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THE USE OF THERMAL ANALYSIS TO STUDY THERMAL PROCESSING EFFECTS ON POLYPROPYLENE*

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Abstract

The thermal stability of a polypropylene copolymer has been examined at several stages during the processing of the material into its final product in order to obtain information on the influence of processing steps such as grinding and thermal heating on the expected lifetime of the material. Mass loss kinetics in an inert atmosphere were able to detect differences in thermal stability, but oxidative differential scanning calorimetry studies proved to be a more sensitive technique. A comparative study of a specially prepared series of samples revealed the importance of additives on measured thermal stability and indicated that both mechanical and thermal processing can cause reduction in measured thermal stability.

Keywords: DSC, polymers, polypropylene, thermal stability

Introduction

Thermoplastic polymers, such as polypropylene, are subjected to several thermal treatments during production and fabrication before the material finally reaches the consumer in the form of a finished product. In addition there is increasing pressure being placed upon resin suppliers to be responsible for the recycling of their materials when the product has reached the end of its initial application. The recycling of this thermoplastic material will once again involve at least one and possibly more thermal treatment processes to produce a second generation product. In this study we have examined the thermal stability of a se-

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ries of polypropylene samples taken from different steps in a typical production process. All samples examined came from the same initial lot of material. The material selected for this study was a high impact polypropylene copolymer suggested for automotive application. The three samples compared were:

(i) The standard base polypropylene polymer as produced from the polymerization process
(ii) Injection moulding grade pellets ready for processing
(iii) An injection moulded test plaque

In order to evaluate the thermal stability of these polymers we decided to employ both thermogravimetry (TG) and differential scanning calorimetry (DSC). The approach employed with the TG experiments was to determine the degradation kinetics of the weight loss process and evaluate the lifetime expectancies based upon the extrapolation of the Arrhenius parameters. While it is recognized that lifetime predictions should be used with caution [1-6] we have found them to be extremely useful for comparing similar polymer systems [7-12]. In addition to performing TG kinetics on the samples, the thermal stability of each specimen was also examined by oxidative induction experiments with a DSC.

Experimental

The basic polymer used in this study was Himont's PRO-FAX SV-152 superior high impact polypropylene copolymer (density = 0.898 g/cm^3 at 23°C) recommended for use in automotive applications because of its high impact strength at low temperatures and controlled crystallization. Three forms of material were supplied by Himont for our specific requirements regarding a kinetic study of mixed polymer systems [13]. The three materials studied were :

(i) "Spheripol", a standard polymeric material in the form of spheres produced by a patented polymerization process of Himont (designated PP1)
(ii) Moulding resin as free flowing pellets (PP2)
(iii) An injection moulded plaque produced from the above pellets (PP3)

In addition sample PP2 was cryogenically ground using a Wiley Mill to produce a fine powder (less than 20 mesh) which was also compared with the above three samples (designated PP2P).

The dynamic programmed TG's were carried out using a TA Instruments 951 TG balance coupled to a 2100 thermal analyser. Because of the known dependence of kinetic parameters on sample mass [14], the samples were standardized at 12±1 mg. The experiments were conducted in nitrogen at a flow rate of 50 ml/min employing heating rates of 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and

50 deg·min^{-1}. The TG data was subsequently analyzed by the isoconversional weight loss method of Ozawa-Flynn-Wall proposed independently by Ozawa [15] and by Flynn and Wall [16].

In addition to measuring the thermal stability of the polymeric materials by TG, the oxidative stability was also measured by the use of DSC to measure the extrapolated onset of oxidative degradation. Two methods of determination were employed using a TA Instruments 910 Differential Scanning Calorimeter coupled to a 2100 thermal analyzer. The DSC was temperature calibrated with indium (156.6°C) and zinc (419.5°C) prior to use. The first method employed a dynamic heating rate from which the onset oxidation temperature was determined. Samples approximately 6±2 mg in size were placed in open aluminum pans and heated at 10 deg·min^{-1} from room temperature to 250°C in a 100 ml/min flow of either oxygen or air. The onset oxidation temperature was then extrapolated from the commencement of the oxidative exotherm. The average of 5 determinations was taken as the oxidation temperature for the sample. In the second method the sample was rapidly heated from room temperature to 200°C in nitrogen at a flow rate of 100 ml/min. While maintaining the temperature at 200°C the nitrogen supply was changed to either an oxygen or air supply of 100 ml/min and the extrapolated time period for the onset of the oxidation exotherm was noted.

