Influence of Low Magnetic Fields on Semicrystalline Polymers

INTRODUCTION

Magnetic and electric fields have been used to bring about changes in polymer systems in two separate areas. The first is an observed ordering effect in liquid crystalline polymers, and the second area has been concerned with induced changes in the mechanical response of epoxy resins and polyolefins.

For liquid crystalline polymers, the rate of polymerization in a magnetic field shows an increase with increasing magnetic field strength.[1] Thin films of liquid crystalline polymer cast in a magnetic field also show changes in orientation over those cast in the absence of fields.[2,3] With increasing field strength,[4] an electric field brings about the transformation of a spherulitic structure to a rodlike structure. Recent literature has suggested that for filled epoxy resins an increase in physicomechanical properties is observed when these materials are cured in a constant magnetic field.[5] Improved properties are also said to be observed for epoxy resins crosslinked in a magnetic field.[6] Other literature[7–10] has reported that polyethylene, crystallized under a constant magnetic field (3000 Oe), yields materials with an increased tensile strength and microhardness and, for HDPE, a decrease in relative elongation.[9,10] For both HDPE and LDPE formed under pressure at 175–180°C, a twofold increase in tensile strength was reported.[8] This paper is a report of our attempts to utilize the claims by other authors that a low-strength magnetic field brings about a change in the mechanical properties of polyethylene. The present study is an investigation of the effect of a magnetic field on the mechanical properties of extruded polyethylene specimens.

Generally, it is assumed that when a polymer is extruded through a die, the chains are oriented parallel to the fiber direction. On emerging from the die, a phenomenon called die swell occurs. The chains revert from a more or less extended chain conformation (in the die), to a more random organization. This process continues until the melt cools enough to crystallize (for semicrystalline polymers). At that time more complex morphological changes can occur.

A number of attempts have been made to maintain (or reintroduce) the high orientation that the chains had in the die. The first of these methods involves pulling the melt as it emerges from the die. The fibers are taken up on a roller, at a high rate, maintaining tension on the melt. A second process similar to the first is to produce highly oriented fibers by hot, slow drawing of conventional fibers[11–13] at a temperature below the melting point of the polymer. A third process, which is slower than the above, consists of extruding polymers at high pressures, at or near their melting points.[14–16] This process is claimed to lead to extended chain crystal formation, for at least part of the sample. All of the above procedures are aimed at maintaining or reintroducing high chain orientation. Given that magnetic fields are capable of controlling or changing molecular organizations, one might postulate that the appropriate field should keep a chain or bundle of chains aligned after they exit the die. When cooled to the point of crystallization, the aligned chains should crystallize while maintaining their orientation.

In an effort to calculate the field strength required to maintain total orientation, we have assumed that this would be equivalent to the magnetic field strength required to prevent die swell. This field strength has been calculated using the volume susceptibilities of polyethylene and the radial pressure associated with a polymer melt as it emerges from an extrusion die. The value of the magnetic field required to totally overcome die swell from these calculations is very large. At this time there is no known method of producing fields of such a magnitude. Knowing this, it would appear that any effort to influence molecular organization using accessible magnetic fields would be doomed to fail. However, there exist reports[8–10] in which quite low fields have been used to modify polymer properties. Apparently small fields can be used to alter properties of polymers. These observations have led us to attempt to modify the mechanical properties of extruded polyethylene specimens using a magnetic field of approximately 10,000 G.

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EXPERIMENTAL

Polyethylene (Marlex 6001) was charged into the barrel of an Instron Capillary Rheometer, Model 3211, which had been heated to 170°C. The polymer was firmly packed to remove any trapped air. A plunger was used to force the polymer through a capillary of diameter 0.0302 in.; the shear rate was approximately 500 s^{-1}.

The polymer melt was extruded directly into air at room temperature. Four different sample preparations were used. One sample set is made by allowing the extruded polymer fiber to "air cool" without passing through a magnetic field (samples are designated AC). Two sample sets were produced by applying a magnetic field to the extrudate after it exited the capillary. The fiber traveled 0.6 cm in air and then passed between two magnets that were 0.6 cm apart and had an approximate field strength of 10,000 G. The magnets had a surface area of 6.45 cm^2 and were aligned so that the poles and the lines of force repelled one another in one case (MR samples) and attracted one another in the second case (MA samples). The final sample set was produced by using a set of aluminum blanks that had the same surface area as the magnets (AB samples). This latter experiment was introduced in order to see if any of the results obtained were due to thermal gradients created by the presence of the magnets and not due to the magnetic fields themselves.

