Evaluation of Aging Behavior of Medium Density Polyethylene in Natural Environment by Principal Component Analysis

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ABSTRACT: To evaluate the aging behavior of medium density polyethylene (MDPE) under aggressive environment, principal component analysis (PCA) method was used to establish a nondimensional expression Z from a data set of multiple properties of MDPE. Natural exposure tests of MDPE were carried out for one year with different test periods at Xisha islands in China. Surface properties and mechanical properties of MDPE were measured. It was found that Z increased stepwise with exposure time extending. Combined with the climatic data in Xisha islands, the shielding effect of the oxidation products generated by the degradation process or the reactivating effect resulting from changes of weather conditions were alternatively executed as the determinant factor to affect the change tendency of Z. In a word, Z can be used to reveal the comprehensive degradation pattern of MDPE in natural environments in a reasonable way. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 19–23, 2012

Key words: aging; degradation; mechanical properties; polyethylene

INTRODUCTION

Although polyethylene (PE) possesses good dielectric properties and good chemical resistance, it is unavoidably subject to the degradation from aggressive environments, in which high radiation [mainly ultraviolet (UV)], temperature fluctuation and rain were the resulting factors to deteriorate PE materials. In most cases, artificial accelerated aging tests were used to study the performance of PE.[1–4] However, the behavior of PE used in natural environments is different from that in accelerated tests due to the versatile climatic conditions.[5–7] Therefore, natural environment exposure test should be carried out to study the aging procedure of PE, which is more suitable to evaluate the service life of PE.

During the natural exposure, the properties of PE on surface appearance, mechanics and chemical structures were usually investigated because the variations of them indicate the durability of PE.[5–7] Especially, fracture-mechanical characteristics are vital to polymer structure elements. The most easy-going approach to evaluation is to select one representative property as the criterion and to monitor its variation. But it is quite difficult to find a specific property to represent all others, and to reduce the redundancy among these properties. In this case, redundancy means that some of the variables (properties) are correlated with one another, possibly because they manifest the same aging feature of PE, which also provides the possibility of variable reduction. Principal component analysis (PCA) is appropriate to reduce a number of observed variables into a smaller number of artificial variables (called principal components), which account for most of the variance in the observed variables. The principal components can be used as predictor or criterion variables in subsequent evaluation.

The aim of this article is to establish a methodology for analyzing and evaluating several properties of medium density polyethylene (MDPE) after natural aging. Correspondingly, an exposure test was carried out at Xisha (Paracel) island in China, an ideal natural accelerating tester for polymers. PCA method was introduced to extract principal components from the aging properties for establishing a comprehensive expression, which was successfully used to evaluate the aging behavior of ethylene–propylene–diene monomers.[8,9] It will be useful in the future to evaluate alterations and failures in natural aged MDPE by a convenient diagnostic techniques.

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EXPERIMENTAL

Exposure test

Natural exposure tests were performed under the tropical environment in Xisha islands with an average temperature of 28°C, an average humidity of 85% and an average sunlight duration per month of 150~280 h. MDPE samples (supplied by Chenguang Research Institute of Chemical Industry, China) were exposed to the natural environment on a shelf with an angle of 45° to the horizontal for 1 year. The specific exposure duration was from October 2007 to September 2008 with six intervals of 1, 2, 3, 6, 9, and 12 months, respectively.

Measurements

Appearance

1. Chromatic aberration measurement: Chromatic aberration were measured with a spectrophotometer (GretagMacbeth COLOREYE XTH, Grand Rapids, MI). The change of color ΔE was calculated by the following equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad (1)$$

where ΔL represents the brightness relationship between light and dark, Δa represents the relationship between green and red and Δb represents the relationship between blue and yellow. The symbol Δ implies the difference between the samples before and after being aged.
2. Gloss measurement: Surface gloss were measured through a portable glossmeter (XGP, China) using a 60°incidence angle.

