Effect of Hindered Amine Light Stabilizer on Properties of HDPE / Kaolin Composites for Hydraulic Gate and its Mechanism Analysis

Li SONG 1,†, Huaqiang LIU 1, Bin YANG 2, Yiping CAI 1
(1 Jiangsu Research Institute of Water Conservancy, Nanjing 210029, China; 2 Jiangsu Water Conservancy Construction Engineering Co., Ltd., Yangzhou 225002, China)

† songli0008@126.com

Abstract. High density polyethylene (HDPE) / kaolin composites with different hindered Amine light stabilizers were prepared by blending granulation. The mechanical properties and dynamic thermodynamic changes before and after aging were discussed and studied. The precipitates were analyzed by FT-IR and H1-NMR, and the precipitation reason and anti-aging difference of different light stabilizers were discussed and compared. The results showed that the mechanical properties retention rates of light stabilizer 2020, light stabilizer 944, light stabilizer 123, light stabilizer 770 and light stabilizer 292 were 87.1%, 81.7% and 79.1%, respectively. Light stabilizer 2020 and light stabilizer 944 with large molecular weight are more easily compatible with the system, not easy to precipitate, and have a better anti-aging effect. At the same time, light stabilizer 2020 with dense hindered amine structure has excellent anti-aging effect. This study provides a reference for the selection of light stabilizer and failure analysis of light aging resistance of HDPE system.

1. Introduction

At present, hydraulic gates can be divided into steel gate, wood gate, reinforced concrete gate and composite material gate. Steel gate has large bearing capacity, impact resistance, stable material performance and quality, but poor anti-corrosion performance and relatively short service life [1-2]. High density polyethylene (HDPE) has good heat resistance and cold resistance [3-4], but also has high rigidity and toughness, as well as recyclability, which is widely used in all walks of life. But its application in the field of the hydraulic gate is blank. Kaolin is widely used to improve the strength of plastics and rubber because of its stable chemical properties, high strength and low price [5]. Hu can et al. [6] improved the tensile strength and flexural strength of HDPE/glass fiber composites by 18.64% and 20.25% respectively through crosslinking pretreatment. Zhang Qingfa et al. [7] improved the mechanical properties of the composites activated with phosphoric acid, tensile strength and tensile modulus were 38.66 MPa and 32.17 MPa, respectively. Because the gate is usually in the outdoor environment and the illumination time is long, which seriously affects the performance of materials [8]. On the basis of summarizing the reported high performance materials, we developed a lightweight, durable and easy to manufacture and maintenance high density polyethylene (HDPE) / kaolin composite material as a new material composite structure gate, and studied its anti-aging properties.
2. Changes of mechanical properties of composites after aging

The effects of different light stabilizers and antioxidants (Table 1) on the mechanical properties of HDPE / kaolin composites were studied. Table 2 shows the tensile strength, elongation at break and impact strength of HDPE / kaolin composites before and after thermal and photo aging.

Table 1 Formula composition of composite materials

| NO. | Base Material                  | Antioxidants | Light stabilizers |
|-----|--------------------------------|--------------|------------------|
| S1  | HDPE+MAC                       | /            | /                |
| S2  | HDPE                          | /            | 2020             |
| S3  | HDPE+MAC                       | 1010+168     | +UV326           |
| S4  | HDPE+MAC+Kaolin               | 1010+168     | +UV326           |
| S5  | HDPE+MAC+Kaolin+EBS           | 2020         | +UV326           |
| S6  | HDPE+MAC+Kaolin+EBS           | 2020         | +UV326           |
| S7  | HDPE+MAC+Kaolin+EBS           | 2020         | +UV326           |

