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THE USE OF TGA TO STUDY THERMAL AGEING EFFECTS OF ORIENTATED POLYPROPYLENE

A. RICHARD HORROCKS AND JENNIFER A. D'SOUZA
Department of Textile Studies,
Bolton Institute of Higher Education,
Bolton, BL3 5AB, England.

ABSTRACT

The effective lifetimes of many orientated polymers like polypropylene films and fibres are defined in terms of the time required for a given environment to promote a sudden change in a macroscopic property; often catastrophic failure may follow such a change. TGA may be used to investigate the microscopic physico-chemical changes which occur during the induction period of thermally-aged polypropylene.

Marked shifts in the temperatures of the onset and maximum rates of mass loss accompanying post-fusion oxidation of aged orientated films are observed which reflect the slight changes in macroscopic properties that also occur during the induction period. The apparent kinetic parameters of unaged and aged film post-fusion oxidations are determined.

INTRODUCTION

Orientated fibre-forming polymers like isotactic polypropylene when subjected to degrading environments often show low or even negligible losses in tensile and other properties prior to their catastrophic failure after an induction period which coincides with their effective end-use lifetimes[1].

The presence of antioxidants increases induction periods and thermal analytical methods have been used in attempts to predict their effectiveness[2-5]. In addition the influence that ageing history has on polymer thermal behaviour has been studied using DTA [3,4], DSC [6-8] and isothermal TGA [9] methods. These studies have shown that degrading agencies, and in particular heat in the presence of oxygen, can reduce induction periods [4,9], shift fusion endotherms [6-8] and modify the character of post-fusion oxidation exotherms [3]

Whilst the use of thermal analytical methods has been criticised with regard to their effectiveness for predicting lifetimes of stabilised polypropylenes [10], it is evident that they offer a means of monitoring their physico-chemical structures during their induction periods when little or no macroscopic property changes are evident. This paper describes the use of TGA as well as DTA to study the effects of oven-ageing on the pre-induction period behaviour of orientated polypropylene fibres.

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EXPERIMENTAL

Orientated Film Production, Physical Properties and Oven-ageing.

Commercial high tenacity tape grade polypropylene (ICI Propathene, GWE26, MFI = 3) was extruded through a slit die at 250°C using a laboratory screw extruder. Conditions were adjusted to give films 50 ± 5 μm thick after stretching at 100°C with varying degrees of orientation. Actual draw ratios of 3.8 and 7.2:1 gave orientated tapes having respective tenacities of 0.19 and 0.51 GPa and breaking strains of 34.7, and 30.0%. Tensile properties of unaged and aged films were determined on 50 x 3mm samples. Densities and derived crystallinities [11] were determined using a Daventest density column.

One metre film lengths were wound around a 25mm diameter glass tube and their outer sides exposed to hot air at 130± 2°C for upto 20 days in a forced draught oven. Restrained, oven-aged film samples were removed after 1 hour and 2, 5, 7, 9 and 20 day intervals. The 1 hour annealed samples were the designated unaged films with which their respectively aged orientated analogues were to be compared.

Thermal Analytical Studies.

A Stanton Redcroft 671 B differential thermal analyser was used under static air conditions and a heating rate of 20°C min^{-1} to record DTA responses of 5 mg samples of unaged and aged orientated films. 20 day aged samples were analysed under static nitrogen conditions. DTA responses of an unstabilised sample of reactor grade, parent polypropylene polymer were recorded for comparison.

Programmed temperature thermogravimetry of unaged (1 hour annealed) and all aged film 5mg samples were undertaken under static air conditions using a Stanton-Redcroft TG 760 instrument at a heating rate of 20°C min^{-1}. Unstabilised polymer and unaged and 20 day oven-aged film 5mg samples were analysed by TGA at heating rates of 5, 10, 20, 30, 50 and 99°C min^{-1}.

RESULTS AND DISCUSSION

Effects of Oven-aging on Orientated Film Physical Properties.

Figures 1(a)-1(c) show the combined changes in film tenacity and breaking strain and simultaneous increases in crystallinity accompanying the 20 day ageing period. The initial fluctuations and subsequent rises in tensile properties are considered to be the consequences of a slow annealing effect occurring over the initial 7 day period. This is accompanied by thermal oxidation which promotes the later sudden tensile property

decreases observed. Unpublished work [12] shows that infrared-sensitive ketonic oxidation products become observable only in the 20 day aged samples. Earlier studies [7,13, 14] suggest that significant generation of such species occurs only prior to the induction period observed in oxidised polypropylene after which catastrophic loss in tensile properties occurs.

