Quantitative Structure Activity Relationship Analysis of Polypropylene during Ultraviolet Aging Based on Tensile Strength

Kui Chen¹, Tianyun Zhang²*, Guangqiao Liu³ and Xiaoping Zheng³

¹School of Bailie Mechanical Engineering, Lanzhou City University, Lanzhou, China
²School of Electronic and Information Engineering, Lanzhou City University, Lanzhou, China
³School of Bailie Petroleum Engineering, Lanzhou City University, Lanzhou, China

*Corresponding author e-mail: 1030220915@qq.com

Abstract. In order to improving ultraviolet radiation (UV) aging resistance of polypropylene (PP) and expanding its application range, it is necessary to research the rule and mechanism of PP in UV aging process. On the base of Fourier transform infrared spectroscopy and differential scanning calorimetry characterization, the variations of structure parameter (crystallinity and carbonyl index) of homo-PP corresponding to different UV aging time were calculated and analyzed. Combined with tensile strength testing, the influences of both crystallinity and carbonyl index on tensile strength in UV aging process of PP were researched. Then the relationship formula between tensile strength and structure parameter was constructed based on linear relationship, and the quantitative structure-activity relationship of PP during UV aging was analyzed. The results show that, with the extending of aging time, the influence of crystallinity on tensile strength of PP declines, while that of carbonyl index is on the contrary. During UV aging, the tensile strength of PP rises slightly with the increase of crystallinity first, then acceleratedly declines for the increase of carbonyl index. It should be noted that, although the crystallinity of PP begins to decline after 100 h UV aging, its effect to tensile strength can’t be ignored while aging time is less than about 300 h.

1. Introduction

Owing to abundant source, low price and density, high comprehensive mechanical properties, and good processability, polypropylene (PP) is now been widely applied in many fields[1]. However, PP is easy to age caused by ultraviolet light and oxygen[2]. Accordingly, in order to improving ultraviolet radiation (UV) aging resistance of PP and expanding its application, it is necessary to research the rule and mechanism of PP in UV aging process.

In recent decades, the main method to analyze photo-oxidation aging of PP is studying the variation of carbonyl index since the reaction of decomposing hydroperoxides into carbonyl groups predominates its UV aging process[3]. However, literature [4] indicates that the photo-oxidation aging of PP can be divided into physical aging and chemical aging. The break of molecular chains and crystal rearrangement of fragments belong to the former, and the forming of new chemical groups in aging process belongs to the latter. Hence, crystallinity is also an important structure parameter used to
characterize aging behavior of semi-crystalline PP. And it is needed to analyze UV aging behavior of PP with crystallinity and carbonyl index together. In this research, we will present variation rules of tensile strength, crystallinity and carbonyl index of PP during photo-oxidation ageing, and quantitative analyze the influences of both crystallinity and carbonyl index on tensile strength of PP based on linear relationship. These are helpful for industrial application of PP.

2. Experiments

2.1. UV accelerated aging experiment
Raw materials and specific experiments of UV accelerated aging see literature [1].

2.2. Tensile strength test
Specific test equipment and process of tensile strength see literature [5].

2.3. Fourier transform infrared spectroscopy characterization
The chemical bonds of all specimens were evaluated by a Nicolet AVATAR 360 FTIR.

2.4. Differential scanning calorimetry characterization
The reheating process of all specimens were measured by DSC (TA Company, Q-10), and specific testing method see literature [1].

3. Results and discussions

3.1. Carbonyl index
Fourier transform infrared (FTIR) spectra of PP corresponding to different UV aging time are shown in Fig. 1. Obviously, the stretching vibration absorption peak of C=O bond located in 1730 cm⁻¹ becomes stronger significantly with the increase of aging time. Regarding bending vibration absorption peak of -CH bond located in 2720 cm⁻¹ as internal standard, the carbonyl index (CI) is obtained by the following equation.

\[ CI = \frac{A_{1730}}{A_{2720}} \]  

where \( A_{1730} \) is the integral area of C=O absorption peak located in 1730 cm⁻¹, \( A_{2720} \) is that of internal standard peak area located in 2720 cm⁻¹. The relationship between carbonyl index and aging time of PP can be obtained by Equation (1) according to Fig. 1, and the results are shown in Fig. 2. Under the work of ultraviolet light and oxygen, PP molecular chains will break due to photo-oxidation degradation, and produce free radicals or excited state molecules accordingly, which will generate hydroperoxides. The hydroperoxides are unstable and can be decomposed spontaneously into carbonyl groups. While carbonyl groups can absorb ultraviolet light strongly in the wavelength range from 260 nm to 340 nm, and make molecular chains of PP further rupture which will drive the increase of carbonyl content further [6]. Therefore, as showed in Fig. 2, carbonyl index acceleratedly increases with the prolonging of aging time.

