Thermo-Oxidative Degradation Behavior of Recycled Polypropylene

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ABSTRACT: This study has been carried out to mimic the thermo-oxidative degradation of polypropylene (co-PP) during service life and recycling. Injection molded specimens were heat aged at 130°C for different times up to maximum of 300 h to simulate the degradation of co-PP during the service life. These aged specimens were mixed with stabilizers in internal mixer and again heat aged up to 300 h. A small increase in melt flow rate (MFR) value was observed for aged co-PP but it showed large increase after recycling. The presence of carbonyl peak at 1713 cm^{-1} confirmed the oxidation of co-PP during aging and it increases with aging time. Carbonyl index (CI) is increased in recycled sample with aging, whereas oxidation induction time (OIT) decreased. The stabilizers used during reprocessing are quite effective in controlling the thermo-oxidative degradation of the polymer during processing and aging. The thermogravimetric analysis shows that the onset of degradation temperature starts at low temperature for recycled sample as compared to virgin co-PP. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3315–3320, 2011

Key words: polypropylene; recycling; aging; degradation; carbonyl index; oxidation induction time

INTRODUCTION

Polypropylene (PP) is widely used for the production of plastic materials such as medical products, bottles, food containers, ducts, chemicals tanks, etc. It is a low cost material having good processability and high mechanical properties, which turns it to be an inexpensive material as compared to other polymer resin. It is the third most important plastic in the world from sale point of view.[1] Its waste products are amongst the most visible in municipal waste due to its high volume to weight ratio and its chemically inert nature.[2] Thus PP waste is perceived as a major problem.

Recycling of co-PP has great potential, because most of its products are produced without fillers. But its degradation during processing and application affects its properties. Degradation of PP is caused by heat, light, oxygen, humidity, etc., and these affect its chemical, optical, physical, and mechanical properties thus reduce its service life.[3–5] Presently, recycling of polymeric products is limited to certain materials only, so lots are still disposed off in a landfill or incinerated. In present society, the pressure for recycling of polymer waste is increasing with passage of time. Since extraction of raw materials affects the environment, as well reduces natural resources. It is very useful for our society to recycle polymeric materials to a greater extent to replace virgin materials. But, it requires appropriate process and awareness about the properties of recycled polymeric materials, which lead to appropriate and useful application and increases the use of recycle materials. Although, the products obtained from recycled polymers are cheap and have moderate quality. Association of plastic manufacturers in Europe is limited to polymeric packaging materials to be recycled.

Thermal aging has been used to simulate degradation during service life. In this method, the material is kept in oven at elevated temperature for certain period of time. Oxidation of polypropylene during heat aging is associated with discoloration and changed its physical, chemical, optical, and mechanical behavior.[6–9]

The objective of this work is to mimic the effect of thermo-oxidative degradation of co-PP and its affect on different properties during the service life and recycling. It has been selected due to its vast applications. Commercial co-PP was injection molded into test specimen and subjected to accelerate thermal aging for different time period to model its service life. These aged specimens were re-stabilized with stabilizers and were reprocessed in internal mixer and aged again for different time period. The properties, such as melt flow rate, oxidation index, oxidation

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TABLE I
Identification Code of Aged and Recycled co-PP

Code	PP_1	PP_2	PP_3	PP_{1R1}	PP_{1R2}	PP_{1R3}	PP_{3R1}	PP_{3R2}	PP_{3R3}
Aging time (h)	100	200	300	100	200	300	100	200	300

induction time, and thermal stability were investigated before and after recycling.

EXPERIMENTAL

Materials

Polypropylene block co-polymer, Topilene (J842) supplied by Hyosung, South Korea, with melt flow rate (MFR) of 16.3 g/10 min (190°C/2.16 kg) was used. The antioxidants used were irganox 1010 and irgafos 168 from CIBA Specialty Chemical, Switzerland. Sandostab PEPQ was supplied by Clariant, Germany.

