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Monitoring Thermo-Oxidative Degradation of Polypropylene by CRYSTAF and SEC-FTIR

Stefan de Goede[1], *Robert Brüll*[2]*, *Harald Pasch,*[2] *Niall Marshall*[3]

[1] SASOL Polymers, P.O. Box 72, Modderfontein 1645, South Africa
[2] German Institute for Polymers, Schloßgartenstr. 6, 64289 Darmstadt, Germany
[3] Schumann SASOL, 1 Klasie Havenga Road, Sasolburg 1947, South Africa

SUMMARY: Samples of a polypropylene homopolymer have been degraded and analysed with regard to chemical composition, molecular weight distribution and chemical composition distribution. FTIR shows the progress of degradation and a decrease in molecular weight can be observed from SEC. CRYSTAF shows that the chemical heterogeneity of the samples broadens with continuing degradation. SEC-FTIR reveals that the degraded species are mainly found in the low molecular end of the molecular weight distribution. The spatial heterogeneity of the degradation process has been proven by the analysis of abrased layers.

Introduction

Polyolefins are of enormous economic importance and constitute about 60 % of the total polymer market. The degradation of polyolefins takes place during processing, application and recycling. It influences the polymer properties and thereby limits the lifetime of the materials.[1] In particular the increasing importance of polymer recycling for the so-called "sustainable development" is a strong motivation to search for analytical methods to analyse the degradation of polyolefins.[2] According to the mechanism one can distinguish photo-oxidative and thermo-oxidative degradation. Beyond this degradation polyolefins can also be attacked by strong acids.[3]

The generally accepted free radical oxidation model of polymers, developed by Bolland and Gee, consists of radical initiation, propagation and termination reactions.[4,5] Following an initiation reaction, which usually results from the thermal or photo-initiated dissociation of chemical bonds, alkyl radicals react with molecular oxygen to form peroxy radicals (ROO·).[6] The propagation reactions result in the formation of oxygen-containing functionalities like ketones, alcohols,

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carboxylic acids, esters and γ-lactones.[7-12]

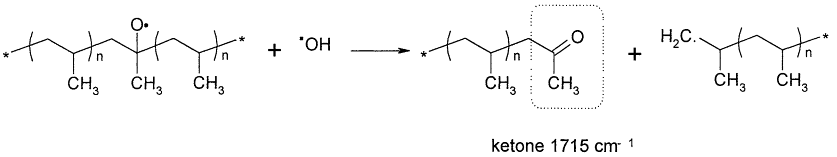

Fig. 1 β-Scission reaction of polypropylene.

The level of degradation can be determined by physical test methods like thermal analysis (e.g. DMA, DSC) melt flow testing, size exclusion chromatography (SEC), oxygen absorption and swelling capacity.[13] Polymers are characterised by their chemical composition, molecular weight distribution and chemical heterogeneity. During the degradation of polymers changes are observed in all three parameters. While the changes in molecular weight distribution and chemical composition have been investigated, there is no information in the scientific literature about the chemical heterogeneity of polyolefin degradation. This information can be obtained either by molecular weight independent fractionation according to chemical composition or separation by hydrodynamic volume and subsequent chemoselective detection. SEC in combination with FTIR provides the possibility of determining the FTIR absorbance as a function of molecular weight. The LC-Transform approach is particularly useful as it eliminates the spectral absorptions of the solvent used.[14,15] CRYSTAF (Crystallisation Analysis Fractionation) has been developed in the early 90s and separates semicrystalline polymers on the basis of crystallisability.[16-18]

In this study we present the analysis of degraded polypropylene samples with the focus on coupled SEC-FTIR and fractionation through CRYSTAF and Temperature Rising Elution Fractionation (TREF).

Experimental

Sample preparation: Samples of unstabilised polypropylene M_w = 81,300 g/mol have been obtained from SASOL Polymers (Modderfontein). They were cast to samples of 2,5 mm thickness and then degraded in a temperature controlled oven.

Analysis: The molar masses of the polymers were determined using a Waters 150C chromatograph at 140 °C with Waters Styragel columns (HT 2 – 6). The solvent used was 1,2,4-trichlorobenzene at a flow rate of 1 ml/min. A CRYSTAF model 200 from Polymer Char S.A. (Valencia, Spain) was used for fractionation. 20 mg of the sample were dissolved in 30 ml 1,2,4-trichlorobenzene. The temperature gradient was 0.1 °C/min. An LC-Transform model 300 from Lab Connections coupled to a Waters 150C chromatograph was used for the SEC-FTIR analysis. The stage temperature was 160 °C, the temperature of the nozzle was 118 °C and the transfer line 150 °C. A Nicolet FTIR, model Nexus, was used for IR-analysis.

Results and Discussion

In the current study 4 samples of unstabilised polypropylene have been aged to different stages. The conditions and characterisation data are shown in Table 1. Fig. 2 shows the FTIR and SEC analysis of the samples.

