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ORIGINAL PAPER

Thermal degradation behavior of polypropylene in the melt state: molecular weight distribution changes and chain scission mechanism

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Abstract In order to clarify the effect of thermal degradation on the structure of polypropylene materials, we investigated the changes in molecular weight distribution. The samples of polypropylene were degraded iso-thermally at 190 °C at different time intervals. The molecular weight distribution was significantly changed with thermo-degradation time, and the carbonyl index increased drastically for 40 min degraded samples, where the molecular weight distribution started splitting into two peaks. The results imply that heterogeneous degradation proceeded in this system. Sequentially, the weight distribution of the oligomeric products observed was discussed on the basis of chain scissions; these results indicate that there are some kinetically favored scissions occurring near the oxygen-centered radicals.

Keywords Polypropylene · Thermo-oxidation · Molecular weight distribution · Chain scission

Introduction

Semicrystalline isotactic polypropylene (i-PP) has been extensively used in the daily life because of its high performance and wide applicability. As a consequence, various processing technologies such as injection, extrusion, spinning, compression, and blow have been employed for i-PP-based products. Recently, much attention has been paid to rotational molding process for large hollow products such as deposits and containers that can not be produced by any other processing methods [1]. During the roto-molding process, a pre-weighted charge of powder samples is placed in a shell-like mold, and slowly rotated about two perpendicular axes,

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meanwhile the plastic is heated and melted to form a coating on the inside surface of the mold without shear force. Therefore, the thermally stable plastics such as polyethylene (PE) and polyvinylchloride, and nylon have been employed for roto-molding processes. The main drawback of the rotational molding is to spend much longer processing cycle time as compared to other conventional processing techniques.

It is well known that the PP materials produced directly from a commercial process are very susceptible to air oxidation. i-PP at molten temperature is often degraded for several dozens of minutes and the accelerated rate of degradation has possibility to lead to poor mechanical properties of the materials. This is the main reason why i-PP-based materials have not been widely used for roto-molding processes. In other words, for the purpose of employing i-PP samples as roto-molding grades, the elucidation of the degradation mechanism of i-PP in the molten state is desirable.

In half past century, the thermal degradation of i-PP based materials has been extensively studied, but most in the solid state ranging between 40 and 150 °C [2–8]. In this temperature range, much information on oxidation and degradation mechanism is now relatively well elucidated: it is a radical chain reaction initiated by the hydroperoxide group [9, 10]. On the other hand, there are few papers concerning i-PP thermal degradation in the melt state, despite it is very important to control various molding conditions. In the last two decades, some researchers started to study the thermal degradation under processing [11–16] and mechanical recycling [17–19].

As well known, many radical reactions can take place during degradation, depending on the polymer species and even the catalyst used for the production [20]. In the case of PE, the heating leads not only to chain scission but to recombination producing cross-linked structure [21, 22]. On the other hand, the degradation of i-PP is preferentially carried out by chain scission, resulting in that the molecular weight distribution (MWD) is shifted to the lower molecular weight side according to the type and extent of the degradation [15, 23–27]. There are reports on molecular weight changes taking place during different processes, whereas most of these researches mainly evaluate the final mechanical and rheological properties of products in injection or extrusion processing. Their processing cycle time was usually in several minutes. The aim of this study is to evaluate the probability of chain scission of a typical commercial polypropylene grades due to the thermal degradation in melt state for a long time, at least half an hour. These data will be indispensable for examining the applicability of i-PP materials to roto-moldings.

Experimental

In this study, we used a commercial grade of isotactic polypropylene with high isotacticity (98–99%) and the weight average molecular weight $M_\mathrm{w} = 416 \times 10^3$ and molecular weight distribution index $M_\mathrm{w}/M_\mathrm{n} = 4.60$.

Weighted quantities of i-PP powders (500 mg) were placed in the aluminum foil plates and the heat treatment was carried out using a windy oven WFO-601SD (Tokyo Rikakikai Corp.) at 190 °C under different degradation time periods.