Preparation of sample

Virgin co-PP was processed in an injection molding machine (TD-800NB, China) with single screw having diameter 32 mm and L/D ratio of 22. The dimension of the 2 mm thick injection molded sample was 8 cm × 5 cm × 1.5 cm. Some injection molded material was saved as control (PP_c) for characterization. The remaining samples were divided into three sets and held at 130°C in ageing oven and were removed after 100, 200, and 300 h. Each 100 h, aging step corresponds to ~ 5 years of indoor aging based on the assumption that the thermo-oxidative aging corresponds roughly to the double of the aging rate for each 10°C rise.[10] After heat aging each set of samples were mixed with combination of antioxidants in Haake Poly Lab internal mixer at 180°C for 10 min at 50 revolutions per minute. The blended material was heat pressed into sheets using hot press at 180°C and 150 bars. Sheets were again subjected to heat aging at 130°C up to maximum 300 h. Table I shows the identification code of aged and recycled samples.

Characterization

Melt flow rate was measured at temperature 190°C under constant load of 2.16 kg using Dynisco (Model D400 1HV) according to ASTM D1238. MFR of each sample was measured five times and average values were reported.

The structure analysis of the co-PP was examined by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of the films were obtained using a FTIR spectrophotometer (Nicolet 6700, Thermo Electron Corporation) using attenuated total reflection technique with diamond crystal. The sample was scanned from 4000 to 500 cm^{-1} at the resolution of 6 cm^{-1}. The average of 132 scan was recorded.

Differential scanning calorimeter (Model Q100, TA Instruments) is used to measure oxidation induction time of the aged and recycled samples according to standard method (ISO 11357-6:2002). First, the sample was held at 50°C for 5 min and then heated from 50°C to 190°C at a heating rate of 20°C/min under a nitrogen flow of 50 mL/min. The sample was held for 5 min for equilibration, and then nitrogen gas was switched to oxygen gas at flow rate of 50 mL/min. The oxidation of the sample showed a sharp increase in heat flow due to the exothermic reaction.

The thermal behavior of the aged and recycled samples was studied by means of thermogravimetric analysis. The thermogravimetric experiments were performed using a (TGA/SDTA851, Mettler, Toledo, Switzerland) instrument under nitrogen flow (50 mL/min). Sample (7–8 mg) was heated at a heating rate of 20°C/min from ambient temperature to maximum of 600°C.

RESULTS AND DISCUSSION

Polypropylene degrades during pelletizing, storage, fabrication, service life, and recycling. All these steps lower its physico-chemical properties and can be monitored by different techniques. Thermal oxidation of PP occurs during heat aging when it was exposed to excess air at elevated temperature. The macroalkyl radicals were generated due to thermal degradation of C—H and C—C bond during polymer life and reacts with molecular oxygen. These reactions form oxygen-containing intermediate such as PO• and POO• radicals.[10] These radicals are very sensitive towards heat and responsible for thermal oxidation of PP. Wide range of products containing different functional groups such as aldehydes, ketones, carboxylic acid, ester, and γ–lactones are formed.[6]

Commercial co-PP was injection molded and oven aged at 130°C for different time period. After oven aging, these samples were reprocessed with stabilizers and aged again at the same temperature for maximum of 300 h. At each stage, melt flow rate, structural and thermal stability were monitored.

