Influence of the Controlled Rheology Process (Vis-Breaking) on Additive Effectiveness in Polypropylene

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SYNOPSIS

Controlled rheology or VIS-breaking is the process whereby polypropylene, peroxide, and other additives such as stabilizers are extruded to simultaneously shorten polymer chain length by chemical action of the peroxide and to blend in additives. Although the influence of additives on the VIS-breaking process has been studied, little attention has been paid to the role of additives present during VIS-breaking on the final resin properties. The effectiveness of a light mineral oil used as a costabilizer for radiation resistance and Irgafos 168 as a melt stabilizer was determined in polypropylene resins prepared with different peroxide levels. It was found that exposure of Irgafos 168 to peroxide during the VIS-breaking process did not hinder the action of Irgafos 168 as a melt stabilizer during injection molding. At low levels of peroxide, the presence of oil led to an improvement of radiation resistance compared to resins that contained no oil. However, at higher peroxide levels, oil-containing resins showed less resistance to radiation than did those without oil. These results were interpreted as an interaction of peroxide with the function of oil in the final resins. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Modification of the molecular structure of polypropylene after polymerization by the action of peroxide-generated radicals is known as *controlled rheology, VIS* (for viscosity) *cracking,* or *VIS-breaking.* The process involves the dry blending of an appropriate peroxide with stabilizers and other additives with the as-polymerized polypropylene. When the composite is melt-extruded, the peroxide thermally decomposes to produce radicals that attack the polymeric chains. Statistically, the larger molecular weight chains are cleaved more frequently than are lower molecular weight molecules, resulting in the overall effect of a decrease in the average molecular weight and a narrowing of the molecular weight distribution.[1] In terms of processability, this *VIS-broken* polypropylene has a higher melt flow index (MFI) (lower viscosity), is less elastic, and is therefore easier to process than the original resin. Other advantages include less shear sensitivity, a wider processing window obtainable, less part warpage, and better physical properties such as tensile elongation, heat-deflection temperature, clarity, gloss, and tolerance to high-energy radiation.[1-5]

Past studies have determined the influences of additives on the VIS-breaking process[4] but have not focused on how the VIS-breaking process affects additive performance in the development of the final polymer properties. This study was undertaken to determine if peroxide interacts with other additives during the VIS-breaking process and to ascertain the additive effectiveness in the final application.

EXPERIMENTAL

Experimental Design

The experimental problem, to assess the influence of the VIS-breaking process on the effectiveness of additives in polypropylene, was particularly suited to the use of statistical experimental design. The principles of experimental design indicated a $2 \times 2 \times 2$ matrix was required to measure the possibility

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Journal of Applied Polymer Science, Vol. 52, 905-915 (1994)
 CCC 0021-8995/94/070905-11

of interactions between three factors. The interactions of interest were between peroxide used in the VIS-breaking process and Irgafos 168 as a thermal melt stabilizer and between peroxide and oil, a costabilizer for radiation resistance. The design matrix was expanded to include three levels of peroxide in order to determine any nonlinearity of the response as a function of peroxide. This resulted in a 3 × 2 × 2 factorial design matrix (Table I). This design allowed the simultaneous measurement of the effects of several variables with relatively few experimental runs.

Polypropylene resins were graciously prepared by Himont, Inc. Specifically, three peroxide levels were chosen to produce resins with melt flow indices (MFI) between approximately 10 and 40 g/10 min. Oil and Irgafos 168 (I168, an in-process thermal stabilizer), when present, were at concentrations typical of commercial resins used in injection-molding manufacturing. The combinations and amounts of additives were established by statistical experimental design (Table I). Peroxide was set at three levels, 10, 18, and 26 g/50 lb polypropylene flake (initial MFI = 0.5 g/10 min). Oil and/or I168 were either absent or present at levels typical for injection-molding resins. Other additives were only sodium stearate as an antacid and a hindered amine light stabilizer. The resins were extruded in a $3\frac{1}{2}$ in. compounding extruder at 70 rpm with die temperature measured at 232°C. The conditions of the extrusion/blending process were held constant for the preparation of all 12 resins.

Table I The 3 × 2 × 2 Factorial Design Coded Levels of Variables for Formulation of VIS-Broken Polypropylenes

Resin No.	Coded Levels[a]		
	Peroxide	Oil	I168
1	−1	−1	−1
2	−1	+1	−1
3	−1	+1	+1
4	−1	−1	+1
5	0	−1	−1
6	0	+1	−1
7	0	+1	+1
8	0	−1	+1
9	+1	−1	−1
10	+1	+1	−1
11	+1	+1	+1
12	+1	−1	+1

[a] Peroxide: 10 g/50 lb, −1; 18 g/50 lb, 0; 26 g/50 lb, +1. Oil, I168: absent (0%), −1; present (0.1% I168, 4.7% oil), +1.

Injection-molded syringes and injection-molded tensile bars were used as test specimens. Syringes (20 cc size) were injection-molded in a 16-cavity hot-runner mold to simulated the heat history seen by a typical polypropylene resin in a production situation. Extruder barrel temperature was set at 220, 238, or 254°C, while the hot-runner manifold was fixed at 260°C. Other conditions were unchanged. The MFI of syringe parts was compared to the MFI of starting pellets to measure the effectiveness of I168 as an in-process thermal melt stabilizer. MFIs were determined according to ASTM-D1238 at 230°C.