The development of the carbonyl concentration was measured following the carbonyl index build-up, which was taken as the absorbance ration of IR band at 1715 and 974 cm^{-1}. Spectra were recorded using 2 cm^{-1} resolution and cumulated number 128 at 21 °C on hot-pressed films with an ORIEL Instrument MIR8000 Fourier transform infrared (FTIR) apparatus.

Molecular weight distribution were measured by high-temperature gel permeation chromatography (GPC) (GPCV-2000, water Alliance Corp.), which was equipped with a guard column (WAT054410, Water Alliance Corp.) and a filter (WAT024388, Water Alliance Corp.). The samples were dissolved in 1,2-dichlorobenzene with 0.3 g/L of antioxidant (4,4′-Thiobis(6-tert-butyl-m-cresol)) at fixed concentration (1 mg/1 mL) and eluted at 140 °C and 0.3 mL/min. The calibration was made with narrow MWD standard polystyrene.

Results

Oxidation leads to the build-up of degradation products in the material. They are easily accessible by FTIR spectrophotometry, which are the carbonyl groups (at about 1713–1722 cm^{-1}). Figure 1 compared IR absorption spectra between the initial state of virginal i-PP and after thermal degradation at 190 °C during 60 min. The heat-treated sample showed a clear absorption band at the 1715 cm^{-1} corresponding to the C=O groups. The heating time dependence of index of the C=O groups are shown in Fig. 2. It is interesting to note that the carbonyl build-up appears after 40 min. As well known, an increase of the oxygen content in polyolefin chains is discernable by FTIR immediately beyond the induction time (t_i). In this study, the degraded samples are denoted as A40, A50, and A60 according to their thermo-degradation time in min.

Figure 3 shows the molecular weight distribution curves of thermo-degraded samples at various annealing time. It should be noticed that the ordinate in the figure indicates the weight fraction of each molecular weight species in eluted polymer

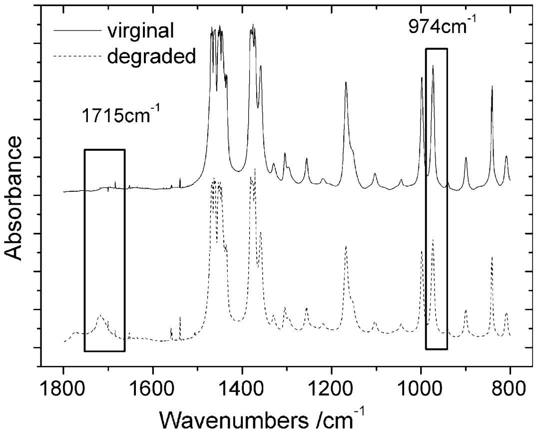
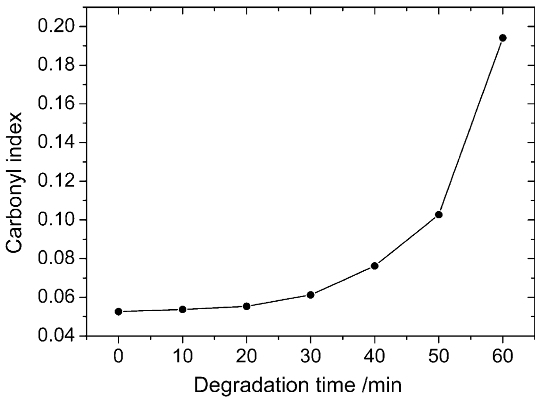


Fig. 1 IR absorption spectra in the range 800–1800 cm^{-1} of pristine i-PP and degraded specimens