Melt flow rate

The comparison of MFR of aged and recycled sample is presented in Figure 1. It shows that the melt viscosity of PP decreases with increasing the heat aging time. The MFR of virgin co-PP (PP_c) is 16.3 and after 100 h aging it increases to 16.5. The MFR
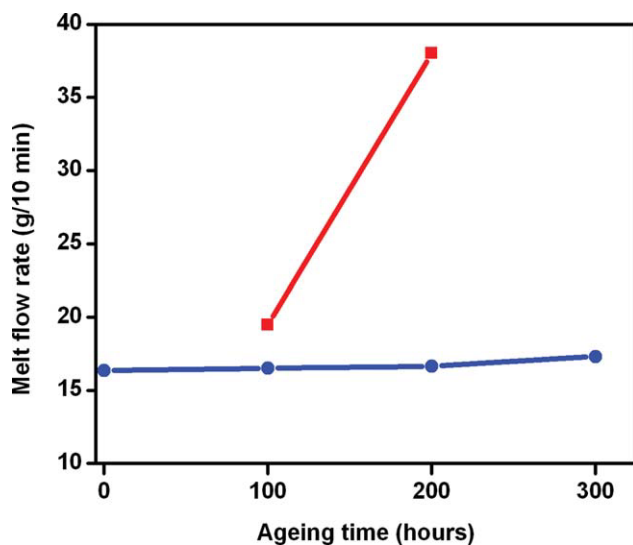
Figure 1 Comparison of MFR of aged PP (blue circle) and recycled PP$_1$ (red square). [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

of sample aged for 300 h showed 17.3. An increase of 1.0 in MFR was observed when PP$_c$ was aged for 300 h. This increase in MFR value shows that aging has a little effect on MFR. The stabilizing effect observed during aging of co-PP might be due to stabilizers added by the manufacturer. These stabilizers are quite effective during processing and aging of co-PP because they maintain its MFR.

Lower MFR value was observed in samples obtained after reprocessing of aged samples with antioxidant. Reprocessing of 100 h aged sample shows that the MFR value increased by 3.0 g for 100 h recycled sample (19.5) and double for 200 h recycled sample (38.3). The MFR value of aged PP$_1$ and recycled PP$_{1R1}$ samples at 100 h is nearly the same. These results revealed that the stabilizers incorporated during reprocessing are quite effective in controlling the thermo-oxidative degradation during processing and aging. Whereas, large increase in MRF value for 200 h recycled sample (PP$_{1R2}$) shows increase in degradation which ultimately affects molecular weight. The MFR of recycled samples PP$_{1R3}$, PP$_{3R1}$, PP$_{3R2}$, and PP$_{3R3}$ were not determined because of their high MRF values and samples become liquid at 190°C. This high increase in MFR of recycled samples might be due to the reaction of alkyl radical R$^\bullet$ generated due to thermal degradation and their reaction with oxygen and/ or cleavage leads to the decrease in molecular weight as reflected by the increase in MFR.[11]

Structural analysis

Thermo-oxidative changes during heat aging of co-PP were monitored by FTIR spectrometry and can be used for the quantification of oxidation. Gener-

ally, oxidation of polymeric material was measured by the quantification of carbonyl region in the range of 1650–1850 cm^{-1}.[12,13] The formation of asymmetrical stretching C $=$ O at 1765 cm^{-1} and symmetrical stretching C $=$ O at 1713 cm^{-1} was found in oxidized polymer sample. Figure 2 shows the IR spectra of PP$_c$, PP$_{inj\ molded}$, and PP$_3$. The IR spectrum of PP$_c$ shows a small carbonyl peak at 1713 cm^{-1} and this peak was disappeared in injection molded specimen. This peak might be from the stabilizer added by the manufacturer, which were consumed during processing. No carbonyl peak was observed in the infrared spectra of 100 h (PP$_1$) and 200 h (PP$_2$) aged samples. Whereas, spectrum of 300 h aged (PP$_3$) sample shows a small peak in the carbonyl region indicating the starting of the oxidation of PP.

Figure 3(a) presents FTIR spectra of recycled sample of PP$_1$. A weak peak is observed in PP$_{1R1}$ and its intensity increases gradually as aging time increases from 200 h (PP$_{1R2}$) to 300 h (PP$_{1R3}$) which shows faster thermal oxidative degradation rate in recycled samples. Figure 3(b) shows similar behavior for recycled samples obtained after reprocessing of PP$_3$ (PP$_{3R1}$, PP$_{3R2}$, and PP$_{3R3}$).