The effectiveness of oil as a costabilizer with a hindered amine light stabilizer for radiation resistance was monitored by the change in tensile properties of nonirradiated and irradiated tensile bars. Type V tensile bars were injection-molded at identical machine conditions (maximum temperature exposure was 220°C), sterilized by ^{60}Co irradiation at 0.5 Mrad/h, and tested 2 weeks after irradiation with an Instron 1122 tensile testing machine. The Instron crosshead speed was 20 mm/min.

Analysis

Data analysis was performed graphically and by mathematical modeling to determine relationships and significant influences between the factors (independent variables) and the responses (dependent variables). Graphical analysis consisted of plotting responses against main factors. Response averages for two (or three) factors gave an indication of trends in main effects, whereas response averages over one (or two) factor(s) showed trends for second-order interactions. Mathematical model fitting to a Taylor series polynomial was performed using Statgraphics v. 5.1, a statistical analysis software package. The terms used in the Taylor series included all factors (peroxide, oil, and I168), peroxide,[2] and all second- and third-order interactions. The coefficients A0, · · · A10 associated with each term are defined in Table II. Factors were expressed in coded form for model fitting so that coefficients of significant terms would reflect the approximate level of importance or influence of the factor with which they were associated.[6] Terms were eliminated from the model polynomial until only significant terms remained (defined by significance level calculations, *t*-values, and Pareto charts).

Table II Factors and Factor Interactions Used in Taylor Series Polynomial for Model Fitting (All Are Expressed in Coded Form)

First Order		Second Order		Third Order	
Coefficient	Factor	Coefficient	Factor	Coefficient	Factor
A0	Constant	A4	Peroxide^2	A8	Peroxide × oil × I168
A1	Peroxide	A5	Peroxide × oil	A9	Peroxide^2 × oil
A2	Oil	A6	Peroxide × I168	A10	Peroxide^2 × I168
A3	I168	A7	Oil × I168		

RESULTS AND DISCUSSION

Principles of Statistical Design

Strategy of Experimental Design—Considerations

Principles of statistical experimental design were applied to determine if the peroxide used in the preparation of controlled rheology polypropylenes could affect the performance of the final resin by interaction with other additives during the VIS-breaking process.

The experimental design was well suited for the following reasons:

1. Experimental design allows the measurement of the effects by several variables at once.
2. Experimental design requires relatively few experimental runs to encompass the area or space of interest, but
3. Provides enough information to indicate major trends and allow development of empirical relationships, particularly when the "true" mechanism of cause and effect is unknown.
4. Experimental design makes it possible to distinguish between a linear or nonlinear response and an interaction of two (or more) factors affecting the response.
5. Graphical and/or mathematical interpretation is possible.

The factors chosen for study were the peroxide level, the absence or presence of oil, and the absence or presence of Irgafos 168, a thermal stabilizer. The 3 × 2 × 2 design matrix is shown in Table I, with peroxide at three levels and oil and Irgafos 168 (I168) at two levels (absent or present). The lowest peroxide level was chosen to produce a polypropylene resin with an MFI of 10–12 g/10 min, such as used in injection molding. The second level was selected to produce an MFI of approximately 20–25 g/10 min, whereas the highest level was an equal increment above the second. The use of three levels of peroxide was to determine the nonlinearity of interactions between peroxide and other additives, if any. The concentrations of oil and I168 were set at values typically used in commercial resins.

Responses

The effectiveness of the in-process thermal stabilizer I168 was monitored by measuring the MFI of the resin before and after injection molding of 20 cc syringes in a 16-cavity hot-runner mold. The MFI of 20 cc syringe parts molded at extruder temperatures of 220, 238, or 254°C was measured to determine the degree of thermal stabilization by I168. Smaller changes in MFI after injection molding would indicate effective thermal stabilization.

Oil was intended to act as a costabilizer in tandem with a hindered amine light stabilizer for radiation stability. As a determination of radiation resistance, the tensile properties were measured before and after irradiation. A decay of the physical properties would be an undesirable result. A minimal decrease was the desired result, although an increase in tensile values was conceivable and would be interpreted as beneficial.

The polypropylene resins were characterized, after preparation and before any treatment, while still in pellet form. This characterization served as the base line for studies of the additive efficiency in terms of their intended function and provided information on the effect of additives on the VIS-breaking process.

Data were analyzed by both graphical interpretation and by mathematical modeling. The model used was a third-order Taylor series polynomial. Factors used and coefficients for each are defined in Table II. In general, mathematical modeling quantitatively confirmed trends observed by graphical

Table III MFI of Polypropylene Resins Before and After Injection Molding

Resin No.	MFI			
		Barrel Temperature		
	Pellets	220°C	238°C	254°C
1	8.7	12.7	13.2	12.8
2	12.6	16.7	18.5	18.8
3	10.9	11.6	12.7	12.6
4	7.2	8.9	8.8	8.8
5	20.0	24.1	25.4	25.4
6	25.1	33.8	33.9	33.9
7	21.8	25	25.8	25.7
8	16.9	21.1	20.5	20.8
9	37.9	46	47	46.8
10	42.8	54.2	55.1	54.7
11	38.2	45	45.3	45.5
12	32.6	38.4	38.9	39

analysis and was used to determine significant influences on the response, the relative magnitudes of those influences, and the effect of interactions. Once the less obvious influences or interactions were identified by modeling, they were easy to identify in the graphical interpretation as well. As an iterative process, analysis by mathematical modeling complemented the graphic analysis well.

