Extraction of Low-Molecular-Weight Oligomers from Polyethylene Film Using Near-Critical Difluorodichloromethane

SHASHANK V. DHALEWADIKAR and MARK A. MCHUGH,* *Department of Chemical Engineering, The Johns Hopkins University, Baltimore, Maryland 21218* and TERRY L. GUCKES, *Exxon Chemical Company, Florham Park, New Jersey 07932*

INTRODUCTION

There is a great deal of interest in using near-critical and supercritical fluid solvents for processing polymers.[1] These unique solvents, which are described in detail elsewhere,[2,3] have been used for fractionating polymers based on the molecular weight (as the molecular weight increases, the solubility in the supercritical fluid decreases[2,4-7]), based on the tacticity of the polymer (generally, atactic polymers are more soluble in supercritical fluids than syndiotactic or isotactic polymers[2,8]), and based on the types of substituent groups attached to the polymer backbone; for example, poly(dimethyl) siloxane is more soluble in supercritical carbon dioxide than poly(phenylmethyl) siloxane of the same molecular weight.[2]

In this paper we report preliminary results on the use of near-critical difluorodichloromethane (Freon 12) for extracting low-molecular-weight oligomers from polyethylene film. Both linear low-density (LLDPE) and low-density (LDPE) polyethylene films are used in this study. Since liquid halocarbons at elevated temperatures, such as tetrachloroethane near 100°C, are generally good solvents for polyethylene film, we chose difluorodichloromethane ($T_c = 112.0°C$, $P_c = 597$ psia) as a representative near-critical solvent for these preliminary tests. Our objective in this short study is to demonstrate the potential of using supercritical fluids for processing or treating polymers.

EXPERIMENTAL

The experimental apparatus used in this study is described in detail elsewhere.[9] The major component of the experimental system is a high-pressure, variable-volume view cell. A piece of polymer film (approximately 20 g) is cut into small strips and is loaded into the view cell. Residual air is removed from the cell by flushing three times with approximately 50 psia of Freon 12. Approximately 30 g of liquid Freon 12 are then transferred into the cell. For the runs with both the LLDPE and LDPE films, the cell contents are pressurized to 2790 psia. Using differential scanning calorimetry (DSC), it was found that the LLDPE film used in this study exhibits a melting temperature

*To whom correspondence should be addressed

of 122°C upon heating and a solidification temperature of 105°C upon cooling. Similarly, the LDPE film exhibits a melting temperature of 111°C upon heating and a solidification temperature of 95°C upon cooling. Therefore, to avoid melting the film during the extraction, the cell temperature is maintained at 92.0 ± 0.1°C for the LLDPE film and at 80.0 ± 0.1°C for the LDPE film.

The system is held constant at these conditions for approximately 30 min with continuous stirring. At that point the stirrer is stopped and the Freon 12 is displaced from the cell into a tared test-tube held in a dry ice-acetone bath. The pressure in the cell is held constant to within ±25 psia by moving the cell piston forward while sampling. By controlling the flow rate of Freon 12 from the cell, it was possible to collect most, but not all, of the solid polymer dissolved in the freon. The extracted polymer precipitates as a white powder from the Freon as the pressure is reduced. The view cell is then cooled, and the dimensionally stable film is recovered from the cell. The original film, the treated film, and the extracted polymer are analyzed using gel permeation chromotography. No attempt is made to close a mass balance for these experiments since our objective is only to demonstrate the potential of using a near-critical or supercritical fluid for extracting low-molecular-weight oligomers from a polymer film.
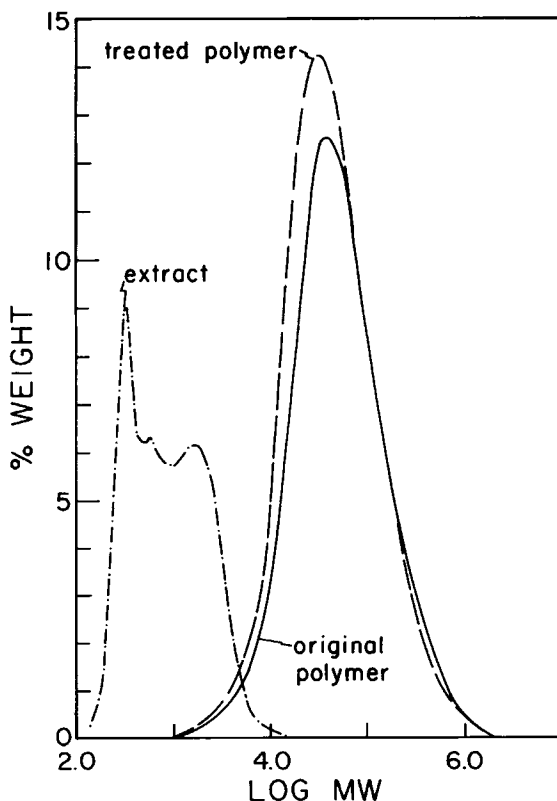