The intensity of the carbonyl peak to that of an internal reference peak can be used to measure extent of polymer oxidation called carbonyl index. It can be calculated from FTIR spectrum by using the ratio of area of carbonyl peak at 1713 cm^{-1} (corresponding to carbonyl C $=$ O groups) and a reference peak at 1376 cm^{-1} (corresponding to C—H bending vibration of methyl group) which is independent of specimen degradation. Carbonyl index can be calculated by using following formula:

$$\text{Carbonyl index(CI)} = OA/ON$$

where OA is the area of carbonyl peak from 1650 to 1850 cm^{-1}, and ON is range from 1315 to
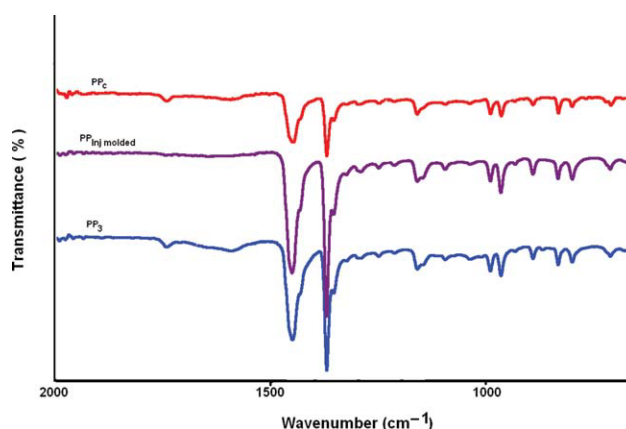

Figure 2 FTIR spectra of PP$_c$, PP$_{inj\ molded}$, and PP$_3$ samples in the 2000–600 cm^{-1} region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 Oxidation induction time curves for PP_c (black square), PP_1 (violet diamond), PP_2 (green star), and PP_3 (red circle) sample measured at 190°C in oxygen (50 mL/min) at a rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
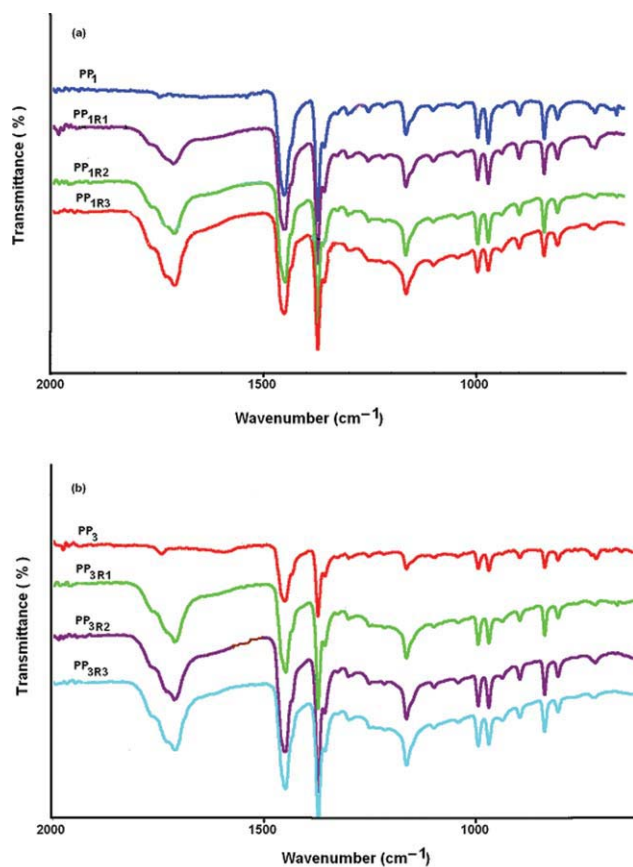
Figure 3 Evaluation of infrared spectra of recycled PP_{1R} (a) and recycled PP_{3R} (b) sample at different aging time in the 2000–600 cm^{-1} region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1420 cm^{-1}.[14] The reprocessing of PP_1 and its subsequent oven aging leads to an increase in CI. The CI for PP_{1R1}, PP_{1R2}, and PP_{1R3} is 0.97, 1.47, and 2.07, respectively. A pronounced increase in CI value was observed during the recycling of 300 h aged PP. The CI of 100 h recycled sample (PP_{3R1}) was 1.55 which was increased to 1.99 for 200 h recycled sample (PP_{3R2}). PP_{3R3} showed maximum CI of 2.30. The increase of CI with aging time shows that co-PP undergoes oxidation reactions. These oxidative reactions followed by degradation of polypropylene as observed by MRF.

