high-density polyethylene because of the overlapping temperature range of peaks related to the T_g of polyacrylic acid and the crystalline polyethylene α relaxation.

EXPERIMENTAL

The low density polyethylene film utilized was 0.025 mm thick, a product of Dow Chemical with the tradename Ziploc.

The film was grafted with methacrylic acid as follows. It was immersed in a solution of methacrylic acid in methanol in a glass tube, (film 0.5 g, methacrylic acid 2 mL, methanol 18 mL). After the tube was purged of air, it was irradiated

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TABLE I
Reaction Conditions for the Preparation of the Graft Copolymers

Sample no.	1	2	3	4
Reaction time (h)	0.5	1.0	1.5	4.5
Radiation dose (Mrad)	0.1	0.2	0.3	0.95
Weight increase (%)	11	24	34	58
Methacrylic acid content (mol %)	3.5	7.3	9.5	15.8

with γ -rays from a ^{60}Co source at various doses. In the absence of irradiation, the polyethylene film absorbed none of the solution after immersion for 24 h. The irradiated films, on the other hand, absorbed about 6% of the solution regardless of the extent of grafting. This indicates that the grafting reaction is controlled by diffusion of monomer into the film and that this diffusion is enhanced considerably as soon as grafting is initiated. It has previously been shown that the composition of the solution absorbed in the film is virtually equal to that outside the film.¹

After grafting, the film was repeatedly refluxed in first methanol and then benzene. This alternative extraction procedure assures the thorough removal of homopolymer from the graft copolymer.² Table I summarizes the polymers prepared.

Dynamic mechanical measurements were carried out using a Vibron dynamic viscoelastometer at the frequency of 11 Hz.

The melting and crystallization point, and the heats of fusion were determined on a Perkin-Elmer DSC 2 Differential Scanning Calorimeter (DSC) at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The values of crystallinity, melting point, and crystallization point of the methacrylic acid grafted low density polyethylene are shown in Table II.

In agreement with other work on grafted polyethylene,³ the crystallinity decreased much less than it does for copolymers of comparable methacrylic acid content. The crystallinity was determined by DSC measurements assuming the heat of fusion in branched polyethylene with a melting point of 109°C to be 47.0 cal/g. The corrected crystallinity was calculated from the relation $(1 - \omega)^{-1} = 1 + (G/100)$, where G is the grafting yield to compare the crystallinities of the

TABLE II
Calorimetric Results on the Graft Copolymers

Sample no.	0	1	2	3	4
MA content (%)	0	3.5	7.3	9.5	15.8
Melting point (°C)	109	108	107	107	107
Crystallization point (°C)	96	95	94	93	91
Heat of fusion (cal/g)	17.4	14.1	14.2	12.1	9.1
Crystallinity (%)	37	30	30	26	19
Corrected crystallinity (%)	37	33	37	34	31
Relative crystallinity	1.00	0.90	1.01	0.93	0.83

TABLE III
 Dynamic Mechanical Relaxation in the Graft Copolymers

Sample no.	0	1	2	3	4
γ ($^{\circ}\text{C}$)	-132	-128	-128	-130	-130
β ($^{\circ}\text{C}$)	-20	-17	-8	-7	-5
α ($^{\circ}\text{C}$)	35	35			
	(shoulder)	(shoulder)			
α' ($^{\circ}\text{C}$)	—	—	>215	>215	>215

polyethylene phases and to eliminate the amorphous grafted polymethacrylic acid side chain.

The retention of crystallinity suggests that the methacrylic acid grafting took place mainly in the amorphous regions of the polyethylene.

The results of dynamic mechanical measurements are shown in Table III and Figure 1.

Three dispersion regions were observed in E'' for the 0 and 3.5 mol % methacrylic-acid-containing samples, and they were labeled γ , β , α in increasing order of temperature. Three dispersion regions were also observed for the 7.3, 9.5, and 15.8 mol % methacrylic-acid-containing samples and these were labeled γ , β , α' in increasing order of temperature. The polyethylene α peak could not be detected clearly in the latter three samples, but the α' peak appeared above 215 $^{\circ}\text{C}$, and the magnitude of this peak increased with increasing graft content. The α' peak above 215 $^{\circ}\text{C}$ was assigned to motions accompanying the T_g of polymethacrylic acid.

The β peak was assigned to motions accompanying the T_g of branched polyethylene, and the position of this peak moved to slightly higher temperatures with increasing graft content, but did not change as much as in comparable random copolymers.⁴ This suggests that the grafted methacrylic acid side chains are better phase separated from the polyethylene than the acid side groups in the ethylene-methacrylic acid copolymers.^{5,6}

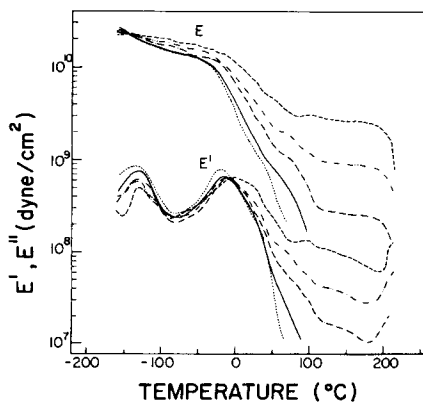


Fig. 1. Temperature dependence of E' and E'' for methacrylic-acid-grafted polyethylene samples at 11 Hz (mol %): (---) 15.8; (- · - · -) 9.5; (· · ·) 7.3; (—) 3.5; (---) 0.

The E'' values of the samples which have 7.3%, 9.5%, and 15.8% methacrylic acid content exhibit two clearly separated peaks, β and α' , again confirming the existence of the methacrylic acid in a separate phase.

The E' values of the samples of 7.3%, 9.5%, and 15.8% methacrylic acid contents exhibit plateaus between the β and α' relaxations, and the plateau value increases in magnitude with increasing graft content. Such results are typically found in the blending of two incompatible polymers.

The position of the γ peak was identical to the γ peak in low density polyethylene and independent of graft content. Therefore, this peak was assigned to local motions of a few CH_2 sequences.

When the initially transparent grafted polyethylene samples of 3.5, 7.3, and 9.5 mol % methacrylic acid content were heated to 90°C for 24 h, they became hazy and inhomogeneous. This result indicates that the grafted polymethacrylic acid is initially dispersed in the polyethylene as incompatible small particles and the particle size increases on heating which presumably decreased the viscosity of the amorphous polyethylene phase sufficiently to allow aggregation of the polymethacrylic acid phase.

The methacrylic-acid-grafted polyethylene films studied here all contained quantities of unreacted polyethylene. The grafted polymethacrylic acid side chains were phase-separated in the form of small particles in the amorphous regions of the polyethylene. This is the reason for the retention of crystallinity and the high stability and strength of the film.

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