Results and discussion

Figure 1 shows the effect of heating rate (β) on the TG curves for the sample PP1. These curves are typical of all the curves obtained, not only with this sample, but also with the other samples examined in this study. These weight loss curves were analyzed by the Ozawa-[15] Flynn-Wall [16] method which we have demonstrated to be a satisfactory approach for TG data of this type [7]. In Fig. 2 the isoconversional data for sample PP1 at conversion values α of 0.05, 0.1, 0.25, 0.5 and 0.80 are plotted. Although very good correlations were found to exist for all the data presented in Fig. 2 with correlation coefficients of 0.999, 0.999, 0.998, 0.998 and 0.999 respectively; it is possible to distinguish a break in these plots at a heating rate of about 1 deg·min^{-1}. This break is especially noticeable in the case of the higher conversional values (i.e. α greater than 0.5). These changes in the slope of the isoconversional plots can influence the measured apparent activation energies (E_a) and the preexponential (log A) factor. The effect of heating rates employed on the calculated apparent activation energies and log A factors are summarized in Tables 1A and B, respectively.

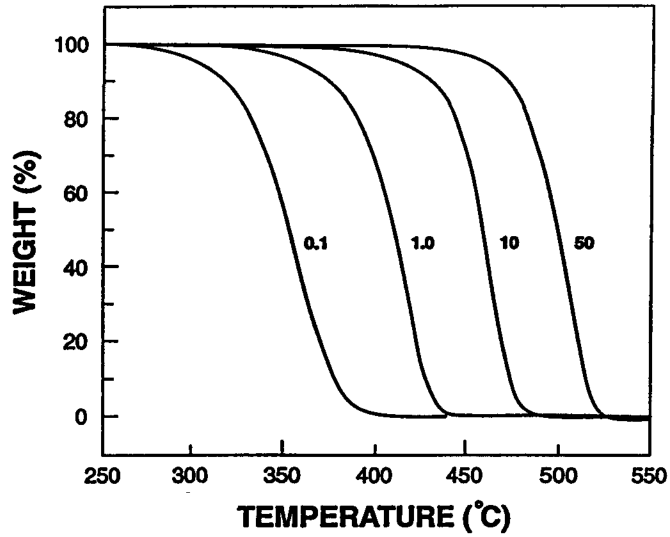

Fig. 1 Weight loss curves for sample PP1 at heating rates of 0.1, 1.0, 10 and 50 deg·min^{-1} in nitrogen

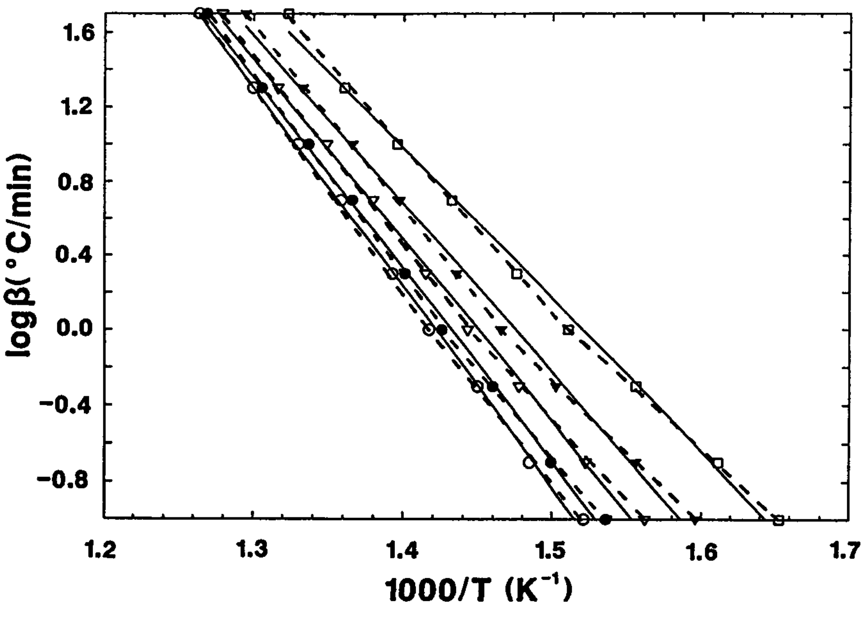

Fig. 2 Isoconversional plots for sample PP1 for α values of 0.05 (□), 0.1 (▼), 0.25 (▽), 0.5 (●)and 0.8 (o). Analysis over full range shown (—) while analysis over heating ranges 0.1–1 and 1–50 deg·min^{-1} shown (- - -)