Function and Effectiveness of I168

Melt Flow Index

Melt flow indices (MFIs) were measured for pellets used in the injection molding of 20 cc syringes and for parts (Table III). Syringes were molded at three different barrel temperatures to assess thermal stability of the materials under conditions simulating a production environment.

Before Injection Molding. The development of MFI during the VIS-breaking process was a function of the additives present in the blend. The amount of peroxide had the strongest influence on the final MFI (Fig. 1) with measurable influences of oil and I168. The steepness of MFI curves as a function of peroxide indicated an increasing importance of peroxide at higher levels. In general, oil had the effect of increasing MFI, whereas I168 produced MFI values lower than the control without either additive. The combined effect of oil and I168 resulted in MFI values higher than the control but lower than those with oil alone. The trends for the different additive sets were not identical, as the nonparallel lines in Figure 1 may be interpreted. For example, the influence of I168 at low peroxide levels was smaller than its influence at high peroxide levels. This indicated an interaction between peroxide and I168. Interaction plots, averaged responses over different levels of the factor measured, clearly show a

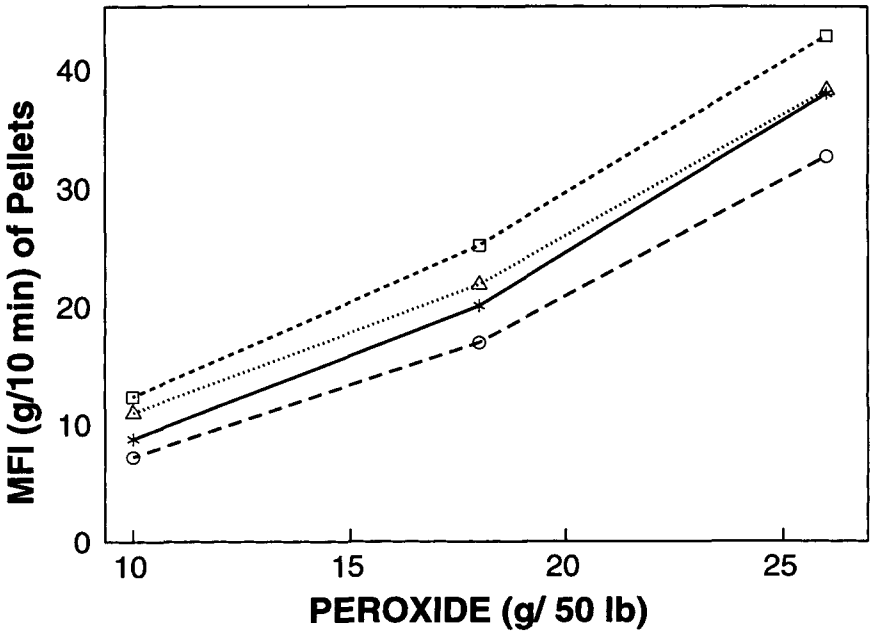

Figure 1 The effect of additives on the development of MFI during the VIS-breaking process: (—*—) no additives; (– –□– –) oil; (– – – ○ – – –) I168; (· · ·△· · ·) oil and I168.

small interaction between peroxide and I168, as the nonparallel lines in Figure 2(b) were interpreted. Parallel lines were interpreted as the absence of interaction, as seen for peroxide and oil, and oil and I168, in Figure 2(a) and (c), respectively.

Mathematical modeling confirmed graphical analysis by developing an equation to describe the response of MFI to the VIS-breaking process. In the model-fitting procedure, all factors were initially included in the model. Coefficients for the model were generated by multiple regression analysis. Factors were eliminated stepwise based on t-value statistics and Pareto charts until only the most influential factors remained, as indicated by t-values and significance level calculations. Because factors were expressed in coded form for regression analysis, the magnitude of the coefficients shown in Table IV are acceptable indicators of the relative importance of each factor or combination of factors.[6] Peroxide and peroxide^2 account for differences in MFI and curvature as a function of peroxide. The next significant influences were oil and I168. The interaction terms were the smallest contributors to modeling the effect of additives on the VIS-breaking process. The peroxide* I168 interaction was the largest of the two interaction terms, confirming the observed interaction from graphical analysis.

