

Quantitative relationship between melting peak temperature and carbonyl index of polypropylene during UV aging based on date fitting

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Abstract. In order to study the quantitative relationship of melting peak temperature (T_m) and structure parameter carbonyl index (CI) of polypropylene (PP) in the ultraviolet (UV) aging process, the T_m of PP change along with CI in UV aging process was fitted directly by using exponential decay function, and indirectly by using both polynomial and exponential decay function through taking aging time as intermediate variable. The results show that, both aging time and T_m decay exponentially with CI , and correlation coefficients of fitting curve obtained increase as the order of exponential decay functions increases. Compared with others, the fifth order polynomial is better in fitting the variation of T_m with aging time. The standard deviations of T_m between test value and calculated value obtained by formulas coming from direct and indirect fitting are 0.2024 and 0.1508 respectively, and the maximum relative errors are 0.20% and 0.16% respectively. The above solution shows that both formulas obtained by direct and indirect fitting can be used in quantitative analysis of T_m and CI , and the latter has a better fitting effect although its form is complex.

1. Introduction

As one of the most widely used general plastic, polypropylene (PP) has the advantages of abundance in raw material, low price, excellent mechanical properties et al. But poor ageing resistance under the influence of ultraviolet light and oxygen leads to properties of PP and its products decline, which limits the application of PP on outdoor products greatly [1, 2]. Therefore, it will be of significance to modification research of PP and prolonging its service life that studying the variation rules of structure and property and quantitative structure-property relationship during ultraviolet (UV) aging.

Deriving from the need of application, current research of aging behavior mainly focuses on mechanical properties. But researches have shown that Photo-oxidative degradation of semi-crystalline PP not only leads to the increase of amorphous form on crystal surface until the regularity of chain is destroyed and crystallinity decreases, but also makes molecular chains located in amorphous region rupture which causes the decline of molecular weights [2, 3]. Thus melting peak temperature (T_m) of PP is an important performance index for its UV aging behavior evaluation since it will move in low temperature region with the prolonging of aging time accordingly. Furthermore, it is widely acknowledged that hydroperoxides decomposition into carbonyl groups predominates UV



aging process of PP [4-6], and studying the variation of carbonyl index (CI) is the main way currently to analyze UV degradation degree of PP.

Based on the background mentioned above, quantitative relationship curve between T_m and CI of PP during UV aging was fitted by Origin software in this paper. The date connected was collected by the following method. PP supplied by Gansu Langang Petrochemical Co. Ltd., is illuminated at room temperature by a 20 W UV lamp with about 20 cm distance, and then taken out for DSC and FTIR characterization after regular time intervals. The T_m is obtained by endothermic peak in reheating curve of DSC. And CI is determined according to the area ratio of C=O stretch vibration absorption and -CH bending vibration absorption in FTIR spectrum.

2. Direct fitting of carbonyl index and melting peak temperature

Figure 1 gives the fitting curves of T_m change along with CI during UV aging of PP. It can be seen that T_m of PP will decay exponentially with CI , and the higher the order number of exponential decay function, the bigger the correlation coefficient becomes, and the better the fitting effect is. The correlation coefficient reaches 0.99427 when the order number of exponential decay function is three. Bring specific parameters obtained via fitting into third order exponential decay function, quantitative relationship formula about T_m and CI is determined as following

$$T_m = 153.32972 + 13.66448e^{-CI/1.32809} - 9.98592e^{-CI/0.93679} + 8.31147e^{-CI/35.28468} \quad (1)$$