Table 1A Apparent activation energies (kJ·mol^{-1})

	Heating rate range/ deg·min^{-1}	Degree of conversion α				
		0.05	0.10	0.25	0.50	0.8
PP1	β=0.1–50	131.6±2.1	138.1±2.6	151.3±3.7	164.4±4.1	178.9±3.3
	β=0.1–1.0	122.6±8.0	124.9±4.7	130.8±1.6	138.8±1.1	156.2±3.0
	β=2.0–50	132.7±4.4	147.3±5.4	168.8±3.7	179.3±2.6	186.4±3.1
PP2	β=0.1–50	146.1±3.3	148.1±3.2	154.3±3.7	165.4±4.0	180.1±3.2
	β=0.1–1.0	142.8±12.0	140.0±14.2	136.4±9.8	140.6±5.1	158.1±2.8
	β=2.0–50	134.9±5.2	146.5±6.8	167.8±5.0	180.3±2.2	187.9±2.0
PP2P	β=0.1–50	148.5±3.2	150.9±3.2	159.4±3.4	170.8±3.8	183.8±3.1
	β=0.1–1.0	168.5±12.2	159.3±14.5	147.5±10.1	149.5±7.4	164.9±7.7
	β=2.0–50	143.6±5.9	153.7±7.8	175.1±5.1	186.7±2.1	197.3±2.3
PP3	β=0.1–50	144.1±3.5	145.7±3.6	153.4±4.0	166.7±3.9	182.4±2.7
	β=0.1–1.0	169.1±11.2	159.2±10.2	144.5±6.1	149.0±3.9	166.4±2.2
	β=2.0–50	143.2±7.5	154.4±9.9	175.7±7.7	187.3±4.7	193.5±3.1

Table 1B Log A values (min^{-1})

	Heating rate range/ deg·min^{-1}	Degree of conversion α				
		0.05	0.10	0.25	0.50	0.8
PP1	β=0.1–50	11.04±0.17	11.62±0.22	12.77±0.31	13.89±0.34	15.10±0.27
	β=0.1–1.0	10.24±0.70	10.50±0.41	11.06±0.14	11.80±0.10	13.28±0.27
	β=2.0–50	11.13±0.34	12.32±0.42	14.06±0.29	14.97±0.21	15.64±0.24
PP2	β=0.1–50	12.15±0.27	12.39±0.26	13.00±0.30	13.97±0.33	15.19±0.26
	β=0.1–1.0	11.84±1.04	11.69±1.24	11.52±0.87	11.95±0.45	13.44±0.25
	β=2.0–50	11.31±0.40	12.28±0.52	13.99±0.39	15.05±0.17	15.76±0.16
PP2P	β=0.1–50	12.41±0.26	12.65±0.26	13.41±0.28	14.38±0.31	15.47±0.25
	β=0.1–1.0	14.17±1.06	13.37±1.26	12.42±0.89	12.65±0.66	13.96±0.68
	β=2.0–50	12.03±0.45	12.85±0.60	14.56±0.39	15.54±0.16	16.09±0.18
PP3	β=0.1–50	12.04±0.29	12.24±0.30	12.95±0.33	14.07±0.32	15.37±0.22
	β=0.1–1.0	14.25±0.98	13.42±0.89	12.23±0.54	12.65±0.35	14.09±0.19
	β=2.0–50	11.96±0.57	12.88±0.77	14.59±0.60	15.57±0.36	16.17±0.29

The E_a and log A values will be noted to have some dependence upon heating rates, however the correlation of the data is greatly dependent on the degree of conversion. In the case of lower conversion values (α less than 0.25) a greater degree of correlation is noted when all 9 heating rates are employed rather than the use of a smaller set of data. However, at high degrees of conversion (α greater than 0.5) the E_a and log A values have a greater degree of correlation when the heating rates are broken down into two segments. This data suggests that, following the degradation associated with the initial weight loss, the degradation kinetics become more complex as competing secondary reactions become more important and the diffusion process, which is heating rate dependent, has an influence on the measured E_a and log A values.

