Variation and Grey GM(1, 1) Prediction of Melting Peak Temperature of Polypropylene During Ultraviolet Radiation Aging

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Abstract. Grey system theory regards uncertain system in which information is known partly and unknown partly as research object, extracts useful information from part known, and thereby revealing the potential variation rule of the system. In order to research the applicability of data-driven modelling method in melting peak temperature ($T_m$) fitting and prediction of polypropylene (PP) during ultraviolet radiation aging, the $T_m$ of homopolypropylene after different ultraviolet radiation exposure time investigated by differential scanning calorimeter was fitted and predicted by grey GM(1, 1) model based on grey system theory. The results show that the $T_m$ of PP declines with the prolong of aging time, and fitting and prediction equation obtained by grey GM(1, 1) model is $T_m = 166.567472 \exp(-0.00012t)$. Fitting effect of the above equation is excellent and the maximum relative error between prediction value and actual value of $T_m$ is 0.32%. Grey system theory needs less original data, has high prediction accuracy, and can be used to predict aging behaviour of PP.

1. Introduction

Polypropylene (PP) has the excellences of abundant resources, low prices, high mechanical properties and easy forming, and has been applied widely in the industry of automobile, household appliance, machinery [1]. However, the existing of large amounts of unstable tertiary carbon atoms leads to the fact that PP is easily aged with the action of ultraviolet light and oxygen, which causes mechanical properties decline, discoloration and the changing of physicochemical properties, and makes PP one of the most ultraviolet aging unresistant polymers [2]. Therefore, it has great significance that researching the rule and mechanism of PP ultraviolet aging, modifying PP to improve its ultraviolet aging resistance and expanding the application range of PP. And these are also one of the major measures to promote the development of PP.

The service life of outdoor PP and its products is about 3 years under the action of ultraviolet light and oxygen [3]. But it can be extended to 5 years and even over 8 years when PP is modified through blend, copolymerization and filling, and so on [4]. Therefore, current PP and its modification research mainly adopt artificially accelerated aging which greatly shortens research time. But literature [5] indicates that artificial accelerated aging can’t reflect the performance variation of materials under natural aging accurately.
Recently, according to experimental data related, forecasting properties of materials through mathematical model is one of the focuses of attention and study \([6–8]\). But simulation and prediction study about aging behaviour of PP was focused mainly on mechanical properties \([9]\), and few about physical properties. Taking melting peak temperature as an example, Grey GM(1, 1) model, one of the typical data-driven modelling methods, is used in determining prediction equation of PP melting peak temperature changing along with ultraviolet radiation aging time.

2. Experiments

2.1. Ultraviolet radiation aging

PP specimens, provided by Gansu Langang Petrochemical Co. Ltd., was illuminated by 20W ultraviolet lamp with a distance of 20 cm under room temperature, and then taken out for Differential Scanning Calorimetry (DSC) characterization after regular time intervals.

2.2. DSC characterization

Differential scanning calorimeter (TA Company, q-10) was utilized to characterize melting peak temperature of different specimens. A specimen of about 3–5 mg was held in aluminum seal during each process at a heating or cooling rate of 10 K/min under nitrogen atmosphere. The specimen was melted at 200 °C for 5 min to eliminate thermal history and cooled to 100 °C, followed then by a reheating process which was recorded to 200 °C.

3. Results and discussions of DSC characterization

The effect of the ultraviolet aging time on the melting behavior of PP was evaluated by DSC. By the reheating DSC curves of PP after different aging time showing in Figure 1(a), the relationship between melting peak temperature and aging time was obtained in Figure 1(b). The melting peak temperature decreases with the extending of aging time. After 400 h ultraviolet aging, it decreases from 165.4 °C to 158.4 °C.

![Figure 1. Reheating DSC curve (a) and melting peak temperature (b) of PP after different UV exposure time.](image)

The decreasing of the melting peak temperature should be mainly due to the following three factors. Firstly, photo-oxidative degradation leads to decrease of crystal surface regularity of crystalline region till to the decomposition, which improves surface free energy of PP. Obviously; melting peak temperature of material declines with the increasing of surface free energy according to Hoffman-Weeks formula \([10]\).
where $T_m$ and $T_m^0$ are melting peak temperature corresponding to thickness being 1 and $\infty$ respectively, $\Delta H$ is fusion heat of unit volume, and $\sigma_e$ is surface free energy. Secondly, photo-oxidative degradation leads to molecular chains break of amorphous region, and causes molecular weight decline. Thus, the melting peak temperature of PP decreases accordingly. Moreover, molecular chains break in amorphous region can also destroy partial entanglement, which may result in lower temperature recrystallization happened at molecular chains of degradation with poor regularity, and brings about more crystallization defects. As a result, the melting peak temperature of PP moves in low temperature region [11, 12].