Fig. 2 Carbonyl build-up of i-PP with degradation time at 190 °C



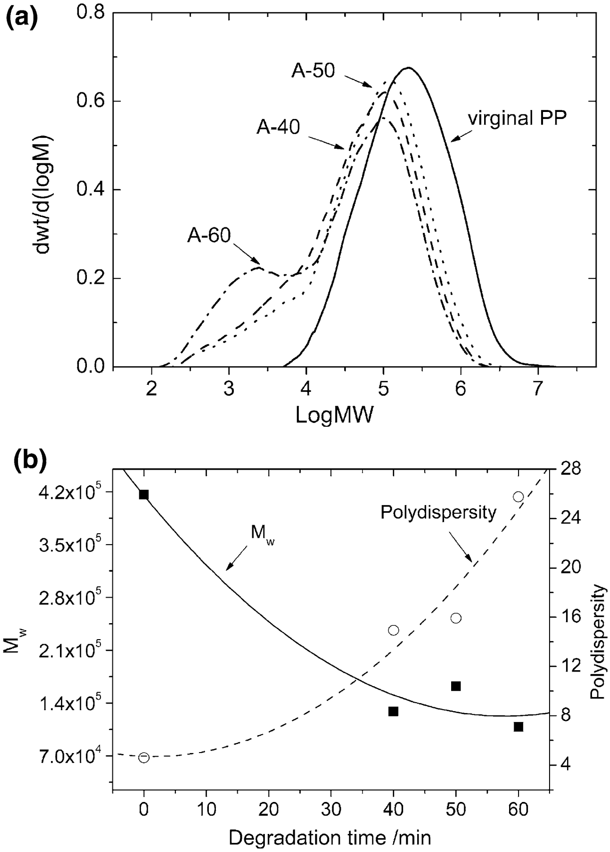


Fig. 3 **a** MWD curves of the virginal i-PP and degraded i-PP; **b** Weight average molecular weight (*open circle*) and polydispersity (*filled square*) changes with degradation time

which passed through the filter prior to the column. The total weight of polymer used for the GPC measurement is kept constant so that the area under the MWD curve is normalized. The presence of hydrogen linked to a tertiary carbon in the

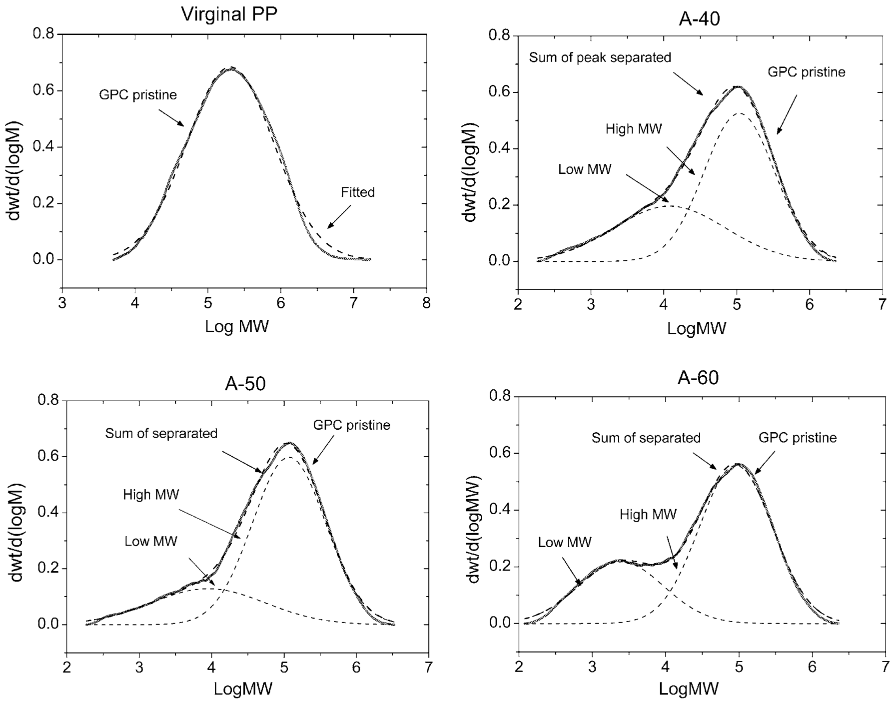


Fig. 4 Peak separation results for thermo-degradation i-PP for 40, 50, and 60 min

backbone chain causes i-PP to be degraded preferentially by chain scission with an overall shift of the MWD curve toward lower values. As shown in Fig. 3, the peak position shifted to the lower molecular weight side and the polydispersity was broadened with increasing the degradation time, suggesting the increase in the scission of polymer chains. The fragments of chains formed during scission were shorter than the original chains and so during the GPC run they were excluded from the higher molecular weight side reducing the weight fraction at this point. Meanwhile, they were retained for a longer time in the GPC columns eluting with other shorter chains, increasing the original weight fraction at this particular molecular weight, even a large amount of lower molecular weight components (log MW < 3.7) were detected for A40, A50, and A60 samples. The fresh oligomeric products are considered to be attributed to the fragments formed during chain scission.