Fig. 1.   Molecular weight distribution curves for the original LLDPE film, the treated LLDPE film, and the extracted material.

RESULTS AND DISCUSSION

The molecular weight distribution (MWD) for the original LLDPE film, the treated LLDPE film, and the material extracted from the film are shown in Figure 1, and the similar MWD for the LDPE film are shown in Figure 2. The sharp peaks in the MWD curves for the extracts of both films correspond to the additives in the films (e.g., stabilizers and antioxidants), which have molecular weights typically in the range of 200–300. Not surprisingly, near-critical Freon 12 only extracts oligomers with a molecular weight up to about 8000. Also, the amount of extract represents only about 0.5 wt% of the original film. Since such a small amount of polymer is extracted and since no attempt is made to quantitatively recover all the extracted material, we do not find a major shift in the MWD curves of the original films. In both these experiments the polymer extracted from the film is recovered as a fine powder. This observation is consistent with those of Krukonis,[10] who finds that the particle size of complex compounds can be regulated by the manner in which they are recovered from a supercritical solution. Krukonis reports that solids that are difficult-to-comminute can be isothermally recrystallized from supercritical solution at moderate temperatures using the pressure-dependent solvent power of a supercritical fluid. We made no attempt to determine or optimize the
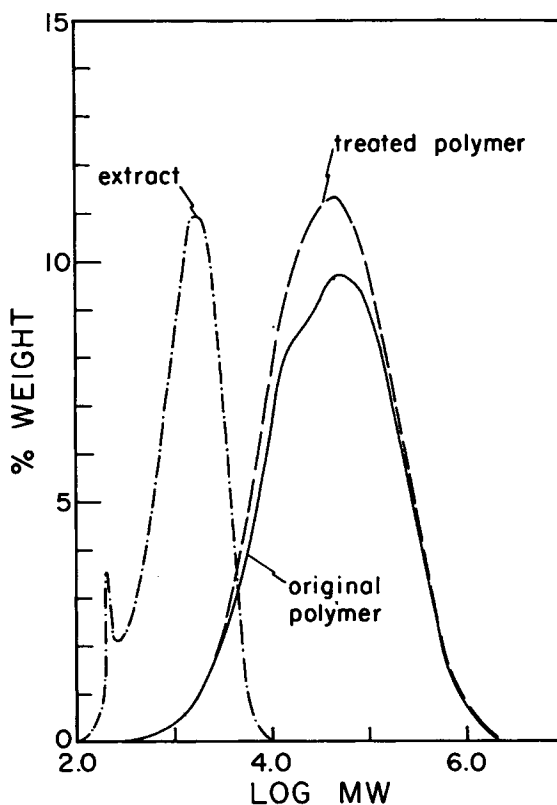

Fig. 2.   Molecular weight distribution curves for the original LDPE film, the treated LDPE film, and the extracted material.

particle size distribution of the recovered extract. The extracted films in this study did not exhibit any dimensional changes. In some tests, however, the films did exhibit a slight haze after being extracted.

CONCLUSION

The results in this short study show that difluorodichloromethane at near-critical conditions can solubilize low-molecular-weight oligomers of polyethylene up to a molecular weight of about 8000. During the extraction process, the physical dimensions of the film remain essentially unchanged. Thus, this process should be applicable for removing low-molecular-weight impurities from films without changing their dimensional integrity. It should be noted, however, that since film additives are also removed from the film, the long-term stability of the film is affected.

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