![Figure 1. FTIR Spectra of PP corresponding to different aging time.](image1)

![Figure 2. Carbonyl index of PP corresponding to different aging time.](image2)
3.2. Crystallinity

The crystallinity \((C)\) is calculated by the Equation (2).

\[
C = \frac{\Delta H_m}{\Delta H_m^0} \times 100\%
\]  

where \(\Delta H_m\), in J/g, is the melting enthalpy of polymer which can be expressed by the area of endothermic peak in the melting heating differential scanning calorimetry (DSC) curve, and \(\Delta H_m^0\), determined as 187.7 J g\(^{-1}\) according to reference [7], is that of polymer with 100% crystallinity. According to the second melting heating DSC curves [1]. The relationship between crystallinity and UV aging time of PP is calculated by Equation (2). As shown in Fig. 3, with the extending of UV aging time, the crystallinity of PP increases first then declines gradually.

Figure 3. Crystallinity of PP corresponding to different aging time.

The crystallinity of PP, rise first and then decline, is the results of competition between two factors [8-10]. On the one hand, compared with crystalline region of semi-crystalline PP, it will be easier for oxygen permeation in amorphous region. And partial entangled molecular chains of PP located in amorphous region will break under ultraviolet light illumination, which not only leads to the decline of molecular weight, but also makes the rearrangement of fragments easier and causes lower temperature recrystallization due to the reduction of chain entanglement concentration. On the other hand, the tacticity of molecular chains located in crystalline region of PP will be destroyed till ultimate decomposition by the photo-oxidative degradation. Combined with Fig. 3, it can be seen that the recrystallization plays an dominant role at the early stage of UV aging, while molecular chains break is dominant after 100 h aging.

3.3. Tensile strength

Fig. 4 is the tensile strengths of PP corresponding to different aging time are shown. It can be seen that with the extending of aging time, the tensile strength of PP rises slightly first, then declines, and gets to the highest when aging time reaches 100 h.

The variation of tensile strength with both crystallinity and carbonyl index are shown in Fig. 5. Combined with Fig. 5 and the analysis above, it is obtained that in the early stage of aging (less than 100 h), although the crystallinity of PP increases obviously because recrystallization rate in amorphous region is faster than that of decomposition in crystalline region, the tensile strength has only a slight increase for molecular chains break in amorphous region, tacticity decline in existed crystalize region and the existing of many defects in new generated crystalize region. The crystallinity of PP increases by 21.6% corresponding to 100 h aging, while the tensile strength increases only by 4.7%. With the further extending of aging time (over 100 h), the characteristic of strong absorption ultraviolet light of carbonyl accelerates the photo-oxidation degradation. Which not only speeds up the break of random
molecular chains further, but also makes the decomposition of existed crystalline region faster than the formation of new crystalline region. Accordingly, the tensile strength of PP begins to decline more sharply. After 400 h UV aging, the tensile strength decreases to 30 %.

**Figure 4.** Tensile strength of PP corresponding to different UV aging time.

**Figure 5.** Variation of tensile strength with both crystallinity and carbonyl index of PP.

### 3.4. Quantitative influences of both crystallinity and carbonyl index on tensile strength

According to the analysis above, the tensile strength of PP changes with structure parameter crystallinity and carbonyl index. Generally, the higher crystallinity and lower carbonyl index lead to higher tensile strength. In order to illustrate the influences of both crystallinity and carbonyl index on tensile strength quantitatively, taking just the influences of both crystallinity $C$ and the inverse of carbonyl index $CI^{-1}$ on tensile strength $\sigma$ to be linear, Equation (3) is constructed.

$$\sigma = aC\% + bCI^{-1}$$

(3)

where $a$ and $b$ are defined as influence coefficients of crystallinity and carbonyl index to tensile strength respectively. By substituting $\sigma$, $C$ and $CI$ corresponding to two neighboring aging time $t_1$ and $t_2$ into Equation (3), linear equations of two variables are established. And $a$ and $b$ solved by this linear equations can be regarded respectively as influence coefficients of crystallinity and carbonyl index to tensile strength corresponding to aging time $(t_1 + t_2)/2$. Accordingly, the variations of both $a$ and $b$ with aging time are given in Fig. 6.