Oxidation induction time

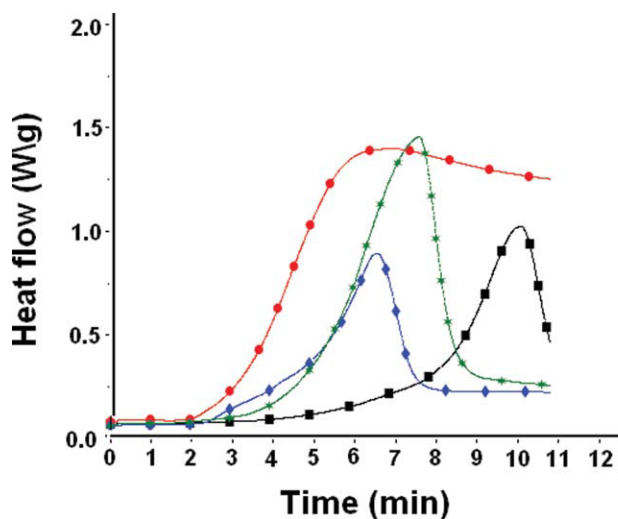Oxidation induction time is used to measure the thermal oxidative stability of polymeric material.

Longer OIT value shows that material is more stable against oxidative degradation.[15,16] Table II shows the OIT values, and Figure 4 shows the OIT curve of co-PP samples when the atmosphere was changed from nitrogen to oxygen.

It shows that PP_c has OIT value of 7.97 min. This high OIT value indicates that virgin PP contains adequate stabilizers which hinder the oxidation of virgin PP. Whereas PP_1, PP_2, and PP_3 have OIT value 5.67, 4.95, and 4.66 min, respectively. This shows that there is decrease in oxidation stability in aged sample with increasing aging time from 0 h to 300 h. This might be due to utilization of the stabilizer during aging. The OIT for recycled PP_{1R1} sample (5.73 min) is nearly equal to PP_1 aged sample (5.67 min). This shows that the stabilizer added during reprocessing were quite effective in controlling the thermo-oxidative reactions. Further aging lowers the OIT to 2.35 min for PP_{1R2} and 0.80 min for PP_{1R3}. This shows that the stabilizers used during reprocessing initially control the thermal degradation of the recycled sample and maintain its OIT as observed in case of PP_{1R1}. This stabilizer system can improve the serviceability and usability of the recycled co-PP. Further aging caused deactivation of the stabilizers and lowered its OIT. The OIT value of

TABLE II
Oxygen Induction Time and Melting Temperature of Control, Aged, and Recycled co-PP