The decrease in MFI by the addition of I168 may be explained by the postulation of two different pathways that lead to polymer chain scission. One pathway may be through a chemically induced chain scission (as occurs in the presence of peroxide), whereas exposure to high temperatures in the melt may cause thermally induced chain scission (as oc-

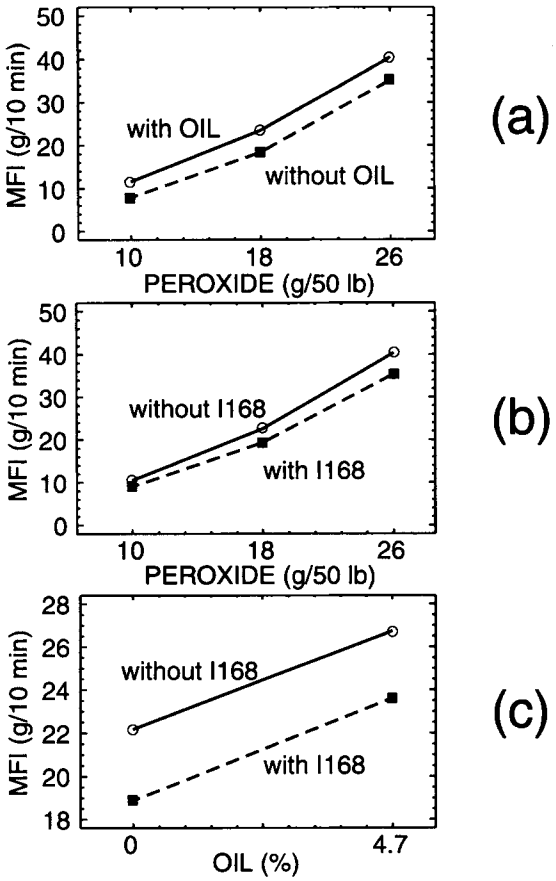

Figure 2 Interaction plots calculated from Table III. (a) Interaction plot for oil and peroxide, averages over all I168 levels. (b) Interaction plot for I168 and peroxide, averaged over all oil levels. (c) Interaction plot for oil and I168, averaged over all peroxide levels.

Table IV Coefficients of Model Fitting Results for MFI Before and After Injection Molding

		After Injection Molding		
Coefficient	Before Injection Molding	220°C	238°C	254°C
A0	20.94 (0.13)[a]	26.0 (1.0)	26.4 (0.7)	26.5 (0.7)
A1	14.06 (0.09)	16.8 (0.7)	16.6 (0.5)	16.6 (0.5)
A2	2.32 (0.07)	2.9 (0.6)	3.1 (0.4)	3.1 (0.4)
A3	−1.60 (0.07)	−3.1 (0.6)	−3.4 (0.4)	−3.3 (0.4)
A4	2.85 (0.15)	3.2 (1.2)	3.5 (0.9)	3.4 (0.9)
A5	0.40 (0.09)	—	—	—
A6	−0.88 (0.09)	—	—	—
A7, A8, A9, A10[b]	—	—	—	—
R^2	0.9996	0.9824	0.9905	0.9914

[a] Standard error estimates for coefficients given in parentheses.
[b] Factors for coefficients A7, A8, A9, and A10 were not significant by the criteria used to establish significance levels (see text).

curs in extrusion).[7] In the absence of I168, both paths would operate to cleave polymer chains. In the presence of I168, the thermally induced path may be suppressed. This would lead to the cleavage of fewer polymer chains, resulting in a lower MFI when I168 was present.

After Injection Molding. The resins were injection-molded into syringes with the barrel melt temperature at three different levels: 220, 238, or 254°C. Change in MFIs for the parts after injection-molding are shown on Table III. The trends observed in the response of MFI to the additive package before injection molding were the same after injection molding. Those resins with oil had higher MFIs than those without oil, and I168 had the effect of lowering MFI compared to cases where I168 was absent. In this set of conditions, oil and I168 had opposite and equal influences, effectively counterbalancing one another, as seen when resins 1 and 3, 5 and 7, or 9 and 11 are compared (Table III).

In terms of the *change* of MFI after injection molding, all three barrel temperatures resulted in the same change in MFI for each resin, indicating that I168 was effective as a thermal stabilizer at these temperatures. I168-containing resins changed the least and about the same amount, regardless of whether oil was also present (Fig. 3). Those resins containing neither oil nor I168 changed an intermediate amount, whereas oil-containing resins changed most. Therefore, I168 was present in sufficient amounts to suppress the development of MFI during the injection-molding process and was not hindered in this function by increasing levels of peroxide, as indicated by relatively straight and parallel lines in Figure 3.

Modeling confirmed and quantitated these observations. Coefficients of significant factors are shown in Table IV. Coefficients for MFI after injection molding were the same regardless of the extrusion barrel temperature. The difference between coefficients for the model before injection-molding and after injection-molding provided an estimate for the relative influence of each factor in the injection-molding process. An average increase of ~ 5 MFI units is indicated by the change in coefficient A0. Increasing peroxide caused a larger change in MFI, estimated at about 2.5 MFI units per incremental increase in peroxide. The presence of oil also caused an increase in MFI, although not as large as with peroxide. The coefficient for I168 (A3) was twice the value after VIS-breaking and injection molding than after VIS-breaking only, showing I168 to be as effective in suppressing MFI development in the injection-molding process as in the VIS-breaking process. Additionally, the interaction term between peroxide and I168 was absent, indicating that per-