Table 2 Kinetic parameters for the thermal degradation of polypropylene in inert atmosphere

Atmosphere	E_a/kJ·mol^{-1}	log A/min^{-1}	Reference
Vacuo	243	-	17
Vacuo	247	14.4	18
Vacuo	284	-	19
Vacuo	209	-	20
N_2	243	-	21
N_2	285	18.60	22
He	213 (a-PP)	-	23
	214 (i-PP)	-	23
Vacuo	257	-	24
N_2	232 (i -PP)	-	24
	214 (a-PP)	-	24
He	265	15.7	25
N_2	160	12.8	26
N_2	230	12.5	27
N_2	233	-	28
He	120–200	-	29

a-PP = atactic polypropylene
i-PP = isotactic polypropylene

Although the major aim of this study was to compare the thermal stability of the polypropylene samples at each stage of the processing cycle, it is of interest to compare the calculated apparent E_a values with those reported in the literature. These values are summarized in Table 2. From this data it can be seen that the reported apparent E_a values are of the order of about 232 kJ/mol with the reported values being dependent upon polymer purity, molecular weight and tacticity. Meanwhile our data presented in Table 1A suggests that the E_a for the initial weight loss is of the order of 144 kJ/mol (the mean of the $\alpha = 0.05$ and 0.1 values). However, more representative values for the overall weight loss range for PP1, PP2, PP2P and PP3 would be E_a values of 164, 166, 171 and 167 kJ/mol, respectively. Clearly these values are much lower than those reported in the literature. However it should be noted that the values reported in the literature are for the homopolymer while the samples being evaluated in this study were produced from an impact modified copolymer, designed for specific characteristics.

The weight loss thermal stabilities of these samples are compared in Table 3. For comparative purposes the kinetic parameters for the $\alpha = 0.05$ have been employed using the data for the whole heating range 0.1–50 deg·min^{-1}. From this data it can be seen that there is little difference between samples PP2 and PP2P. This would infer that, based upon kinetic TG data as a measure of thermal stability, the mechanical action used to produce the powdered sample was not responsible for any loss in thermal stability. This result was not too surprising in view of the fact that liquid nitrogen was used to quench the sample during the actual mechanical action. Comparison of sample PP2 and PP3 on the other hand does show a very slight loss in thermal stability of PP3 as measured by kinetics, although extremely small. However, when the data for the PP1 material is considered a noticeably reduction in thermal stability is noted in comparison to the other two samples. For example, PP1 has a reduced apparent activation energy, a faster rate constant and consequently a greater reduced life prediction than the other two samples. A similar trend is noted with the higher α values.

Table 3 Comparative kinetic data

	E_a/kJ·mol^{-1}	log A/min^{-1}	Rate constant	Lifetime prediction	
			@300°C×10^2/min	@200°C (min)	10 year T/°C
PP1	131.6	11.04	10.94	161	88
PP2	146.1	12.15	6.81	492	105
PP2P	148.5	12.41	7.41	504	107
PP3	144.1	12.04	7.95	386	102

The reason for this apparent anomalous behaviour is believed to lie in the composition of the samples being examined. In proceeding from PP1 to PP2 in the production process, although a thermal processing step is involved, it is also

Table 4 Thermal oxidative stability of polypropylene samples in oxygen

Sample	PP1	PP2	PP2P	PP3
Oxidation temperature (°C)	198.8	228.1	217.0	227.0
	198.1	225.2	216.5	225.7
	198.1	229.4	216.1	224.7
	196.4	227.6	215.6	226.3
	202.7	225.0	215.6	223.2
Average	198.8	227.1	216.2	225.4
Standard deviation	2.1	1.7	0.5	1.3
Oxidation time at 200°C(min)	0.85	13.3	3.62	10.8
	1.20	11.5	5.16	8.58
	0.63	11.2	5.14	11.3
	0.50	9.88	5.32	9.94
Average	0.8	11.5	4.8	10.2
Standard deviation	0.3	1.2	0.7	1.0
Oxidation time at 180°C(min)	4.54	62.0	22.4	43.5
	3.13	61.8	22.2	56.1
	2.97	51.5	17.1	42.9
	3.42	43.5	21.1	73.5
Average	3.5	54.7	20.7	54.0
Standard deviation	0.6	7.7	2.1	12.4