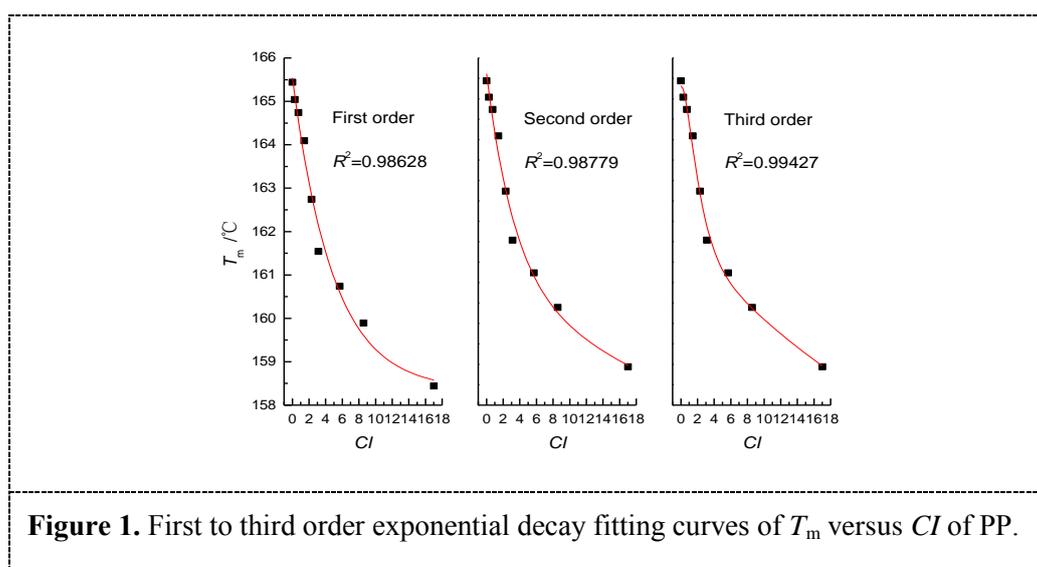


Figure 1. First to third order exponential decay fitting curves of T_m versus CI of PP.

3. Indirect fitting of carbonyl index and melting peak temperature

In order to further improve fitting effect, regarding aging time as intermediate variable, quantitative relationship of PP between T_m and CI was determined indirectly via fitting relationship curves of T_m change along with aging time and aging time with CI .

A second or higher order polynomial fitting method is proposed to show the decline of T_m over aging time since there existing a certain discreteness in the declining date. Figure 2 is second to seventh order polynomial fitting curves of T_m with UV aging time of PP. It can be found that correlation coefficient of regression fitting curve increases with the increase of polynomial order. When the order is up to seven, correlation coefficient reaches 0.99995 and standard deviation is 0.04936. But the stability of curve declines with the increase of order. Especially, when the order of polynomial is higher than five, fitting curve appears strong jitter and shows strong instability. Hence, from the point of ensuring higher correction coefficient, lower standard deviation and reducing the influence of high order terms, fifth order polynomial with correction coefficient 0.99955 and standard deviation 0.0864 is selected as fitting formula as following