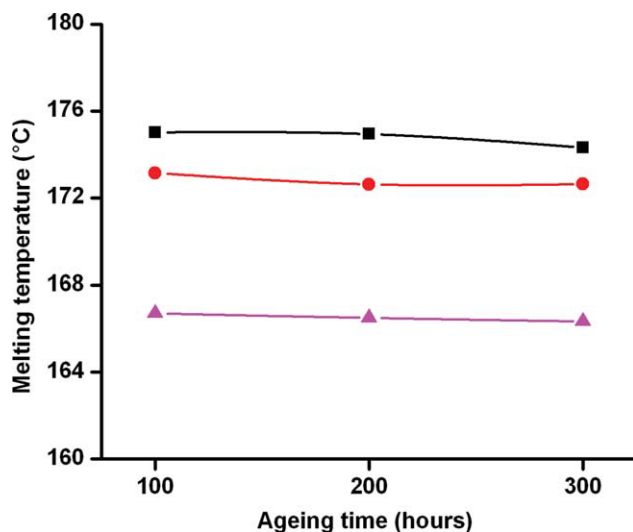| Code	PP_c	PP_1	PP_2	PP_3	PP_{1R1}	PP_{1R2}	PP_{1R3}	PP_{3R1}	PP_{3R2}	PP_{3R3}
OIT (°C)	7.97	5.67	4.95	4.66	5.73	2.35	0.80	0.27	0.26	0.17
T_m (°C)	176.1	175.0	175.4	174.9	173.2	172.6	172.6	166.7	166.5	166.3

Figure 5 Melting temperature of aged PP$_1$ (black square), recycled PP$_{1R}$ (red circle), and PP$_{3R}$ (pink triangle) samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 Thermogravimetric curves of PP$_c$, PP$_3$, PP$_{1R1}$, and PP$_{1R3}$ in nitrogen at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

less than one was observed in PP$_{3R}$ samples and after 300 h aging it was lowered to 0.17 min.

The melting temperature (T_m) of aged and recycled samples is shown in Figure 5. It can be seen from this figure that T_m is insensitive to the aging time in all cases. The T_m of PP$_c$ is 176.1°C and after 300 h aging it reduces to 174.9°C. This small decrease in T_m shows that degradation reactions occur in the amorphous region of the co-PP. Similar behavior in T_m was observed in PP$_{1R3}$ and PP$_{3R3}$. This lowering in T_m in recycled sample further confirms the occurrence of thermo-oxidative degradation.

Thermal gravimetric analysis

Figure 6 shows the TGA curves of PP$_c$, PP$_3$, PP$_{1R1}$, and PP$_{1R3}$. It can be seen from this figure that the onset of degradation temperature (T_{onset}) for control sample (PP$_c$) is around 427°C and it decreases to 377°C in 300 h aged co-PP (PP$_3$). This shows that the thermo-oxidative treatment given to the samples during aging cause chain scission of PP. This in turn decreases the average molecular weight of PP and lowers its thermal stability as observed in Figure 6. The T_{onset} for recycled sample aged for 100 h (PP$_{1R1}$) and 300 h (PP$_{1R3}$) was 412°C and 398°C, respectively. By comparing PP$_{1R1}$ with PP$_3$,
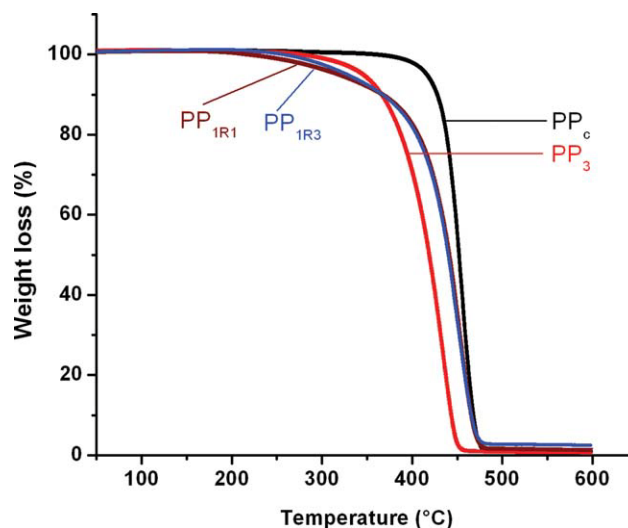
an improvement of 35°C was observed in T_{onset} of PP$_{1R1}$. The introduction of stabilizer during recycling also influenced the rate of degradation.