The MWD curves of thermo-degradation i-PP can be decomposed into two peaks using the Gaussian distribution function, except for the pristine i-PP. The results of peak separation are shown in Fig. 4. The sole higher molecular weight component of pristine i-PP is separated into two portions: lower molecular component and higher molecular component for the thermo-degradation samples. As for higher molecular weight component, the peak position hardly changed and it was around 1×10^5. As for lower molecular weight component, on the other hand, the peak position gradually shifted to the lower side with increasing the degradation time.

Furthermore, it is worth note that all the peak positions of the degraded samples overstep the MWD range of pristine i-PP. Thus, the oligomeric products formed during scission contributed to the most of the lower molecular weight component.

The peak position of lower and higher components and their peak areas are plotted against the thermo-degradation time in Fig. 5. As is shown in Fig. 5, the fraction of higher molecular weight component of A40 was 30% decreased compare to the pristine i-PP. But both the peak position and fraction of higher molecular weight component hardly changed when extended the thermo-degradation time. The molecular weight of the lower component, on the other hand, decreased from log MW = 4.08 of A40 to log MW = 3.39 of A60, and the fraction was almost constant, suggesting that chain scission occurs heterogeneous during the degradation process. There are some kinetically favored scission points on the chain. Consequently, the single-modal MWD profile of pristine i-PP turns to the multi-modal profiles of degraded samples. In addition, the peak position of lower component shifted to the lower side, but no shift in the higher component. This point will be discussed in detail in next session.

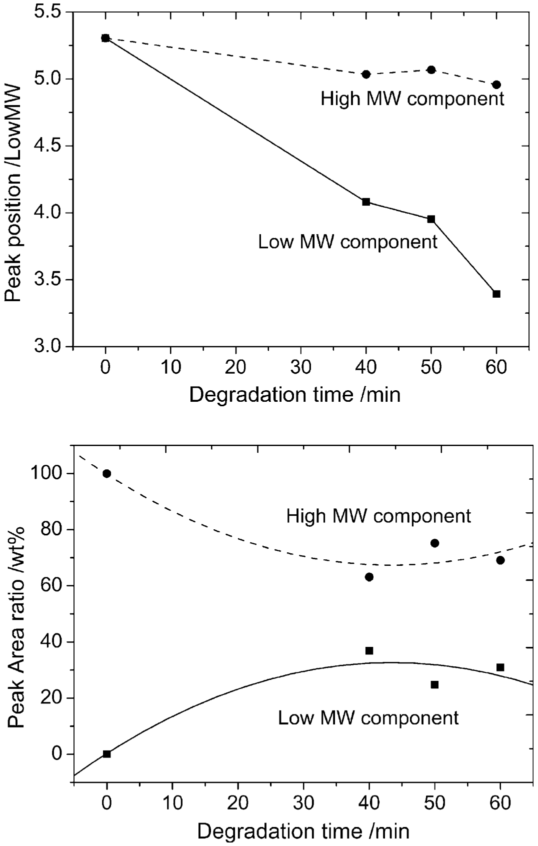


Fig. 5 Variation of peak position and peak area with degradation time at 190 °C

Discussion

The changes in MWD of the thermo-degraded samples strongly suggest that the heterogeneous degradation proceeded in this system. Here, we discuss how the chain scission propagates during the thermo-degradation of the present i-PP samples.