4. Fitting and prediction of grey GM(1,1) model

Grey system theory regards uncertain system in which information is known partly and unknown partly as research object, extracts useful information from part known, and thereby revealing the potential variation rule of the system [13]. Up to now, it has been widely applied in many fields. Taking time series as independent variable and melting peak temperature as dependent variable, melting peak temperatures of PP during ultraviolet aging are simulated and predicted with grey GM(1, 1) model. The specific process sees reference [13]. It is obtained that evolution parameter $a$ and grey action quantity $b$ of grey regression equation

$$a(k+1) = \left(1 - e^a\right) \frac{h}{a} e^{-ak}, \quad k=1, 2, \ldots, n$$

are 0.0060 and 167.0608 respectively. Thus, simulation and prediction equation can be expressed as

$$T_m = 166.567472e^{-0.00012t}$$

where $T_m$ is melting peak temperature, and $t$ is aging time. Table 1 is simulation result obtained from Equation (3). Precision inspection shows that the accuracy grade of this model is first.

| Aging time (h) | Actual value | Predicted value | Residual error | Relative error (%) |
|---------------|--------------|-----------------|----------------|-------------------|
| 50            | 165.04       | 165.5710        | -0.5310        | 0.3217            |
| 100           | 164.74       | 164.5805        | 0.1595         | 0.0968            |
| 150           | 164.09       | 163.5960        | 0.4940         | 0.3011            |
| 200           | 162.74       | 162.6173        | 0.1227         | 0.0754            |
| 250           | 161.54       | 161.6446        | -0.1046        | 0.0647            |
| 300           | 160.74       | 160.6776        | 0.0624         | 0.0388            |
| 350           | 159.89       | 159.7164        | 0.1736         | 0.1086            |
| 400           | 158.44       | 158.7610        | -0.3210        | 0.2026            |

It can be seen from Table 1 that, the maximum relative error of predicted value and actual value obtained from grey GM(1, 1) model is 0.32%, which is negligible. Therefore, grey GM(1, 1) model can be utilized in melting peak temperature prediction of PP during ultraviolet aging.
5. Conclusions
During the process of ultraviolet aging, the melting peak temperature of semi-crystalline PP declines with the increasing of surface free energy of crystalline region, and (or) molecular chains breaking and the formation of randomly ranged crystal of amorphous region.

The quantitative relationship between melting peak temperature and ultraviolet aging time of PP are obtained based on grey GM(1, 1) model. The maximum relative error between predicted value and actual value of melting peak temperature is 0.32% accordingly.

Owing to needing less experimental data and being easy to test, grey GM(1, 1) model is a simple and reliable way for melting peak temperature prediction during ultraviolet aging process since. But fitting and prediction of grey GM(1, 1) model can only be done via the time series. This insufficiency limits the further application of this method.

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References
[1] Wang Y Z, Yue C E, Ma D, Sun Z Y and Chen G L 2014 Study on anti-UV aging effect and reaction mechanism of PP-g-AN in PP/PP-g-AN blends Eng. Plast. Appl. 42 82-87
[2] Kotek J, Kelnar I, Baldrian J and Raab M 2004 Structural transformations of isotactic polypropylene induced by heating and UV light Eur. Polym. J. 40 2731-2738
[3] Leng L C, Zhang Y M, Han G T, Zhao J and Gao S W 2014 Study of different hindered amine light stabilizer modified anti light aging of polypropylene Appl. Chem. Ind. 43 864-868
[4] Hu X J 2003 Study on weathering quality of Polypropylene Synthetic Mater. Aging Appl. 32 1-3
[5] Azuma Y, Takeda H, Watanabe S, Nakatani H 2009 Outdoor and accelerated weathering tests for polypropylene and polypropylene/tale composites: A comparative study of their weathering behavior Polym. Degrad. Stab. 94 2267-2274
[6] Rajaneesh A, Satrio W, Chai G B and Sridhar I 2016 Long-term life prediction of woven CFRP laminates under three point flexural fatigue Compos. Part B-Eng. 91 539-547
[7] Ma X and Liu Z B 2016 Research on the novel recursive discrete multivariate grey prediction model and its applications Appl. Math. Model. 40 4876–4890
[8] Celina Mathew C 2013 Review of polymer oxidation and its relationship with materials performance and lifetime prediction Polym. Degrad. Stab. 98 2419-2429
[9] Chen K, Zhang T Y, Hu Y X and Zheng X P 2013 Application of residual error grey prediction model in aging behaviour prediction of plastic Mod. Chem. Ind. 33 119-122
[10] Zoepfl F J, Marković V and Silverm Joseph 1984 Differential scanning calorimetry studies of irradiated polyethylene I. Melting temperatures and fusion endotherms J. Polym. Sci. Pol. Chem. 22 2017-2032
[11] Rabello M S and White J R 1997 The role of physical structure and morphology in the photodegradation behaviour of polypropylene Polym. Degrad. Stab. 56 55-73
[12] Xu L X and Zhong M Q 2006 Study on the effect of nano-TiO₂ on UV aging resistance of polypropylene J. Zhejiang Univ. Techno. 34 302-305
[13] Chen K, Zhang T Y, Zheng X P and Hu Y X 2013 Application of grey theory for the prediction of plastic aging behavior China Plastics Ind. 41 113-116