Table 5 Thermal oxidative stability of polypropylene samples in air

Sample	PP1	PP2	PP2P	PP3
Melting point (°C)				
Extrapolated onset	154.1±0.7	151.1±1.3	153.4±0.7	152.9±3.0
Endotherm minimum	166.7±0.5	168.3±0.4	166.7±0.2	168.4±2.3
Oxidation temperature (°C)	199.7	235.1	220.4	238.2
	202.0	234.4	222.8	234.6
	204.6	237.9	225.7	230.2
	214.5	235.6	224.6	235.5
	205.9	237.9	226.8	236.3
Avarage	205.3	236.2	224.1	235.0
Standard deviation	5.1	1.5	2.3	2.7

likely that additives such as heat and light stabilizers as well as antioxidants are added to the material to improve the processing performance of the material. The presence of these additives in samples PP2, PP3 will consequently contribute to the measured thermal stability of these samples PP2 and PP3 in comparison to PP1 and result in slower degradation kinetics and longer lifetime predictions. In order to verify the presence of such additives, the DSC oxidation studies were performed. The results of these studies are summarized in Tables 4, 5 and Fig. 3 where the measured induced oxidation temperatures were measured under dynamic heating rate conditions of 10 deg·min^{-1}, along with the isothermal oxidative induction times measured at 180 and 200°C according to ASTM D3895-80 [30].

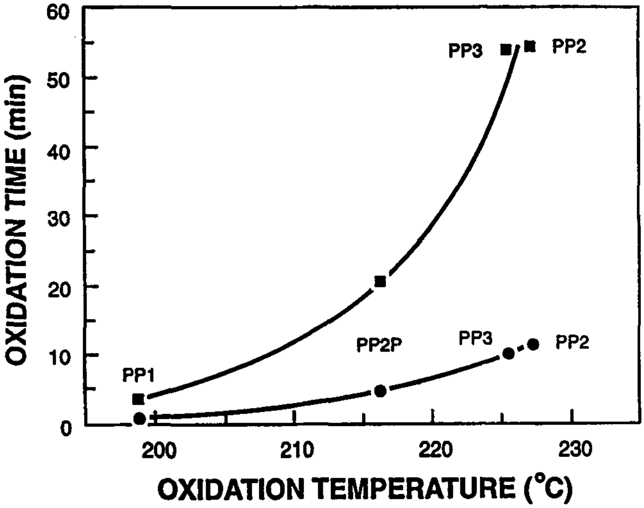

Fig. 3 Relationship between oxidation time at 200°C (•) and 180°C (■) and oxidation temperature at 10deg·min^{-1} for samples examined in oxygen

These results are exceedingly interesting and informative in that they confirm the greater thermal stability of sample PP2 in comparison to PP1. This data which was obtained in two oxidative environments unlike the TG data, clearly shows that the standard polymeric spheres PP1 have less oxidative thermal stability than the pellets PP2 since both the onset oxidation temperature and onset oxidation times are significantly less for the spheres than for the pellets. This data would tend to suggest that only low levels of additives such as heat stabilizers or antioxidants are present in the polymeric sphere sample PP1 while indicating that they have been incorporated in the pellet production stage.

The thermal oxidative data presented in Tables 4 and 5 also suggest that samples PP2P and PP3 have slightly decreased thermal oxidative stabilities in comparison to the PP2 sample. This observation is based upon the slightly reduced oxidation temperatures and times noted for PP2P and PP3 in comparison to sample PP2. This suggests that the mechanical grinding action to produce the powder, and the thermal processing to produce the plaques were sufficient to cause a slight reduction in the measured thermal oxidative stability of samples PP2P and PP3 with the reduction in thermal stability being much more pronounced with the powder (PP2P). This effect probably arises due to the production of hydroperoxide groups during the mechanical and thermal treatment processes. These hydroperoxide species can then initiate the thermal decomposition process, and result in decreased thermal oxidative stability.