2.2.2 Mechanical properties

1. Tensile strength: The tensile specimens were tested according to ISO 37:1994 at room temperature (23 °C) with a crosshead speed of 500 mm min^{-1} using a computer-controlled universal testing machine (type WDS, China) equipped with pneumatic grips. The elongation at break (ε) can be calculated by eq. (2):

$$\varepsilon = \frac{G - G_0}{G_0} \times 100 \qquad (2)$$

where G_0 is original elongation length before test; G is the elongation length after break.
2. Flexural strength: The exposure side of sample was pressed with the preloading of 5 N and the speed of 5 mm/min. the flexural strength (σ)was obtained through eq. (3):

$$\sigma = \frac{3P \cdot L}{2b \cdot h^2} \qquad (3)$$

where P is loading press, L is cross length, b is the width of sample, and h is the thickness of it.
3. Hardness: The indentation hardness (Shore D) of the exposed side of the plate samples was determined by means of a pocket hardness meter (type TH210, China) according to ISO 7619:1986. At least five locations were recorded and the average value was used in the following PCA procedure.

Evaluation method

PCA is a methodology that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components. PCA is often used to reduce data dimensionality by performing true Eigen vector-based multivariate analyses. Its operation can be thought of as extracting hidden, simplified structures within the data in a way which best explains the variance in the data.[10] For manifesting the aging characteristics of PE, changes in chemical and physical properties were usually monitored. For example, the increase of carbonyl group was used to indicate the aggravation of aging process of PE. However, any of them only reflected one side of the aging behavior. If considering all the effect of them, the evaluation might be contradictory. Principle component analysis (PCA) right simplified this problem. It could reduce the redundancy in these properties and extract a smaller number of principal components (artificial variables), by which a comprehensive expression can be built up that represents most content of multiple original properties.

In this article, the programming work of PCA was performed using Matlab software (version 7.5, MathWorks).

RESULTS AND DISCUSSION

PCA results

According to the methodology of PCA, a comprehensive value was achieved to characterize the performance of PE during the aging process. The experimental results of aging properties were listed in Table I, in which sample No.1 corresponded to original sample as a control, and sample No.2 to 7 related to the aged sample with the exposure duration

TABLE I
Aging Properties of MDPE After Natural Exposure with Different Time Period

Sample No.	X1	X2	X3	X4	X5	X6
1	0	26.2	45.7	30.3	127	8.81
2	3.04	20.4	48.9	30.3	106	8.96
3	4.9	17.9	50.8	29.8	81	9.01
4	6.22	17.8	50.5	28	71	9.4
5	4.6	19	51.7	23.7	30	9.04
6	4.1	9.5	52	21.2	20	10.7
7	8.44	7.2	54.2	16.7	14	9.4

TABLE II
Results of Main Components Extraction

Main component	Eigenvalue	Variance	Accumulative variance
1	4.7448485	0.790808085	0.790808085
2	0.8155081	0.135918015	0.926726101
3	0.2776717	0.046278618	0.973004718
4	0.1211172	0.020186204	0.993190922
5	0.0406288	0.00677147	0.999962392
6	0.0002256	3.7608E-05	1

of 1, 2, 3, 6, 9, and 12 months, respectively. The measured properties were presented by variable X, including color aberration (X1), gloss (X2), hardness (X3), tensile strength (X4), elongation at break (X5), and flexual strength (X6).

Based on the data set in Table I, PCA was applied to identify the most meaningful basis to re-express a data set, after filtering out noise and revealing hidden structure within the data set. The detailed analysis procedure is shown as follows:

1. Normalised the original data in Table I, calculated the covariance matrix, its eigenvector and eigenvalues (listed in Tables II and III).
2. Based on the eigenvalue, variance and cumulative variance of each component can be calculated from eqs. (4) and (5), the result of which is listed in Table II. The first few components account for meaningful amounts of variance are retained, interpreted, and used in subsequent analysis.

$$\text{Variance of component (Yi)} = \frac{\lambda_i}{\sum_{i=1}^{6} \lambda_i} \quad (\mathrm{i} = 1, 2 \ldots 6) \qquad (4)$$

$$\text{Cumulative variance of component } (\mathrm{Y_m}) = \frac{\sum_{\mathrm{i=1}}^{\mathrm{m}} \lambda_i}{\sum_{i=1}^{6} \lambda_i} \qquad (5)$$

where λ_i is the eigenvalue corresponding to principal components Y_i, and $\sum_{i=1}^{6} \lambda_i$ is the sum of eigenvalues.