$$T_m = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5 \tag{2}$$

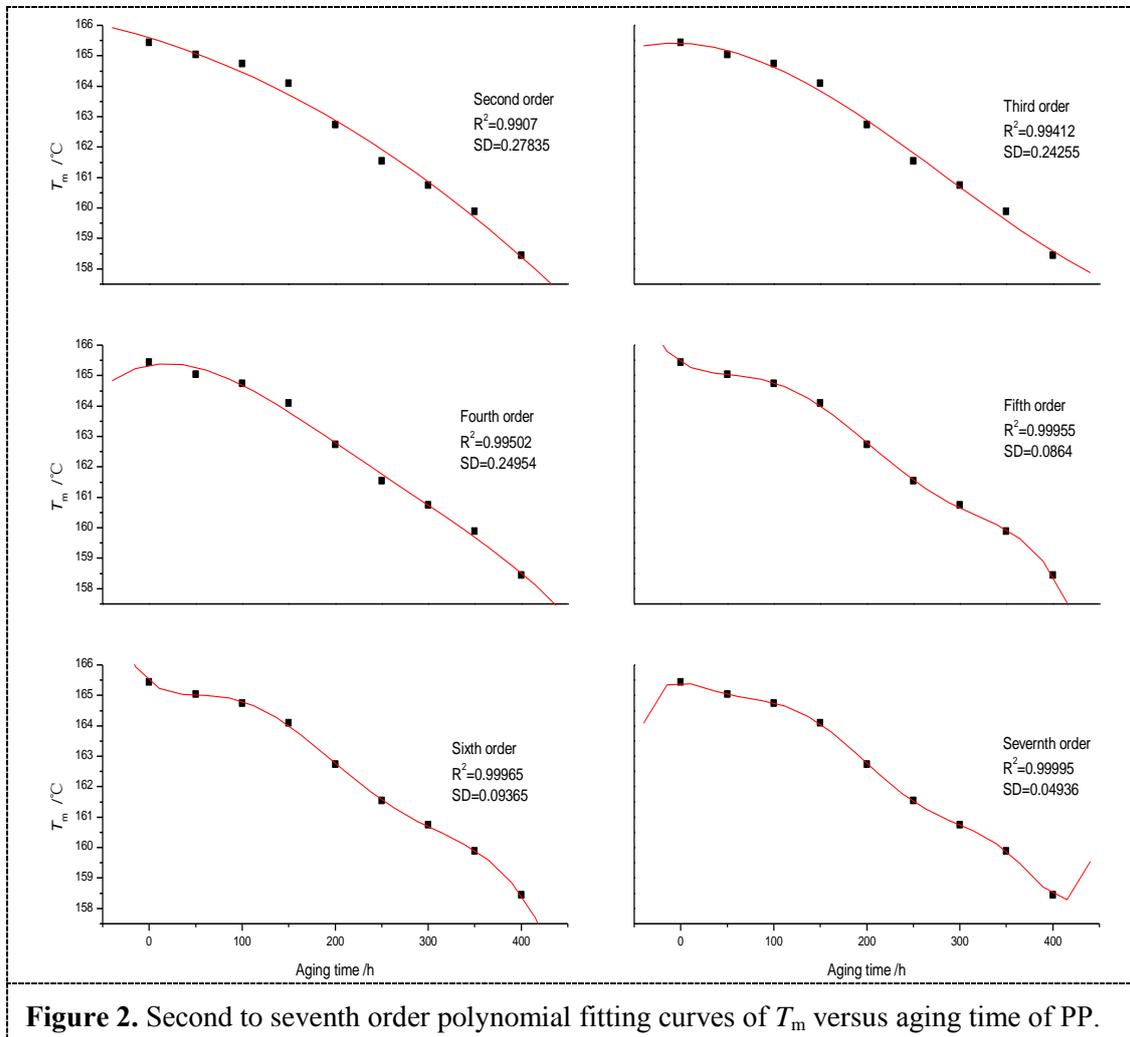


Figure 2. Second to seventh order polynomial fitting curves of T_m versus aging time of PP.

In order to eliminate aging time and obtain quantitative relationship formula of T_m change along with CI , a scatter plot diagram of aging time versus CI is made. Figure 3 is first to third order exponential decay fitting curves of UV aging time with CI of PP. It can be seen that aging time of PP will decay exponentially with CI , and the higher the order number of exponential decay function, the bigger the correlation coefficient becomes. The correlation coefficient reaches 0.99838 when the order number of exponential decay function is three. Therefore, regarding third order exponential decay function as quantitative relationship formula of UV aging time change along with carbonyl index, and substituting it into Formula (2), quantitative relationship formula of T_m versus CI is determined as Formula (3). The values of parameters in Formula (3) are shown in Table 1.

$$T_m = a_0 + a_1(t_0 + d_1e^{-CI/A_1} + d_2e^{-CI/A_2} + d_3e^{-CI/A_3}) + a_2(t_0 + d_1e^{-CI/A_1} + d_2e^{-CI/A_2} + d_3e^{-CI/A_3})^2 + a_3(t_0 + d_1e^{-CI/A_1} + d_2e^{-CI/A_2} + d_3e^{-CI/A_3})^3 + a_4(t_0 + d_1e^{-CI/A_1} + d_2e^{-CI/A_2} + d_3e^{-CI/A_3})^4 + a_5(t_0 + d_1e^{-CI/A_1} + d_2e^{-CI/A_2} + d_3e^{-CI/A_3})^5 \tag{3}$$

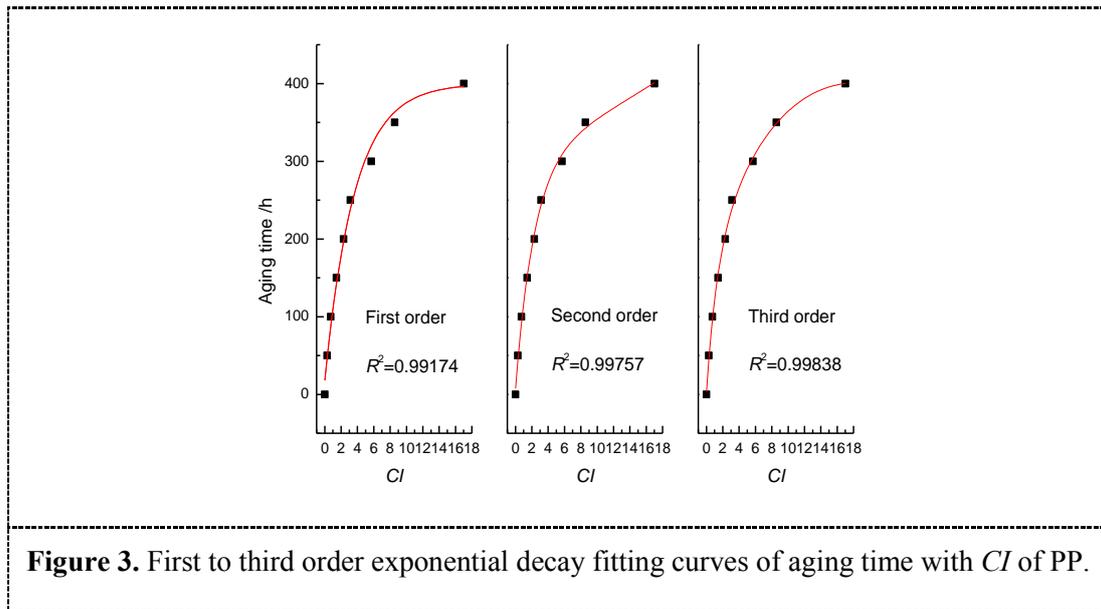


Figure 3. First to third order exponential decay fitting curves of aging time with CI of PP.