Confirmation of these oxidative processes on the heating of polypropylene samples PP1 in oxygen in the DSC were confirmed by X-ray Photoelectron Spectroscopy (XPS). Sectioned spheres of PP1 were heated to 250°C at 10 deg·min^{-1} in both oxygen and helium and the DSC results are shown in Fig. 4. After cooling to room temperature the samples were subjected to XPS analysis using a Kratos AXIS XPS spectrometer. The sample heated in oxygen showed a highly oxidized surface with approximately 15% of the carbon atoms being oxidized. Carbon oxygen single bonds (C–O) dominated at 10.8% with carbon oxigen double bonds (C=O) and carboxylic acid (COOH) functional groups were indicated.

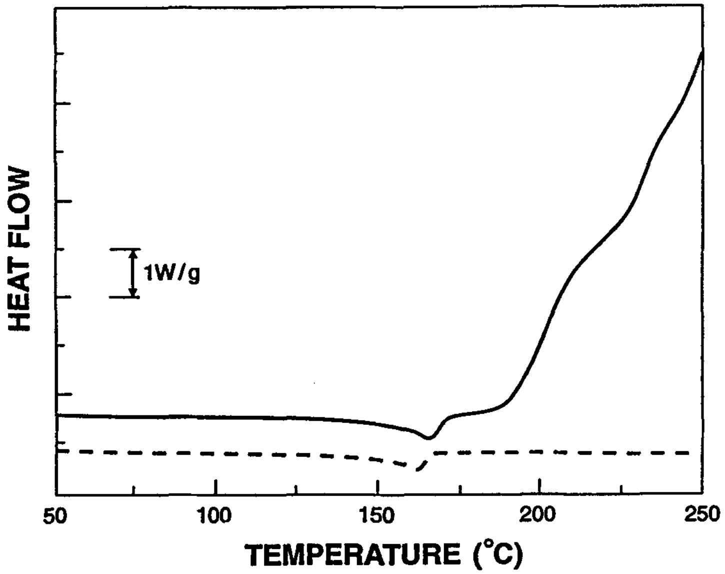

Fig. 4 DSC oxidative stability curves for PP1 at 10 deg·min^{-1} in oxygen (—) and helium (- - -)

Conclusion

The thermal analysis of a series of polypropylene samples by TG weight loss kinetics and DSC thermal oxidative studies have revealed that thermal and mechanical processing of the polymeric material during processing operations can influence the resultant thermal stability of the polymer and its expected lifetime. Consequently each step in the production process needs careful control to reduce the formation of possible degradation initiators. The implication of these findings in terms of recycling processes, becomes important when it is realized that the polymeric materials are subjected to several mechanical and thermal actions during the processing stages and lifetime of the polymer. Based upon our findings it can be expected that each step during processing and reprocessing can have an accumulative effect on the overall thermal stability of subsequent products. While it appears that additives such as antioxidants and heat stabilizers will play a key role in prolonging the lifetime of these polymers they themselves may not be sufficient to minimize the effects of degradation products such as hydroperoxides which can accumulate during the polymer processing and recycling operations and which can have an adverse effect on the polymers thermal stability.

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Zusammenfassung — Bei verschiedenen Schritten der Verarbeitung von Polypropylen-Kopolymer zum Endprodukt wurde die thermische Stabilität untersucht, um Informationen über den Einfluß von Verarbeitungsschritten, wie z.B. von Mahlen und Erhitzen auf die voraussichtliche Lebensdauer des Materiales zu erhalten. Mit Hilfe der Gewichts- verlust-Kinetik in inerter Atmosphäre können Unterschiede in der thermischen Stabilität nachgewiesen werden, jedoch erwiesen sich oxidative Scanningkalorimetrie-Untersuchungen als empfindlicher. Die Vergleichsstudie einer speziell hergestellten Serie von Proben erwies den Einfluß von Additiven auf die thermische Stabilität und zeigte, daß sowohl die mechanische als auch die thermische Bearbeitung ein Absinken der thermischen Stabilität verursachen kann.