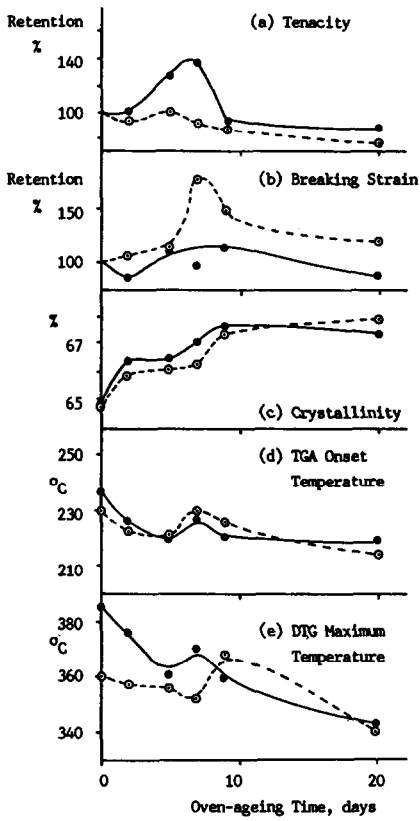

Figure 1: The influence of oven-ageing on the physical and thermal properties of orientated polypropylene films; draw ratio 3.8 (—●—) and 7.2 (-⊙-).

Following an initially rapid increase in crystallinity after annealing for 1 h a more gradual rise to an asymptotic value occurs during the 4 to 5 day period. A small rapid rise accompanies that for tensile properties and their maximisation; this rise is followed by a slower increase beyond 9 days ageing. The slight increase within the 7 to 9 day period is probably a consequence of the now significant thermal oxidation present [1, 7, 14]. The effect of film orientation is real but inconsistent and so requires further elucidation.

Thermal Analytical Behaviour of Aged Films.

The DTA responses of unstabilised raw polymer and unaged and 20 day aged

orientated films are shown in Figure 2. The inherent oxidative sensitivity of unstabilised polypropylene is evident when compared with the antioxidant-containing films. Oven-ageing enhances the intensity of the low temperature region of the post-fusion oxidative exotherm . Under nitrogen slight shifts to lower temperatures of the onsets of exothermic character are observed for each orientated film after ageing. Little effect of ageing is observed with respect to this exothermic intensity however. That exotherms are observed at all in the film samples when compared to the DTA response of the unstabilised polymer under nitrogen, are probably consequences of both the presence of antioxidant and the melt extrusion histories. Slight changes in the fusion endotherms also are induced by oven-ageing as noted previously [6-8] although as expected, they are little influenced by the atmosphere present.

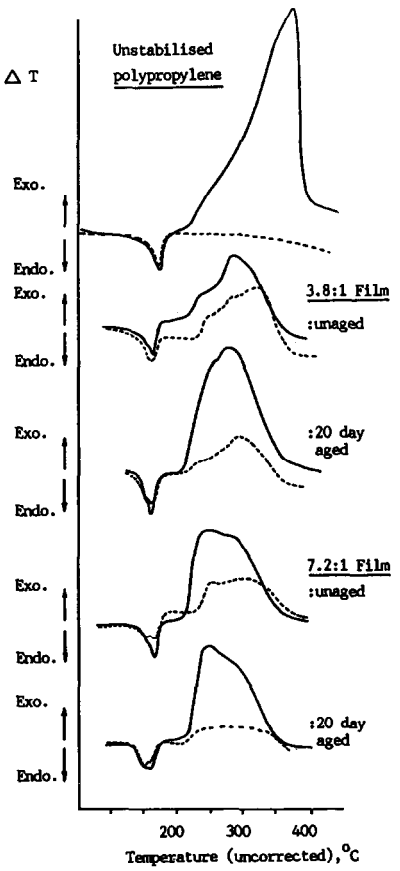

Figure 2: DTA responses of unstabilised polymer and orientated film at 20°C min^{-1} in static air (——) and nitrogen (·····).

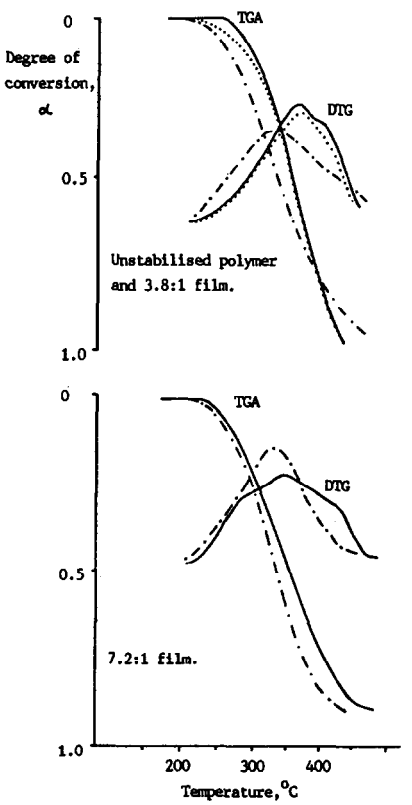

Figure 3: TGA and DTG responses for unstabilised polypropylene (·····) and unaged (——) and 20 day aged (— · —) films at 20°C min^{-1} in static air.