Table 1 Degradation conditions and characterisation of polypropylene samples

Sample	**T [°C]**	**Time [days]**	**CO-Index**	**M_w**	**M_w/M_n**
1	70	4	0.13	71,500	2.81
2	110	4	0.64	64,300	2.63
3	70	105	0.76	52,200	3.31
4	130	1	1.43	21,000	4.12

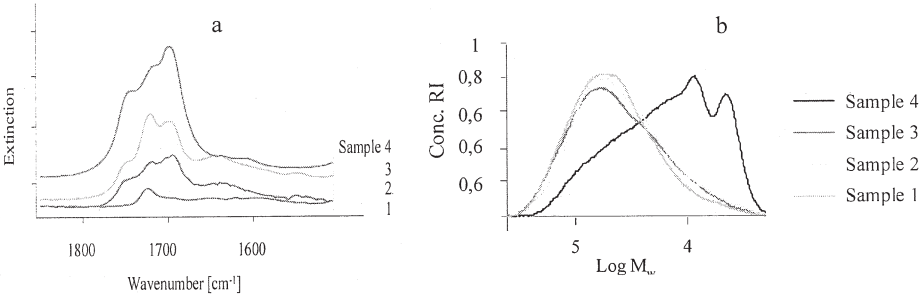

Fig. 2 Carbonyl region of the FTIR-spectra(a) and SEC-traces (b) of the degraded samples.

As seen in Fig. 2, the intensity of the carbonyl vibration increases with prolonged degradation. The spectra clearly show the presence of a carbonyl absorption at 1716 cm^{-1}. This absorption band is associated with the development of a ketone following β-scission (Figure 1), the most common oxidation mechanism experienced by polypropylene. Further absorptions can be seen with progressing degradation (samples 2-4) at ca. 1740 cm^{-1} and 1780 cm^{-1}. These are associated with peracids and γ-lactones respectively, both of which are secondary oxidation products.[19,20] The molecular weight is reduced with progressing degradation and the molecular weight distribution broadens, particularly in sample 4.

However, both techniques do not take into account the chemical heterogeneity, that means the distribution of degradation products over the molecular weight distribution. The SEC-FTIR-analysis of two degraded samples is shown in Fig. 3.

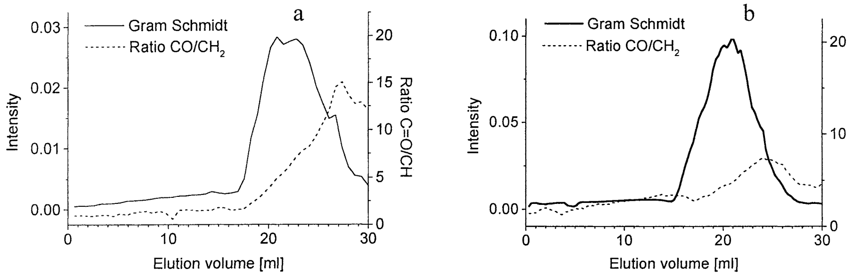

Fig. 3 SEC-FTIR of sample 2 (a) and 4 (b).

The Gram Schmidt plot is a sum over all absorptions and corresponds with the concentration of the sample in the eluate. Chemigrams can then be generated to investigate the intensity of a particular absorption along the molecular weight axis. The Gram Schmidt plots in Fig. 3a and b reveal the decrease in molecular weight with progressing degradation. In order to locate the carbonyl groups chemigrams have been taken for the carbonyl-region (1600-1800 cm^{-1}). For the CH-concentration the chemigram for the band centered around 1167 cm^{-1} has been drawn. The ratio of both chemigrams then reflects the relative concentration of degraded species. Overlaying the ratio of these chemigrams with the Gram-Schmidt-plot shows that the degraded fraction of the polypropylene is mainly found in the low molecular weight end while the high molecular weight part is virtually undegraded, particularly in sample 2.

Fractionation by CRYSTAF is another approach to gain insight in the chemical heterogeneity. In contrast to SEC the sample is fractionated according to crystallisability, which is a function of the chemical composition. CRYSTAF is a fractionation technique, which has been introduced into polymer analysis in the early 90s. The solution of the sample is cooled according to a programme and the concentration of the material in solution measured. Fig. 4 shows the concentration profiles of two samples at different stages of degradation.

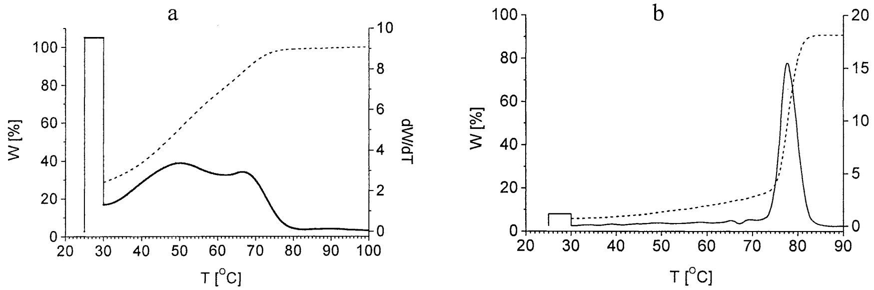

Fig. 4 Concentration profiles of polypropylene samples 2 (a) and 4 (b) obtained by CRYSTAF.