Table 2 Mechanical properties of the composites samples before and after thermal aging

| Sample Number | Condition | S1       | S2       | S3       | S4       | S5       | S6       | S7       |
|---------------|-----------|----------|----------|----------|----------|----------|----------|----------|
| Tensile Strength /MPa | Before Aging | 28.5     | 28.3     | 28.2     | 28.1     | 28.5     | 28.9     | 28.7     |
| Elongation At Break /%   |           | 510      | 503      | 506      | 505      | 508      | 508      | 515      |
| Impact Strength /J/cm   |           | 65.1     | 64.5     | 64.9     | 64.9     | 65.2     | 65.2     | 65.4     |
| Tensile Strength /MPa | After Thermal | 19.1     | 22.5     | 23.2     | 21.9     | 22.5     | 22.2     | 22.3     |
| Elongation At Break /%   |           | 310      | 402      | 433      | 399      | 405      | 410      | 401      |
| Impact Strength /J/cm   |           | 46.2     | 55.1     | 55.8     | 52.9     | 55.1     | 55.2     | 54.1     |
| Tensile Strength /MPa | After Light | 19.1     | 19.5     | 25.2     | 21.9     | 22.5     | 23.8     | 21.5     |
| Elongation At Break /%   |           | 349      | 350      | 435      | 395      | 406      | 415      | 390      |
| Impact Strength /J/cm   |           | 43.2     | 45.1     | 55.8     | 50.9     | 51.1     | 52.8     | 49.8     |

According to the test data in the table 2, the tensile strength, elongation at break and impact strength of the samples before aging are about 28.5MPa, 508% and 65.0J/cm respectively with a small floating. When the composite was thermally aged, the mechanical properties of the composite is decreased. The average retention rates of tensile strength, elongation at break and impact strength of S1 to S7 is 66.3%, 81.6%, 84.6%, 79.5%, 81.1%, 80.7% and 79.4% respectively, as shown in Fig. 1. Because S1 is not added with antioxidant, the thermal aging resistance of composite is weak, and the mechanical properties of the composites are decreased obviously after thermal aging. There was no significant difference in
mechanical properties of S2-S7 after thermal aging, and the three indexes were 22.5MPa, 402% and 55.1J/cm. The main reason is that the hindered amine light stabilizer and antioxidant 1010/168 have good synergistic effect, and improve the thermal aging resistance of the system [9]. The mechanical properties of the composite materials are significantly different after photoaging. The average retention rates of the three mechanical properties of S1 to S7 are 67.3%, 69.5%, 87.1%, 78.2%, 79.1%, 81.7% and 75.6%, respectively, as shown in Fig.2. Light stabilizer 2020 significantly improves the photo aging resistance of the sample. The light aging resistance of light stabilizer 944 is only inferior to that of light stabilizer 944, which is due to 2020 has more dense hindered amine structure. The anti-aging properties of light stabilizers 123, 770 and 292 are weaker in turn. This shows that the light stabilizers with high molecular weight and dense hindered amine structure can be better compatible with the material system and have excellent light stability. Next we focus on the characterization and research of the composite after photoaging.

3. Dynamic mechanical properties before and after aging
In order to further study the difference of mechanical properties of the composites after photoaging, the dynamic mechanical properties of the samples were analyzed. Fig.3 shows the curve of storage modulus of HDPE / kaolin composite with different light stabilizers after light aging. As shown in the figure, the storage modulus of the composite decreases with the increase of temperature. It is difficult for molecules to move at low temperature, so the material shows greater rigidity at this time. With the increase of temperature, the molecular motion intensifies, and the inter chain sliding property of HDPE increases. The rigidity is weakened and the material shows greater flexibility [10]. However, the composites with different light stabilizers exhibit different storage modulus at the same temperature. At low temperature, the composite without antioxidant and light stabilizer (S1) has higher storage modulus, while the composite with light stabilizer 2020, 994, 123, 770 and 292 has lower storage modulus, which increases in turn. The main reason is that the light stabilizer improves the light aging resistance of the composite and delays the aging brittleness of the composite. In the low temperature range -70 ℃ to 20 ℃, the difference of storage modulus is more obvious, which has more guiding significance for the research of material aging differentiation.