**Figure 6.** Variation of influence coefficients of both crystallinity and carbonyl index with aging time.

Fig. 6 shows that, with the extending of aging time, $a$ declines obviously while the result is just contrary to $b$. Therefore, the influence of crystallinity on tensile strength declines with the prolonging of aging time, while that of carbonyl index to tensile strength is on the contrary, which is
consistent with the analysis above. The above conclusion indicates that Equation (3) established can be used in quantitative structure activity relationships analysis in UV aging process of PP. Fig. 6 also shows that, although the crystallinity begins to decline after 100 h aging, its influence on tensile strength should not be ignored until aging time is about 300 h.

4. Conclusion

During UV aging, the tensile strength of PP rises slightly first for the increase of crystallinity, then declines quickly for the accelerated photo-oxidation degradation induced by carbonyl. And the tensile strength of PP decreases to 30 \% after 400 h UV aging.

Through proposing influence coefficients of structure parameter crystallinity and carbonyl index to tensile strength respectively, the relation equation between tensile strength and structure parameter is established based on linear relationship. And the quantitative structure activity relationships in UV aging process of PP is analyzed by the equation established. Although the crystallinity of PP begins to decline when aging time exceeds 100 h, its influence on tensile strength should not be ignored until aging time is about 300 h.

5. Acknowledgments

The article was financially supported by No. 51865025 of the National Natural Science Foundation of China, No. 18JZ3RA223, 218, 230 of the Gansu Natural Science Foundation, No. 2018D-19 of the Scientific Research Project of Bureau of Gansu Education, No. 114 of Talent Innovation and Entrepreneurship Project Lanzhou.

References

[1] Chen K, Zhang T Y and Zhang Z R, Variation and grey GM(1, 1) prediction of melting peak temperature of polypropylene during ultraviolet radiation aging, IOP Conference Series: Materials Science and Engineering, 281 (2017) 225-229.
[2] Kotek J, Kelnar I, Baldrian J and Raab M, Structural transformations of isotactic polypropylene induced by heating and UV light, Eur. Polym. J., 40 (2004) 2731-2738.
[3] Zhang T Y, Chen K, Zhang Z R and Shi R, Quantitative relationship between melting peak temperature and carbonyl index of polypropylene during UV aging based on date fitting, IOP Conf. Series: Materials Science and Engineering, 322 (2018) 94-98.
[4] Leong Y W, Abu Bakar M B, Mohd Ishak Z A and Ariffin A, Characterization of talc/calcium carbonate filled polypropylene hybrid composites weathered in a natural environment, Polym. Degrad. Stab., 83 (2004) 411-422.
[5] Zhang T Y, Chen K, Liu G Q and Zheng X P, Injection molding process optimization of polypropylene using orthogonal experiment method based on tensile strength, IOP Conference Series: Materials Science and Engineering, 612(2019)1416-1420
[6] Norman S A, Michele E, Amaya A, Gonzalo S, Christopher M L, Verran J, Stratton J, McIntyre R B, Degradation and stabilization of polymers and coatings: nano versus pigmentary titania particles, Polym. Degrad. Stab., 85 (2004) 927-946.
[7] Yang R C, Wu L, Niu S R and Ma J Z, Thermal-oxidative aging kinetics of montmorillonite/polypropylene nanocomposites, Acta Metallurgica Sinica, 27 (2010) 70-75.
[8] Rabello M S and White J R, The role of physical structure and morphology in the photodegradation behaviour of polypropylene, Polym. Degrad. Stab., 56 (1997) 55-73.
[9] Xu L X and Zhong M Q, Study on the effect of nano-TiO₂ on UV aging resistance of polypropylene, J. Zhejiang Univ. Techno., 34 (2006) 302-305.
[10] Obadal M, Čermák R, Raab M, Verney V, Commercure S and Fraïssé F, Structure evolution of α- and β-polypropylenes upon UV irradiation: A multiscale comparison, Polym. Degrad. Stab., 88 (2005) 532-539.