A comparison of the plots in Fig. 4 shows, that the change in chemical heterogeneity is reflected in the CRYSTAF-measurements. The chemical composition distribution of the crystallisable fraction becomes broader, the peak crystallisation temperature drops and the amount of soluble fraction increases.

The oxidation of semi-crystalline polymers is not homogeneous, partly due to the heterogeneous nature of the solid polymer but also because oxidised regions of the sample are more susceptible to further oxidation. The heterogeneous nature of polymer oxidation has been studied spatially using, for example, IR-analysis of microtomed slices or infrared microscopy.[20-23] To analyse the gradient within the samples, layers of 0.3 mm thickness have been abrased. Fig. 5 shows the SEC-FTIR-plots of two layers, taken at 0.3 mm and 1.2 mm into sample 4.

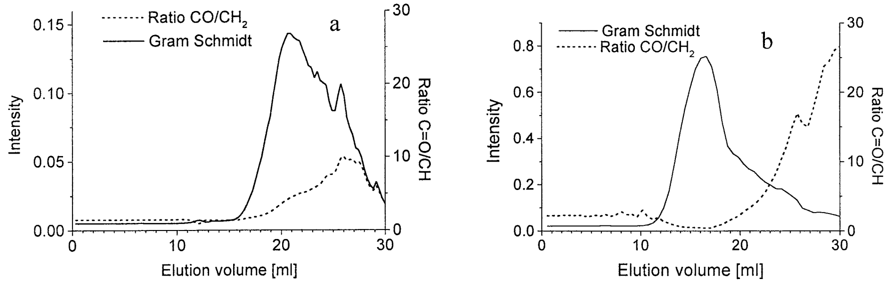

Fig. 5 SEC-FTIR of the layers at 0.3 mm (a) and 1.2 mm.

From Fig. 5 can be seen that the degradation within the sample is heterogeneous. The Gram Schmidt plot indicates a reduced molecular weight for the surface layer compared to the core of the sample. For both layers the highest concentration of degraded species is found in the low molecular weight region. It is interesting to note that for the sample taken at 1.2 mm the high molecular weight fraction is almost undegraded while for the surface layer the degraded species also affect the high molecular weight portion. The CRYSTAF traces for two fractions are shown in Fig. 6.

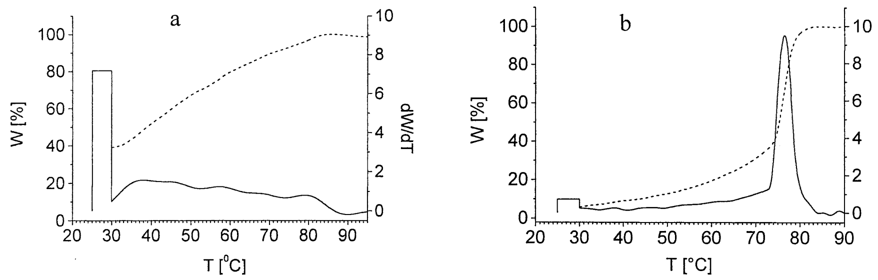

Fig. 6 CRYSTAF-traces of the layers at 0.3 (a) and 1.2 mm (b).

CRYSTAF impressively reveals the gradient of degradation from the surface to the core of the sample. The surface layer consists almost exclusively of non-crystallisable material while the inner part of the sample is still highly crystalline.

CRYSTAF is a relatively simple and useful technique for the separation of species based on crystallisability. However, it is not possible in the analytical version to isolate sufficiently large fractions for further analysis. Therefore TREF (Temperature Rising Elution Fractionation), a technique similar to CRYSTAF in that it fractionates semicrystalline polymers according to their crystallisability, has been used to separate sample 4 into seven fractions for further analysis using GPC and FTIR.

Table 2 TREF of sample 4 and FTIR and SEC-analysis of the fractions.

Fraction	**Elution Temp.**	**CO-Index**	**M_w**	**M_w/M_n**
1	40	0.33	21,000	4.67
2	80	0.53	10,500	3.23
3	90	0.26	20,500	2.19
4	94	0.19	21,800	4.78
5	98	0.07	39,300	2.01
6	102	0.04	62,200	2.12
7	107	n.a.	98,500	2.21

Analysis of the fractions by IR shows that the fractions at low elution temperature have a higher normalised area under the carbonyl absorption peaks. Initially the highly degraded fractions are eluted, while the fractions at high elution temperatures show only a small carbonyl index. The 1715 cm^{-1} ketone absorption is present in all but the highest molecular weight fraction. However, absorptions associated with peracids and lactones only appear in the lower molecular weight (and less crystallisable) fractions. This is consistent with a view that the lower molecular weight fraction consists of highly oxidised polymer chains, which are unable to crystallise, while the higher molecular weight fractions are less oxidised.

Conclusion

From the results it can be concluded that both, CRYSTAF and TREF, are efficient techniques to fractionate degraded polypropylene according to the degree of decomposition. SEC-FTIR has been proven to be very useful to study the distribution of degraded species along the molecular weight axis. These are mainly found in the low molecular tail of the molecular weight distribution.

Acknowledgement

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