![Figure 3. Storage modulus of the composites samples after light aging](image)

4. Qualitative analysis of precipitates
In order to further analyze the precipitates qualitatively, we scrape the precipitates out and enrich them, and then carry out ATR-IR test on them, as shown in Fig. 4. According to the infrared spectrum, all precipitates contain 720 cm⁻¹, 1472 cm⁻¹, 2850 cm⁻¹ and 2910 cm⁻¹ characteristic peaks, which are the infrared characteristic peaks of polyethylene, indicating that the precipitates will inevitably introduce the composition of composite substrate in the scraping process. The infrared spectra of the precipitates of S4 after photoaging show that 1215cm⁻¹ and 1163cm⁻¹ are from the N-C stretching vibration in the
structure, respectively. And 1720 cm\(^{-1}\) is from the C = O stretching vibration of the ester bond in the structure\(^{11-12}\). The results show that 1153 cm\(^{-1}\) is derived from the N-C expansion vibration in the structure of light stabilizer 123. 1720 cm\(^{-1}\) is derived from the C=O expansion vibration of ester bond in the structure. The results show that 1169 cm\(^{-1}\) is from N-C expansion vibration in structure and 1731 cm\(^{-1}\) is from C=O expansion vibration of ester bond in structure. In addition, the precipitates of S3, S4, S5 and S6 samples after photoaging are found to be the elastic vibration of phenol O-H in the structure of antioxidant 1010 near 3598 cm\(^{-1}\). It is shown that the light stabilizers of S4, S5 and S7 (770, 123 and 292) of the samples are precipitated obviously during the photoaging process.

In order to further characterize the precipitates, we analyzed them by \(^1\)H-NMR. According to the analysis of test spectrum in Fig. 5, the characteristic chemical shifts of precipitates are about 0.90 and 1.25 ppm, which should be the characteristic peaks of -CH\(_3\) and -CH\(_2\)- of HDPE. The characteristic chemical shift of S2, S3, S4, S5, S6 and S7 is about 7.01 ppm, which should be the chemical shift of hydrogen on the benzene ring in the structure of antioxidant 1010 and 168. In addition, the characteristic shifts of S4 and S7 are quite different from those of other groups. And 1.51/1.80, 2.25 and 5.11 (5.18) ppm are from the chemical shifts of hydrogen at A/B/C and D positions of light stabilizer 770, 123 and 292 respectively (shown in Fig), and 3.64 ppm is the chemical shift of hydrogen at the position of light stabilizer 292\(^{13-14}\). Therefore, after photoaging, the light stabilizers 2020, 944 and 123 do not appear obvious precipitation, while the light stabilizers 770 and 292 precipitate obviously, so the mechanical properties of the response samples are also weakened most obviously.
5. Discussion on precipitation mechanism
In the composite system, light stabilizer plays a key role in anti-aging. The precipitation of light stabilizer directly leads to the failure of light aging resistance, which leads to the obvious decline of mechanical properties of the composites [15]. Light stabilizers 770, 123 and 292 are all small molecule amine stabilizers. With the increase of temperature, the chain movement of stabilizers and polyethylene is intensified, and small molecule stabilizers are more likely to migrate to the surface of material [16]. Light stabilizers 2020 and 944 are macromolecular amine stabilizers, which are compatible with polyethylene matrix. Even if the molecular chain move violently, it is relatively difficult to precipitate, so as to better protect the composite material and delay the aging of the material caused by light radiation. Therefore, the precipitation of light stabilizer is the main reason for the degradation of light aging resistance of HDPE / kaolin composites.