3. Based on the data in Table III, each principal component can be defined as a linear combination of optimally weighted observed variables. The optimal weight is produced from the eigenvectors matrix, which means for a given set of data, no other set of weights could produce a set of components that are more successful in accounting for variance in the observed variables.
4. The evaluation expression can be established by the weighted sum of retained main components as eq. (6), in which the weigh is the variance of each main component.

$$Z = \sum_{i=1}^{m} (\lambda_i / \sum_{i=1}^{p} \lambda_i) Y_i \qquad (6)$$

According to the PCA result shown in Tables II and III, the variance of each principal component is identified. It can be seen that the variances of the first and second components are 79.1 and 13.6%, respectively. That is, the cumulative variance of the first two components reaches 92.67%. Commonly, when the cumulative variance is more than 85%, the number of principal components can be determined on behalf of all components. That means the first two principal components, marked as Y_1 and Y_2, could cover most information expressed by the six variables. Based on the Eigen-vectors of the covariance

TABLE III
Matrix of Eigenvector

	Components					
Variables	1	2	3	4	5	6
X1	0.381283	−0.53593	0.46931	−0.09861	−0.57943	−0.0411
X2	−0.44404	−0.09436	−0.20039	0.545975	−0.49286	0.461268
X3	0.440188	−0.25324	0.118287	0.331322	0.521577	0.588467
X4	−0.42138	−0.04038	0.690496	0.414229	0.271145	−0.31452
X5	−0.4405	−0.0334	0.325991	−0.63344	0.07456	0.54016
X6	0.303451	0.79812	0.377554	0.097906	−0.26502	0.220355

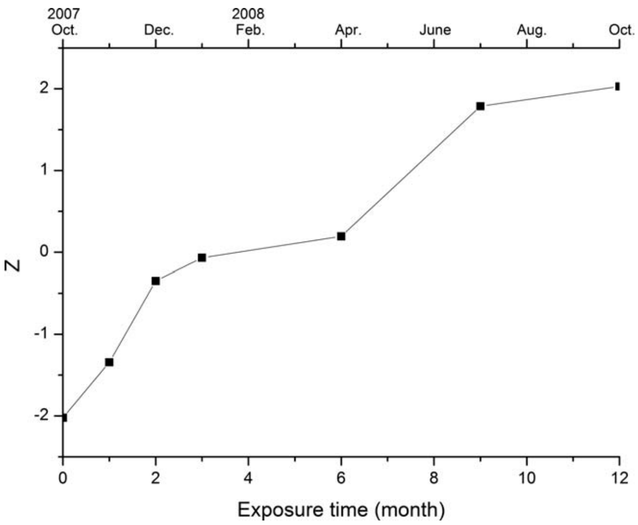

Figure 1 Change of Z value with the passing exposure time (Z value was obtained from the comprehensive expression (eq. 8) for evaluating MDPE aging behavior).

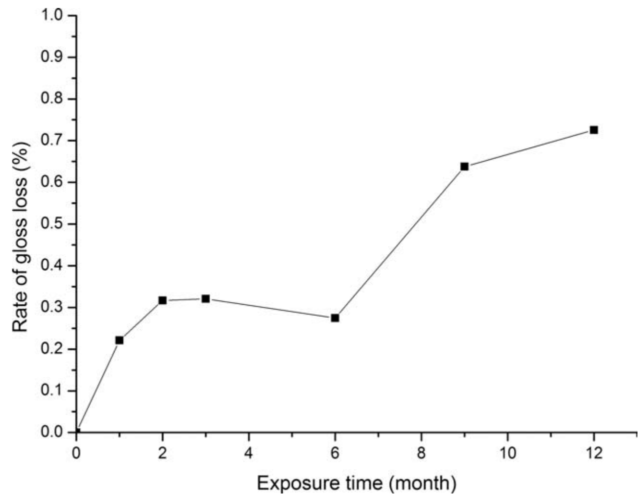

Figure 3 The relationship between aging time and the rate of gloss loss for MDPE under the environment of Xisha Islands.

matrix, the polynomial expression [eqs. (7) and (8)] was established to reveal the relationship between the principal component and the six characteristic variables.