Table 1. Values of parameters in Formula (3).

| Polynomial coefficient | | | | | | |
|------------------------|---------------------------|--------------------------|---------------------------|--------------------------|----------------------------|----------|
| a_0 | a_1 | a_2 | a_3 | a_4 | a_5 | |
| 1.65438×10^2 | -1.89400×10^{-2} | 3.56608×10^{-4} | -3.24091×10^{-6} | 1.01212×10^{-8} | -1.05641×10^{-11} | |
| Time migration | | Deflection | | Attenuation constant | | |
| t_0 | d_1 | d_2 | d_3 | A_1 | A_2 | A_3 |
| 0 | -1.63626×10^2 | 1.31240×10^4 | -1.29568×10^4 | 1.32235 | 23.56421 | 21.98159 |

4. Comparing of fitting effect

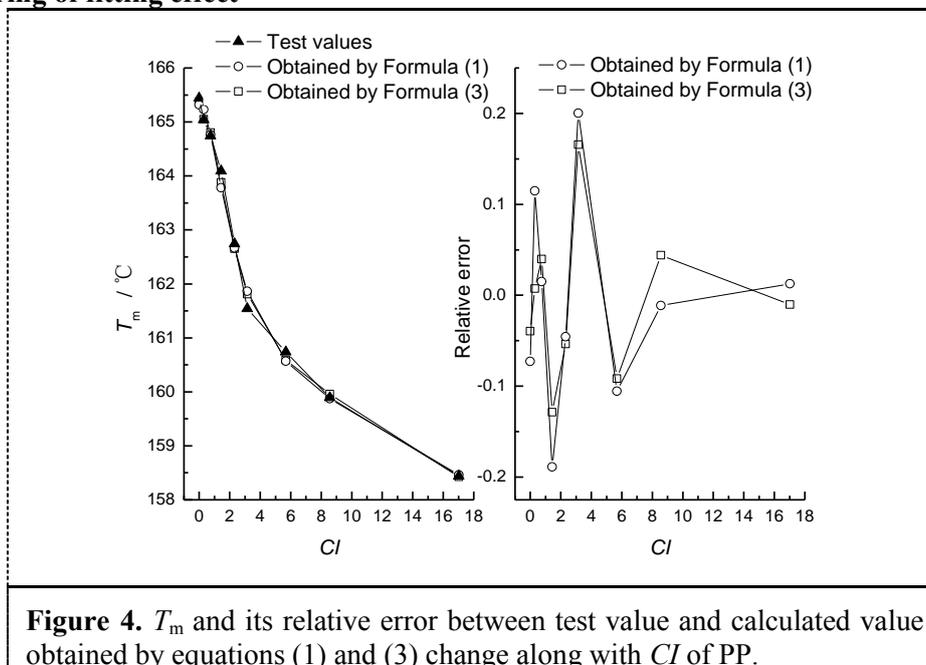


Figure 4. T_m and its relative error between test value and calculated value obtained by equations (1) and (3) change along with CI of PP.

All values of T_m corresponding to each CI of PP during UV aging can be obtained by Formula (1) and (3) respectively. Figure 4 shows the calculational results of T_m and relative errors between calculated value and test value. It can be seen that all relative errors are tiny, the maximum relative errors between test value and calculated value obtained by Formula (1) and (3) and are 0.20% and 0.16%

respectively, and standard deviations are 0.2024 and 0.1508 respectively. All the above solution shows that both Formula (1) and (3) can be quantitative relationship formula of T_m change along with CI , and Formula (3) has a better fitting effect.

5. Conclusion

Melting peak temperature of PP decays exponentially with the increase of carbonyl index during ultraviolet aging, and the higher the order number of exponential decay function, the bigger the correlation coefficient of fitting curve becomes. Melting peak moves in low temperature with the extension of PP aging time, and both correction coefficient and instability of polynomial fitting curve increase with the increase of polynomial order. Overall, Polynomial of 5th order has a better fitting effect. Aging time of PP decays exponentially with carbonyl index, and the higher the order number of exponential decay function, the bigger the correlation coefficient becomes.

Quantitative relationship formula of melting peak temperature of PP change along with carbonyl index during ultraviolet aging is determined by direct fitting and indirect fitting regarding aging time as intermediate variable. The calculation of standard deviation and relative error between calculated and test value of melting peak shows that quantitative relationship formulas obtained by direct fitting and indirect fitting can both be used in quantitative analysis between melting peak temperature and carbonyl index, and the latter has a better fitting effect although its equation is complex.

Acknowledgments

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