Table III presents the temperature of the sample at different percentage of weight loss. PP$_c$, showed 5% weight loss at 418°C and it was lowered to 347°C after 300 h aging. In recycled samples, the thermal degradation temperature at 5% weight loss was further lowered. This lowering of temperature in recycled samples confirmed the presence of low molecular weight volatizing products. Thermal degradation temperature at 10% weight loss for control sample was 429°C, and for PP$_3$, it was lowered to 369°C. The temperature at 10% weight loss for PP$_{1R1}$ and PP$_{1R3}$ is 372°C and 368°C, respectively. The increased weight loss in aged and recycled samples at lower temperature showed that thermo-oxidative aging produce low molecular weight products which volatilize at lower temperature.

CONCLUSIONS

In conclusion, thermo-oxidative degradation of co-PP during aging greatly affects its molecular weight and primary structure. The thermo-oxidative treatment induced changes in molecular weight and polymer structure resulting an increased MFR and

TABLE III
Thermal Degradation Temperature Profile of Control, Aged, and Recycled Sample

Sample	$T_{on\ set}$ (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)
PP$_c$	427	418	429	454	469
PP$_3$	377	347	369	421	445
PP$_{1R1}$	412	318	372	442	465
PP$_{1R3}$	398	313	368	439	466

decrease long-term stability. Lowest MFR was observed for aged co-PP as compared to recycled one. Similarly, carbonyl index was increased in recycled sample with aging, whereas oxidation induction time decreased. The thermogravimetric analysis shows that the onset of degradation temperature starts at low temperature for recycled sample as compared to virgin co-PP. During and after recycling, the thermo-oxidative degradation of co-PP can be controlled by incorporation of proper stabilizers. It also increased the OIT of the recycled polymer showing that the stabilizer system used in this study is quite effective. In this way, serviceability and the usability of the recycled co-PP can be improved using this stabilizer system.

References

1. Zebarjad, S. M.; Sajjadi, S. A.; Tahani, M. J Mater Process Tech 2006, 175, 446.
2. Papaspyrides, C. D.; Poulakis, J. G. In: The Polymeric Materials Encyclopedia; Salomone, J. C. Ed.;CRC Press Inc: New York, 1996; p 7403.
3. Boldizar, A.; Gevert, T.; Markinger, M. Polym Recycling 1995, 1, 249.
4. Vasile, C.; Odochian, L.; Agherghinei, I. J Polym Sci Part A: Polym Chem 1988, 1639, 26.
5. Manabe, N.; Yokota, Y.; Nakatani, H.; Suzuki, S.; Liu, B.; Terano, M. J Appl Polym Sci 1831, 2006, 100.
6. Gächter, R.; Müller, H.; Plastics Additives Handbook, 4th ed.; Hanser: Munich, 1993.
7. Fearon, P. K.; Marshall, N.; Billingham, N. C.; Bigger, S. W. J Appl Polym Sci 2000, 79, 733.
8. Incarnato, L.; Scarfato, P.; Gorrasi, G.; Vittoria, V.; Acierno, D. Polym Eng Sci 1999, 39, 1661.
9. Kartalis, C. N.; Papaspyrides, C. D.; Pfaendner, R.; Hoffmann, K.; Herbst, H. J Appl Polym Sci 1999, 73, 1775.
10. Jansson, A.; Möller, K.; Gevert, T. Polym Degrad Stab 2003, 82, 37.
11. Zweifel, H.; Stabilization of Polymeric Materials; Springer-Verlag: Berlin, 1998.
12. Nagy, E. V.; Li, S. A.; Trans Soc Biomater 1990, 13, 109.
13. Gillis, A. M.; Furman, B. D.; Li, S.; Trans Orthop Res Soc 1998, 23, 359.
14. Kurtz, S. M.; Muuratoglu, O. K. Biomater 2001, 22, 2875.
15. Yang, M. S.; Gao, X. W. Polym Degrad Stab 2008, 93, 1467.
16. Edidin, A. A.; Jewett, C. W.; Kwarrteng, K.; Kalinowski, A.; Kurtz, S. M. Biomater 2002, 21, 451.