6. Conclusion
(1) The results show that the anti-aging properties of HDPE / kaolin composites blended with different light stabilizers are different. And light stabilizer 2020 is best, 944, 123, 770 and 292 are weaker in turn;
(2) The dynamic mechanical test can accurately evaluate the aging embrittlement index of materials, and the FTIR and H1-NMR analysis of precipitates can provide guidance for the failure cause analysis of materials.
(3) The higher the molecular weight of amine light stabilizers with different structures, the more difficult it is to precipitate in the process of light aging. Light stabilizers 2020 and 944 are more difficult to precipitate, which makes the materials have better light aging resistance. Light stabilizers 123, 770 and 292 are easier to precipitate, which leads to the failure of light aging resistance. At the same time, the structure of hindered amine with denser structure has better resistance to light aging.

Acknowledgments
This work was financially supported by Independent research funding projects of Jiangsu provincial public welfare research institutes (2019z014) of China.

References
[1] Huang C B. Application of cast iron gate in water saving reconstruction project of irrigation area [J]. Water conservancy construction and management, 2013, 33 (3), 79.
[2] Xiong R E, Yan G H. Dynamic characteristics and shape optimization of water stop structure of hydraulic gate [J]. Vibration, test and diagnosis, 2011, 31 (006), 798.
[3] Tao S P. Study on temperature distribution and crystallization behavior of HDPE during injection molding [D]. Sichuan University, 2004.
[4] Yi X S. Study on injection molding self reinforcing process of high density polyethylene [J]. Polymer materials science and engineering, 1990, 000 (4),56(in Chinese).
[5] Ye S Z, Zhou Y H, Chen F L. Research progress on surface modification of kaolin [J]. Rubber industry, 2004 (12), 53.
[6] Hu C, Zhou Y, Zhang T, Jiang T, Zeng G. Effect of synergistic modification on mechanical properties of sisal REINFORCED HDPE composites [J]. Plastics industry, 2020 (08), 126.
[7] Zhang Q, Ren X, Wu J, et al. Mechanical properties of activated carbon / HDPE composites [J]. ActaCompositaeSinica, 2020, 37 (11),2816(in Chinese).
[8] Basfar A A, Ali K M I,Mofi S M. UV stability and radiation-crosslinking of linear low density polyethylene and low density polyethylene for greenhouse applications[J]. Polymer Degradation & Stability, 2003, 82(2), 229.
[9] Yoshihiko T., Yasuyuki I., Shin T., et al. Structural change of a polymeric hindered amine light stabilizer in polypropylene during UV-irradiation studied by re-active thermal desorption-gas chromatography [J], Polym. Degrad. Stab,. 2004, 83, 221.
[10] Pandey J K, Reddy K R, Kumar A P. AN OVERVIEW OF THE DEGRADABILITY OF POLYMER NANOCOMPOSITES[J]. Revista Internacional De Prótesis Estomatológica, 2005, 3(2), 106.

[11] Shi W, Zhang J. effect of hindered amine light stabilizer and antioxidant on UV stability of polymer [J]. Plastics science and technology, 2010 (03), 97.

[12] Wang Weihong, Zhang Chenxi. Effect of natural aging on properties of wood flour / HDPE composites and application of additives [J]. Forestry science, 2012 (04), 102.

[13] Wang JJ. Synthesis and application properties of hindered amine light stabilizer gw-540 [J]. Journal of Suzhou University: Medical Edition, 1998 (11): 1150.

[14] Liu E D, Shao Y C, Zhang S F, et al. Synthesis and properties of 2,4-bis (4-biphenyl) - 6 - (2-hydroxy-4-alkoxyphenyl) - 1,3,5-triazine ultraviolet absorber [J]. Fine chemical, 2011, 28 (3), 284.

[15] Gjsman P, Meijers G, Vitarelli G. Comparison of the UV-degradation chemistry of polypropylene, polyethylene, polyamide 6 and polybutylene terephthalate[J]. Polymer Degradation & Stability, 1999, 65(3), 433.

[16] Basfar A, A K. Natural weathering test for films of various formulations of low density polyethylene (LDPE) and linear low density polyethylene (LLDPE)[J]. Polymer Degradation and Stability, 2006, 91(3),437.