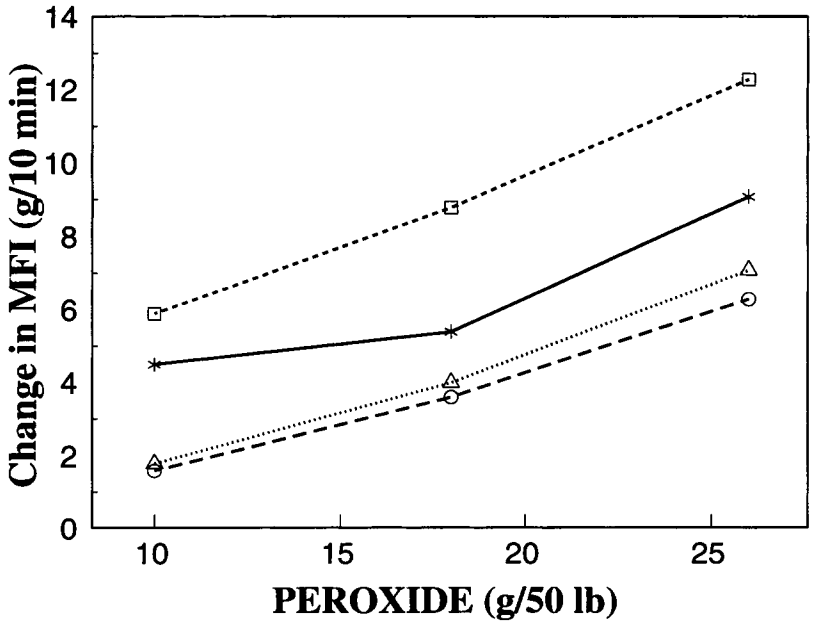

Figure 3 Change in MFI after injection molding into syringe test sample. Extruder barrel temperature at 238°C. Change in MFI with extruder barrel at other temperatures was qualitatively the same. Key same as for Figure 1.

oxide, regardless of the amount used in VIS-breaking, did not interfere with the intended function of I168 as an in-process thermal stabilizer for injection-molding.

Function and Effectiveness of Oil

Tensile properties were measured on Type V tensile bars molded under the same conditions for all resins. Properties were measured before and after irradiation by a ^{60}Co source to 2.5 and 5 Mrad total or integrated dose. The tensile properties were divided into two categories: (1) tensile yield and (2) tensile break. Tensile-yield properties included % elongation at yield, stress or strength at yield, and modulus. Tensile break properties included % elongation at break, stress at break or tensile strength, and work or energy to break or toughness. All property responses were analyzed. Modulus was found to be representative of results for % elongation at yield and stress at yield just as similar conclusions were reached whether toughness, % elongation at break, or tensile strength were analyzed. Therefore, only analyses for modulus and toughness are reported (Table V).

Modulus

Figure 4 shows the dependence of modulus on the experimental design before irradiation. Modulus is clearly distinguished by the absence or presence of oil. Oil decreased the modulus by ~ 25%. Modulus also appeared to decrease with increasing peroxide. There was no interaction between oil and peroxide, as the roughly parallel sets indicated. The effect of increasing peroxide and oil may be ascribed to a plasticizing effect of smaller molecules, as in oil or produced at higher peroxide levels. The effect of I168 on modulus may be through a small interaction with peroxide or may be indistinguishable from background of the measurement.

Irradiation was found to cause a slight increase in modulus for most resins although oil was still the most influential factor on modulus (Table V). Examination of Figure 5 shows that influences can be ranked in order of greatest influence: Oil, then dose, followed by peroxide. An interaction between peroxide and oil for irradiated samples may be indicated by different responses of modulus in the absence or presence of oil. In the absence of oil, values of modulus were more scattered, although the increase of modulus with dose was still evident. Effect of dose was approximately the same for resins with and without oil, indicating no interaction between oil and dose.

Regression analysis using the polynomial in Table II revealed similar trends. Analyses were stratified by dose to simplify interpretations of important factors (Table VI). Coefficients of significant factors indicated the same order of influence as that of graphical analysis, i.e., oil > dose > peroxide. Oil affected a decrease in modulus approximately two times greater than the second most influential factor, which was peroxide[2], as indicated by comparison of

Table V Tensile Properties at Yield and at Break for Type V Polypropylene Tensile Bars Before and After Irradiation

Resin No.	Modulus (kg/cm^2) by Dose			Work (kg-cm) by Dose		
	0	2.5	5	0	2.5	5
1	4049 (262)[a]	4053 (547)	4596 (449)	260 (20)	165 (14)	135 (16)
2	3165 (405)	3036 (299)	3127 (358)	288 (7)	198 (7)	156 (14)
3	2811 (280)	3050 (272)	3261 (486)	283 (6)	208 (7)	157 (12)
4	4117 (207)	4234 (443)	4425 (570)	272 (19)	198 (15)	127 (18)
5	3756 (368)	3953 (655)	3985 (439)	281 (18)	221 (19)	212 (17)
6	2821 (362)	3060 (276)	2967 (323)	280 (13)	222 (7)	208 (6)
7	2675 (237)	3122 (306)	3143 (223)	242 (6)	209 (14)	177 (8)
8	3497 (455)	4428 (313)	4182 (412)	274 (12)	219 (13)	184 (21)
9	3767 (258)	4214 (430)	4188 (467)	281 (5)	247 (10)	215 (14)
10	2570 (209)	3060 (318)	3202 (307)	260 (7)	223 (8)	202 (20)
11	2864 (400)	3172 (195)	3064 (235)	260 (5)	222 (5)	195 (8)
12	3831 (364)	3987 (261)	4591 (453)	275 (5)	243 (12)	211 (19)

[a] Standard error for the mean (10 replicates) is given in parentheses.