According to Lehrle et al. [28], when a scission at some distance (x-mer) from the end of the chain molecule occurs at time t, the weight fraction w_x of x-mer is given by

$$w_x = \frac{N_x}{N} x\alpha = x\alpha^2 (1-\alpha)^{x-1} \tag{1}$$

where α is the probability that a bond is broken at time t, N_x is the number of x-*mers*, and N is the number of all molecules. Therefore, in the case of random scission mechanism, the plot of $\ln(w_x/x)$ against $(x-1)$ leads to the consistency of the α values calculated form the intercept and the slope. If all molecules did not start to be degraded at the same time and a large amount of intact chains is retained, the degraded chains gradually increase with time. Let β be the fraction of degraded molecules at time t. Then we have

$$\beta w_x = x\alpha^2 (1-\alpha)^{x-1} \tag{2}$$

Taking logarithm of Eq. 2 leads to the following linear relation:

$$\ln(w_x/x) = 2\ln\alpha - \ln\beta + (x-1)\ln(1-\alpha) \tag{3}$$

The values of α and β can be calculated from the slope and the intercept of the $\ln(w_x/x)$ versus $(x-1)$ relation.

As shown in the GPC results, the fragment of chains formed during chain scission develops a novel shoulder on the lower molecular weight side (log MW < 3.7). Thus, the novel lower molecular weight components are the oligomers produced by the degradation. According to Eq. 3, we plot $\ln(w_x/x)$ against $x-1$ in Fig. 6. The probability of chain broken (α) and the fraction of degradation chains (β) are estimated from the slope and the intercept of the linear relation (see Table 1).

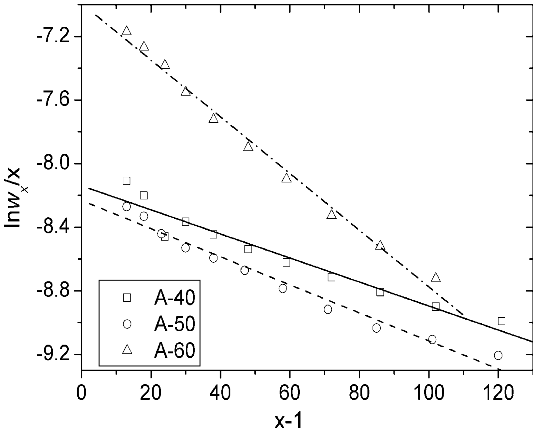


Fig. 6 $\ln(w_x/x)$ plotted against the $(x-1)$

Table 1 Probability of the chain broken (α) and fraction of degradation chains (β)

Sample	Carbonyl index	α	β
A40	0.120	0.0075	0.19
A50	0.150	0.0088	0.29
A60	0.305	0.018	0.34

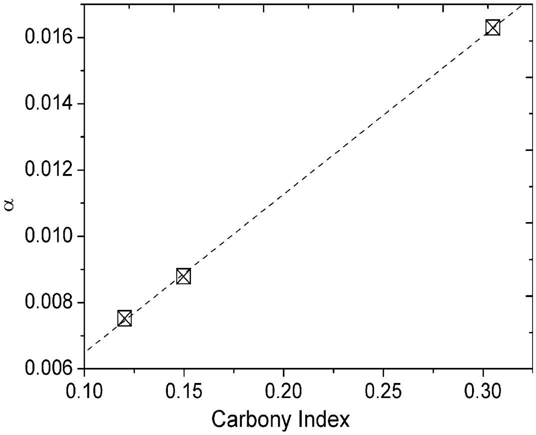
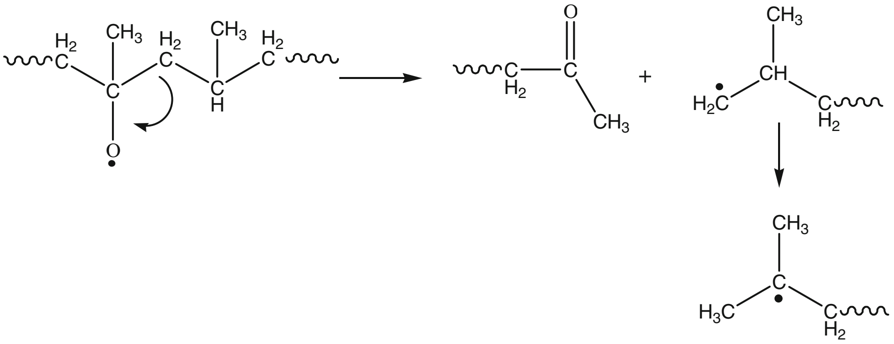
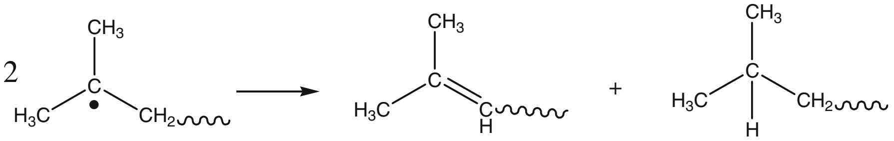