An Instron universal testing system (Model TM-S) was used to study the initial modulus, tensile strength at yield, drawing stress, and elongation at yield of the separate sample sets. Table I indicates the parameters used for testing.

TABLE I
Parameters Used for Instron Tensile Testing

	Drawing stress	Initial modulus	Tensile stress at yield	Elongation to yield
Full load (kg)	2	10	10	10
Chart speed (cm/min)	100	100	100	100
Crosshead speed (cm/min)	1	5	5	5
Grip length (cm)	2	1	1	1

RESULTS AND DISCUSSION

Thirty samples were prepared under identical conditions for each of the four separate treatments. Each sample was tested on the Instron system and values of initial modulus, tensile strength (stress), elongation at yield, and drawing strength (stress) were obtained. Using standard statistical methods, the sample means for the separate treatments were calculated. The values of these means and associated standard deviations appear in Table II.

TABLE II
Statistical Means and Associated Standard Deviations for Separate Sample Sets

Treatment	MR	MA	AB	AC
Modulus (psi)	158,400	155,400	142,400	128,300
σ	24,000	19,100	14,900	17,500
Yield strength (psi)	4062	3972	4074	4167
σ	138	150	152	175
Elongation to yield (psi)	12.8	13.4	12.1	12.5
σ	1.2	0.9	1.3	1.4
Draw strength (psi)	3269	3239	3252	3317
σ	74	124	68	353

Based on the observed means and standard deviations, it is difficult to discern any major differences between the various treatments. However, there are a number of statistical methods which can be used to indicate similarities or differences between sample means. We have applied two methods to the data sets. The first method uses pooled standard deviations of all 120 samples (of one test) to establish an individual 95% confidence interval for each of the four separate treatment means. The second method is the standard Student t test. Briefly the t test is used to determine, with significance level = 0.05, whether the samples have come from normal distributions with the same mean. For example, we test the hypothesis H_0, that the mean of sample AB is equal to the mean of sample AC, and all other pairwise combinations of the four treatments.

An analysis of both the 95% pooled interval and the t test leads to essentially the same conclusions for the four treatments and four tests. If we deal first with modulus data, we could not reject H_0 for MA and MR samples, i.e., the hypothesis that both means are from the same normal distribution could not be disproved. In contrast, we can reject H_0 for either of the magnetic samples compared with AB or AC samples. We also reject H_0 for AB vs. AC samples. Similar conclusions hold for the tensile strength at yield data.

For elongation to yield data, H_0 cannot be rejected for MA vs. MR or for AB vs. AC samples. However, H_0 is rejected for either MA or MR vs. AB or AC. With regard to draw strength data, H_0 cannot be rejected for any pair of samples.

In general, for all tests we can see no difference between samples prepared in attractive or repulsive fields. If field affects crystallization, then, since PE is weakly diamagnetic, we would expect to see different effects as a result of the two different types of field.

Three of the four tests do show significant differences between samples formed in a field and those formed in the absence of a field. In two of these three tests we also have significant differences between AB and AC samples. If the differences between magnetic field samples and no field samples were solely due to the absence of field, then no difference is anticipated between AB and AC samples. Presumably then, some part of difference is due to the presence or absence of the metal itself rather than just the field.

In an ideal case one would like to be able to turn a field on or off and maintain all other conditions constant. In this case we were using permanent magnets and such experiments were not possible. However, we did match the overall shape of the magnets. Further thermal conductivity of the magnets and the aluminum blanks differed by a factor of only 2.5. In contrast the difference between metal and air is a factor of approximately 10,000. Note that, even though heat transfer presumably plays a role, one can clearly identify differences between samples prepared in a field and those out of the field.

CONCLUSIONS

The data indicates that the low field strength used has an effect on the fibers produced. This effect is not entirely due to the magnetic field, but includes a component due to possible changes in heat transfer properties in the presence of metal blocks. However, one can clearly demonstrate the separation of magnetic field effects and heat transfer effects for changes in modulus, tensile strength at yield, and elongation to yield. Further work is planned to determine if the trends observed for polyethylene are seen in other polyolefins. The use of higher field strengths would presumably enhance these effects.

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