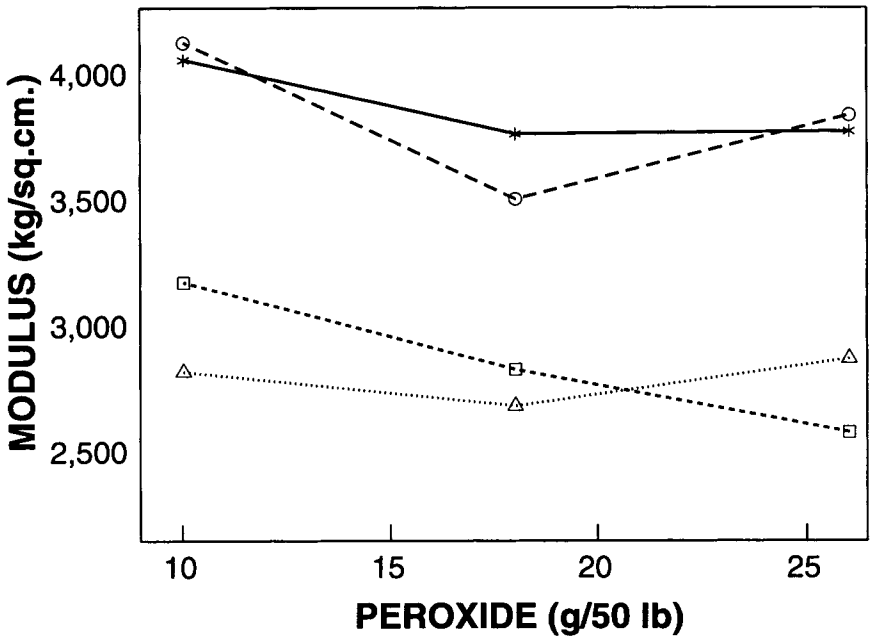

Figure 4 The effect of additives on tensile modulus of Type V tensile bars before irradiation. Key same as for Figure 1.

coefficients A2 and A4. At the 2.5 Mrad level, oil was the only term required to describe the response. This emphasized the significance of oil on modulus and indicated that higher-order terms with coefficients A8, A9, and A10 at other dose levels may be present to account for scatter in the response and not imply any mechanistic interactions. The change in coefficient A0 over dose level indicated the slight increase that radiation produced in modulus. The presence of different coefficients in models for each

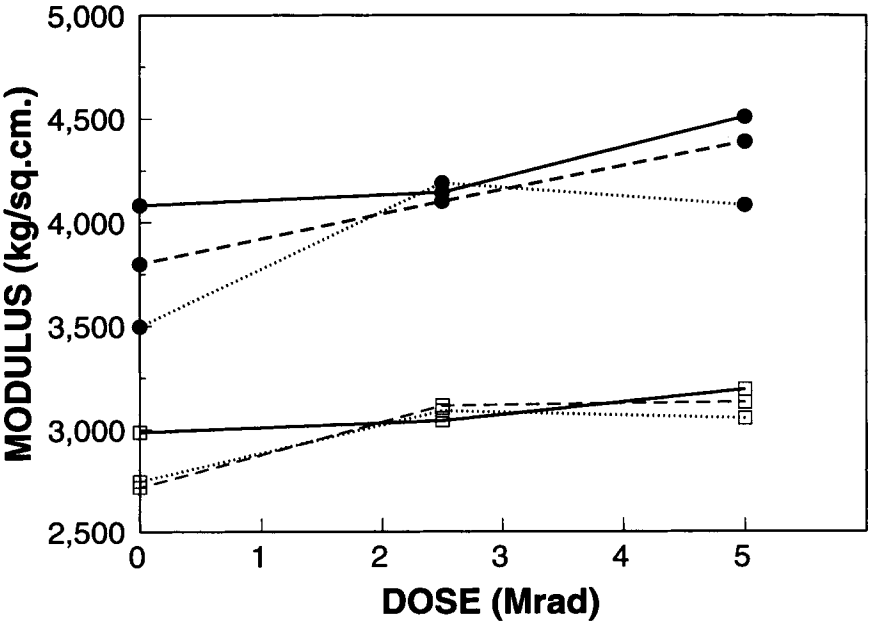

Figure 5 Response of modulus to irradiation segregated by peroxide levels and absence or presence of oil: (——) low peroxide; (– – –) midlevel peroxide; (• • •) high peroxide; (●) without oil; (□) with oil.