Fig. 7 α value plotted against the carbonyl index

As shown in Fig. 7, we found a linear relationship between the carbonyl index and α value. As well known, there are various paths which can lead to chain scission [29]. The linear relation in Fig. 7 implies that there are some kinetically favored scissions occurring near the oxygen-centered radicals.



Self-termination:



Sequentially, the new carbon-centered radical can reenter the oxidation cycles and leads to a further chain scission, possibly involving the self-termination reactions to the extent that severe degradation will occur. That is the reason why the peak position of lower molecular weight component shows the thermo-degradation time dependence. Furthermore, the oxidation reaction not only occurs on the secondary carbon-centered radicals formed by chain scission but also reacts with the primary volatile point on other chains. In other words, more and more chains are initiated to enter the oxidation reaction with increasing the thermo-degradation time, that is, the β value accelerated increases along with the degradation time.

Conclusion

The thermal degradation of polypropylene has been investigated under isothermal condition at 190 °C. The effect of thermo-degradation on the molecular weight and its distribution was discussed in depth. It was found that the single-modal GPC profile of the pristine i-PP turned to the multi-modal profiles of the degraded samples, which indicated that the heterogeneous degradation proceeded in this system.

Such partial thermo-degradation was estimated through the deviation from the fragmentation predicted statistically on the basis of chain scission. A linear relationship between the carbonyl index and probability of chain broken (α) was found in the paper, which indicated that there are some kinetically favored scissions occurred near the oxygen-centered radicals. In addition, the probability of chain broken can be predicted from the carbonyl index data determined by FTIR analysis.

References

1. Crawford RJ (ed) (1996) Rotational moulding of plastics, 2nd edn. Research Studies Press Ltd, England, pp 1–12
2. Billingham NC, Calvert PD (1990) In: Scott G (ed) Development in polymer stabilizations. Applied Science Publishers Ltd, London
3. Gillen KT, Wise J, Clough RL (1995) General solution for the basic autoxidation scheme. Polym Degrad Stab 47(1):149–161
4. Commereuc S, Vaillant D, Philippart JL, Lacoste J, Lemaire J, Carlsson DJ (1997) Photo and thermal decomposition of iPP hydroperoxides. Polym Degrad Stab 57(2):175–182
5. Shyichuk AV, Stavychna DY, White JR (2001) Effect of tensile stress on chain scission and crosslinking during photo-oxidation of polypropylene. Polym Degrad Stab 72(2):279–285
6. Fayolle B, Audouin L, George GA, Verdu J (2002) Macroscopic heterogeneity in stabilized polypropylene thermal oxidation. Polym Degrad Stab 77(3):515–522
7. Elvira M, Tiemblo P, Gomez-Elvira JM (2004) Changes in the crystalline phase during the thermo-oxidation of a metallocene isotactic polypropylene. A DSC study. Polym Degrad Stab 83(3):509–518
8. Suzuki S, Nakamura Y, Hasan ATM K, Liu B, Terano M, Nakatani H (2005) Dependence of tacticity distribution in thermal oxidative degradation of polypropylene. Polym Bull 54:311–319
9. Achimsky L, Audouin L, Verdu J, Rychly J, MatisovaRychla L (1997) On a transition at 80 °C in polypropylene oxidation kinetics. Polym Degrad Stab 58(3):283–289
10. Bertin D, Leblanc M, Marque SRA, Siri D (2010) Polypropylene degradation: theoretical and experimental investigation. Polym Degrad Stab 95(5):782–791