$$Y_1 = 0.381283X_1 - 0.44404X_2 + 0.440188X_3 - 0.42138X_4 - 0.4405X_5 - 0.303451X_6 \quad (7)$$

$$Y_2 = 0.53593X_1 - 0.09436X_2 - 0.25324X_3 - 0.4038X_4 - 0.0334X_5 + 0.79812X_6 \quad (8)$$

Using corresponding variance of main components as the weight factor, the evaluation expression Z for MDPE aging properties can be established according to eq. (6), as shown in eq. (9).

$$Z = \frac{\lambda_1}{\sum_{i=1}^{6}\lambda_i}Y_1 + \frac{\lambda_2}{\sum_{i=1}^{6}\lambda_i}Y_2 = 0.791Y_1 + 0.136Y_2 \quad (9)$$

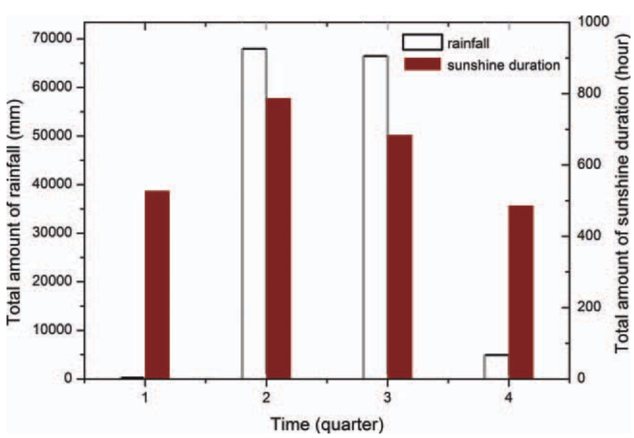

Figure 2 Climatic conditions of the tropical area for exposure tests in 2008. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Based on it, Z is plotted with exposure time t, shown in Figure 1. It should be noted that the bottom and top axis in Figure 1 are corresponding to the exposure duration and the calendar time, respectively. By this way, the tendency of Z can be analyzed with the variation of climatic conditions based on calendar time. In general, the evaluation expression Z increases stepwise with the exposure time extending, which indicates the aging tendency of MDPE with four phases.

Discussion

As mentioned above, the aging procedure of MDPE can be divided into four phases, each of which includes three months. In the first quarter of the exposure period, the quick elevation of Z can be attributed to the photo oxidation of PE, by which oxidation products formed on the sample surface. In the next quarter, the aging rate slowed down because the thickening oxidation layer prevented the UV light from reacting with the bulk of the PE.[11] At this phase, the shielding effect of the oxidation product was the controlling factor for the aging behavior of MDPE. The oxidation process was reactivated and quickened rapidly, however, after half a year's exposure. This might be ascribed to alteration of climatic conditions, as shown in Figure 2. It was recorded that the peak value of the total amount of radiance intensity, sunshine duration and rainfall in 2008 appeared in April with the specific value of 583.93 MJ/m^2, 269.2 hours and 3426 mm. This means that the effect of photo oxidation on MDPE was stronger during this phase due to the elevated radiance intensity and sunshine duration. The diffusion of rain water into the bulk of the sample was also fastening due to the sudden increase in rainfall. The climatic conditions were, therefore, the predominant factor affecting the aging rate of PE during the third quarter of the exposure period. Following this period, the rate of degradation remained relatively constant after the formation of more compact oxidation products.[11] As a comparison, the gloss loss of PE presents a similar tendency, in which the variation slope is larger at the first and third phases than that at other phases (Fig. 3). Based on the principle indicated by Z, it can be understood that the gloss keeps unchanged due to the formation of oxidation products at the second phase, and looses increasingly because the rinse-off of the products by the rain started in April 2008, aggravates the degradation of MDPE.

CONCLUSIONS

PCA is an effective method to extract relevant information from six characteristic properties of MDPE. The evaluating parameter Z can be used to describe the aging process of MDPE. During 1-year exposure, the aging rate of MDPE increased stepwise and was controlled by various factors during the exposure period. The shielding effects of oxidation products and the variation of climatic conditions were alternately dominant in the rate and progress of degradation over time.

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