Table VI Coefficients of Model Fitting Results for Tensile Modulus and Tensile Toughness of Irradiated Polypropylenes

Coefficients A0 · · · A10 for Responses	Modulus by Dose			Toughness by Dose		
	0	2.5	5	0	2.5	5
A0	3187 (26)[a]	3614 (38)	3569 (53)	271 (3)	217.8 (0.2)	195 (2)
A1	−139 (18)	—		—	20.8 (0.1)	31 (1)
A2	−439 (26)	−531 (38)	−514 (53)	—	−2.3 (0.2)	—
A3	−101 (26)	—	—	−11 (5)	−3.8 (0.2)	−15 (2)
A4	210 (31)	—	238 (65)	—	−4.8 (0.3)	−21 (2)
A5	—	—	—	−9 (3)	−11.0 (0.1)	−10 (1)
A6	81 (18)	—	—	—	−6.0 (0.1)	—
A7	—	—	—	—	−2.6 (0.1)	—
A8	82 (18)	—	−106 (37)	—	3.3 (0.1)	—
A9	−105 (31)	—	−129 (35)	—	2.0 (0.3)	3 (1)
A10	110 (31)	—	—	11 (6)	8.5 (0.3)	13 (2)
R^2	0.9919	0.9453	0.9738	0.4811	0.9996	0.9882

[a] Standard error estimates for coefficients given in parentheses.

level of dose also implied some interaction between dose and other factors. Regression analysis with a third-order polynomial including dose terms resulted in the model shown below:

$$\text{Modulus} = 3466 - 547 \times \text{oil} + 200 \times \text{dose} + 136 \times \text{peroxide}^2 - 92 \times \text{peroxide} \times \text{dose}^2$$

$$R^2 = 0.927$$

The coefficients in the equation above show the same ranking of influences as shown in Table VI and as indicated by earlier graphical analysis, i.e., oil > dose > peroxide.

A mechanistic interpretation of the effect of dose on modulus may be in terms of changes in molecular structure. It is accepted that chain scission predominates over cross-linking in irradiation of polypropylenes.[8] However, it is unknown how chain branching may be influenced by irradiation. An increase in chain branching, even accompanied by chain scission of linear segments, may result in an increase of entanglements and an increase of modulus.

Toughness

The response of toughness to the initial VIS-breaking process was complex (Table V). Some trends were evident (Fig. 6) but consistency of those trends was lacking. For example, toughness appeared to respond differently to the absence or presence of I168 at different peroxide levels in unirradiated resins, suggesting a small interaction between I168 and peroxide. The influence of I168 on toughness in resins without oil was significantly different than those with oil. On an average, toughness decreased with increasing peroxide level for those resins that contained oil (short dash and dotted lines in Fig. 6). The general trend in resins that contained no oil was an increase in toughness with increasing peroxide. However, at higher peroxide levels, toughness was consistently greater for those resins without oil than those with oil. This was in contrast to the lowest peroxide level where oil-containing resins exhibited superior toughness. This indicated the importance of peroxide and a possible interaction between peroxide and oil.

Mathematical modeling of toughness to the initial VIS-breaking process (before irradiation) gave poor results. The model fit for toughness of unirradiated samples ($R^2 = 0.481$, Table VI) was most likely due to the narrow spread of the response and the uncertainty of the means (Table V). The response was not strongly dependent on the independent factors used here. An alternative interpretation is that toughness may be more influenced by some factor not recorded, such as a unique response of each resin to molding conditions. Although the model fitting was poor, it did identify interactions between peroxide and oil and between peroxide (actually peroxide^2) and I168, as graphical interpretation

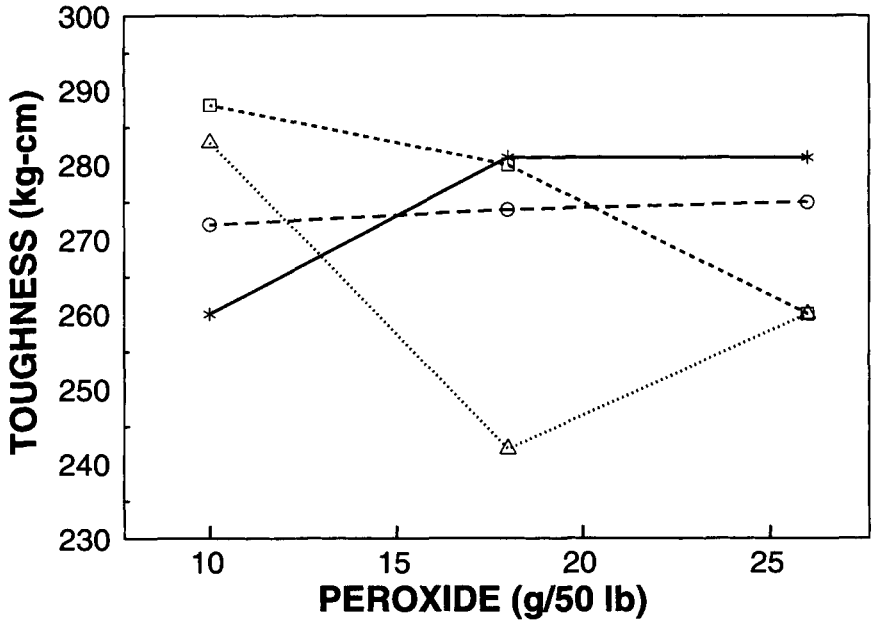

Figure 6 Toughness or energy to break Type V tensile bars as a function of additives, before irradiation. Key same as for Figure 1.

suggested. The magnitude of the coefficients suggested that the interactions were small.