TGA/DTG mass responses are typified by those for the unstabilised and 8:1 unaged and 20 day aged films shown in Figure 3. Comparison of Figures 2 and 3 shows that the DTA exotherm maxima in air correspond to the onsets of mass loss and that the DTG maxima occur at significantly higher temperatures. However it is interesting to note that the DTG maxima are close to the DTA exothermic maximum of unstabilised polypropylene in air. The presence of antioxidant in the film enhances the temperature at which the onset of mass loss occurs but has no effect on that for maximum loss rate. Ageing at 130°C decreases both these temperatures for orientated films. However the changes in TGA/DTG responses during the whole 20 period are not simple and plots of onset and maximum rate of mass loss temperatures as a function of ageing time are shown in Figures 1(d) and 1(e). Comparison with the physical property changes in Figure 1(a) - 1(c) shows that the associated physico-chemical structural changes are mirrored by the variations in TGA/DTG behaviour. Further work is necessary to explain the causes of these observations and again film orientation seems to influence the effects in a complex manner.

In an attempt to observe the effect of oven-ageing on the post-fusion oxidative character of the unstabilised polymer and the unaged and 20 day aged film, the respective TGA responses undertaken at various heating rates were analysed according to the method of Ozawa [15] at the degrees of conversion, α, of 0.1, 0.25, 0.5 and 0.75. The derived apparent activation energies and assumed first order reaction Arrhenius factors are listed in Table 1.

TABLE 1 : Apparent Activation Energies and Arrhenius Factors

Film Draw Ratio	Ageing Time;days	Degree of conversion, α 0.1 E[a]	0.1 log A[b]	0.25 E	0.25 log A	0.5 E	0.5 log A	0.75 E	0.75 log A
3.8	0	72.3	5.7	68.4	5.4	70.9	5.6	79.1	6.2
	20	70.5	5.7	65.9	5.4	69.5	5.7	72.6	5.8
7.2	0	73.9	6.0	72.8	5.9	73.5	6.0	73.8	6.0
	20	75.2	6.2	69.1	5.8	64.5	5.4	52.7	4.4
Unstabilised Polymer	0	64.0	4.9	56.5	4.3	54.8	4.3	56.8	4.5

Notes : (a) kJ mol^{-1}

(b) A values have units min^{-1}

These results suggest that the post-fusion oxidation is isokinetic over the

range α = 0.1 - 0.75 in unaged films. Oven-ageing, however, whilst hardly influencing the apparent kinetic parameters for α = 0.1, significantly reduces them at higher degrees of conversion and orientation. The unstabilised polymer also shows a similar deviation from isokinetic character.

These results agree with the DTA and TGA/DTG responses in Figures 1 - 3 which show that oven-ageing increases the oxidation sensitivity of the polymer, presumably as antioxidant effectiveness reduces.

CONCLUSIONS

These preliminary studies of the thermal analytical behaviour of oven-aged polypropylene films suggest that TGA offers a means of investigating the small physico-chemical structural changes which take place during the induction period prior to catastrophic failure. It is anticipated that the use of TGA can thus be made to monitor the behaviour of orientated polypropylene films, tapes and fibres during their use and thereby attempt to predict their initial and remaining lifetimes.

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REFERENCES

1. J.W. Tamblyn and G.C. Newland, J. Appl. Polym. Sci., 9 (1965) 2251.
2. F. Geleji, Z. Holly, G. Ocskay and T. Weir, J. Polym. Sci., Pt. C, 16 (1968) 3695.
3. V.E. Althouse, Am. Chem. Soc., Div. Polym. Chem. Preprints, 4 (1963) 256.
4. J.B. Howard, Polym. Eng. Sci., 13 (1973) 429.
5. J. Holcik and M. Kosik, J. Polym. Sci., Symp. No. 57 (1976) 191.
6. K.D. Pae and J.A. Sauer, J. Appl. Polym, Sci., 12 (1968) 1901.
7. M.G. Wyzgoski, J. Appl. Polym. Sci., 26 (1981) 1689.
8. M. Mucha and M. Kryszewski, Acta Polym., 36 (1985) 648.
9. J. Rose and F.R. Mayo, Macromol., 15 (1982) 948.
10. D.A. Gordon, Am. Chem. Soc., Adv. Chem. Ser., 85 (1968) 224.
11. M.N. Huda, M.J.Dragaun, S. Bauer, H. Muschik and P.Skalicky, Coll. Polym. Sci., 263 (1985) 730.
12. A.R. Horrocks and J.A. D'Souza, to be published.
13. D.L. Faulkner, Polym. Eng. Sci., 22 (1982) 466.
14. H.J. Oswald and E. Turi, ibid., 5 (1965) 152.
15. Ozawa T., Bull. Chem. Soc. Japan, 38 (1965) 1881.