11. Cramez MC, Oliveira MJ, Crawford RJ (2002) Optimisation of rotational moulding of polyethylene by predicting antioxidant consumption. Polym Degrad Stab 75(2):321–327
12. Ciolacu CF, Choudhury NR, Dutta DK (2006) Colour formation in poly(ethylene terephthalate) during melt processing. Polym Degrad Stab 91(4):875–885
13. Oliveira MJ, Botelho G (2008) Degradation of polyamide 11 in rotational moulding. Polym Degrad Stab 93(1):139–146
14. Xu X, Ding Y, Qian Z, Wang F, Wen B, Zhou H, Zhang S, Yang M (2009) Degradation of poly(ethylene terephthalate)/clay nanocomposites during melt extrusion: effect of clay catalysis and chain extension. Polym Degrad Stab 94(1):113–123
15. Gonzalez-Gonzalez VA, Neira-Velazquez G, Angulo-Sanchez JL (1998) Polypropylene chain scissions and molecular weight changes in multiple extrusion. Polym Degrad Stab 60(1):33–42
16. Oliveira MJ, Cramez MC, Garcia CB, Kearns MP, Maziers E (2008) Effect of the processing conditions on the microstructure and properties of rotational molded polyamide 11. J Appl Polym Sci 108(2):939–946
17. Xiang Q, Xanthos M, Miltra S, Patel SH, Guo J (2002) Effect of melt reprocessing on volatile emissions and structural/rheological changes of unstabilized polypropylene. Polym Degrad Stab 77(1):93–102
18. Dintcheva NT, La Mantia FP, Scaffaro R, Paci M, Acierno D, Camino G (2002) Reprocessing and restabilization of greenhouse films. Polym Degrad Stab 75(3):459–464
19. Awaja F, Pavel D (2005) Recycling of PET. Eur Polym J 41(7):1453–1477
20. Ying Q, Zhao Y, Liu Y (1991) A study of thermal oxidative and thermal mechanical degradation of polypropylene. Die Makromol Chem 192(5):1041–1058
21. Miyagawa E, Tokumitsu K, Tanaka A, Nitta K (2007) Mechanical property and molecular weight distribution changes with photo- and chemical-degradation on LDPE films. Polym Degrad Stab 92(10):1948–1956
22. Daivd C, Trojan M, Caro A (1992) Photodegradation of polyethylene: comparison of various photoinitiators in natural weathering conditions. Polym Degrad Stab 37(3):233–245
23. Canevaro SebastiaoV (2000) Chain scission distribution function for polypropylene degradation during multiple extrusions. Polym Degrad Stab 70(1):71–76
24. Machado AV, Maia JM, Canevarolo SV, Covas JA (2004) Evolution of peroxide-induced thermomechanical degradation of polypropylene along the extruder. J Appl Polym Sci 91(4):2711–2720
25. Iedema PD, Willems C, Vliet G, Bunge W, Mutsers SMP, Hoefsloot HCJ (2001) Using molecular weight distributions to determine the kinetics of peroxide-induced degradation of polypropylene. Chem Eng Sci 56(12):3659–3669
26. Shibayama M, Imamura KY, Katoh K, Nomura S (1991) Transparency of recycled polypropylene film. J Appl Polym Sci 42(5):1451–1458
27. Hinsken H, Moss S, Pauquet JR, Zweifel H (1991) Degradation of polyolefins during melt processing. Polym Degrad Stab 34(1–3):279–293
28. Lehrle R, Williams R, French C, Hammond T (1995) Themolysis and methanolysis of poly (β-hydroxybutyrate): random scission assessed by statistical analysis of molecular weight distributions. Macromolecular 28(13):4408–4414
29. Pasquini N (2005) Polypropylene handbook, 2nd edn. Carl Hanser Verlag, Munich, pp 267–271