Interaction between peroxide and oil was more apparent in irradiated samples. Figure 7 shows the interaction plot for peroxide and oil where I168 levels have been averaged. At the lowest peroxide level, resins with oil had greater toughness than did those without oil. At the midlevel of peroxide, toughness was about equal for all resins. At the highest peroxide level, samples *without* oil had greater tough-

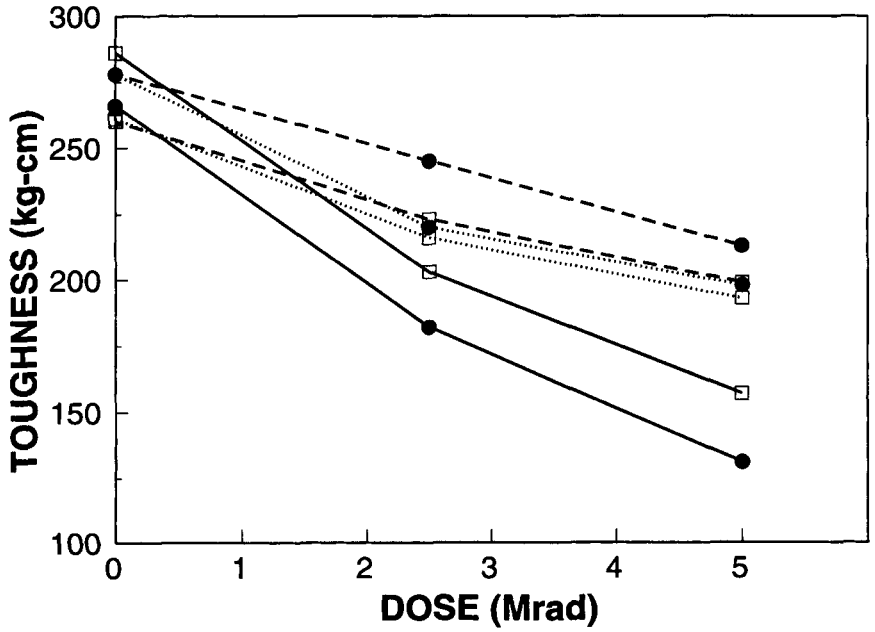

Figure 7 Interaction plot for the response of toughness as a function of peroxide, oil, and irradiation: (——) low peroxide; (– – –) midlevel peroxide; (· · ·) high peroxide; (●) without oil; (□) with oil.

ness than those with oil. Additionally, the parallel lines within each peroxide level (without and with oil) indicated that there was little or no interaction between oil and dose, whereas the difference between each peroxide level indicated an interaction between peroxide and dose. The dependence of toughness as a function of dose was dependent upon the amount of peroxide used to prepare the resin. The ranking of influences from the interaction plot in Figure 7 is dose > peroxide > oil.

Similar interaction plots for peroxide and I168 (averaged over oil levels) and for oil and I168 (averaged over peroxide) as a function of dose (not shown) indicated no discernable interactions between peroxide and I168 or between oil and I168.

Regression analyses for toughness were also fit for each level of dose (Table V). At dose = 2.5 Mrad, all terms were used to describe the response. There were no terms that were statistically different and that could be eliminated from the model. The only interesting information from this model was that peroxide and the interaction term between peroxide and oil were the terms with the largest coefficients, A1 and A5. At 5 Mrad, peroxide and peroxide^2 were the terms with the largest coefficients. Oil appeared only in the interaction terms peroxide × oil and peroxide^2 × oil and had the smallest coefficients (A5 and A9) of the significant terms. The constants A0 for all doses represented the overall effect of dose on toughness. The order of influence observed graphically was confirmed by model fitting to be dose > peroxide > oil.

As with modulus, different significant coefficients for different dose levels implied interaction between dose and other factors. Graphical analysis had suggested a strong peroxide–dose interaction. Use of a third-order polynomial that included dose resulted in a reduced model with significant factors shown below:

$$\text{Toughness} = 214 + 16 \times \text{peroxide} - 45 \times \text{dose} + 11 \times \text{dose}^2 - 10 \times \text{peroxide} \times \text{oil} + 17 \times \text{peroxide} \times \text{dose}$$

$$R^2 = 0.925$$

The only terms present were peroxide, oil, dose, and interactions of these terms. The coefficient for the peroxide*dose interaction was the largest of the two interaction terms identified. Improved radiation resistance (improved toughness) at higher peroxide levels was suggested by the positive value of the coefficient. The observation that oil was present in only the peroxide × oil interaction term and that the coefficient for that term is negative suggested that toughness overall might benefit from the absence of oil. These were observed in the interaction plot of Figure 7.

SUMMARY

The effectiveness of oil as a costabilizer for radiation resistance was found to be influenced by the VIS-breaking process through the use of statistical experimental design for formulation analysis. At low peroxide levels, corresponding to MFI ≈ 12 g/10 min, oil-containing resins had higher toughness values (particularly when irradiated) than those resins that contained no oil. This tendency was reversed at higher peroxide levels, where resins without oil showed better resistance to radiation-induced loss of tensile properties. The thermal melt stabilizer Irgafos 168, while influencing the results of the VIS-breaking process and acting as an effective melt stabilizer during injection-molding, was unaffected by the peroxide content.

The author would like to thank Dr. Perry Haaland for insightful conversations in the use of statistical analysis and C. Daudt of Himont, Inc. for preparation of the polypropylene resins.

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Received August 13, 1993
Accepted October 29, 1993