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Data Interpretation

Application of smoothing methods for estimation of service life for polymers from tensile testing

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Abstract

We propose a procedure for extracting reliable information regarding service life of a polymer product from an experimental scatter plot obtained by mechanical tests. Consideration was given to the change in elongation at break as a result of natural weathering for stabilized polymers. We suggest using locally weighted regression scatter plot smoothing to estimate the service life (threshold time)—weathering time at which the elongation at break of a polymer reduces by half. For the first time the construction of realistic confidence intervals (accuracy of the estimations) for the service life obtained from tensile testing of aged polymers is discussed. The proposed approach is general and applicable to other degradation processes.

Keywords: Coatings; Weathering; Service life; Tensile testing; Elongation at break; Scatter plot smoothing; Loess (lowess); Confidence intervals

1. Introduction

In the plastics industry strong efforts are being made to develop long lasting materials stable against the degradative influence of light and heat. Seen from the point of application, life time predictions based on data from mechanical tests, for example tensile testing, are the most important information requested, where expensive natural and artificial aging and weathering tests are often made to get the required information. Mechanical properties, especially elongation at break, are sometimes considered to be more sensitive to degradation of polymers than chemical methods [1–4] and the most sensitive property to thermally initiated aging for filled polymer compounds [5]. The monitoring of mechanical data during weathering leads to the accumulation of plenty of data. Typical experiments often consist of a great amount of scattered points.

In this paper, locally weighted regression scatter plot smoothing has been considered to approach the problem of estimating the service life from the weathering tests. Here we consider the change in elongation at break as a result of natural weathering for stabilized polymer samples. It has become almost a rule to consider that the useful life of the material ends when it reaches 50% of its original mechanical properties [2,3]. Therefore, for the comparison of the lifetime of the samples, the weathering time was estimated at which the elongation of polymers reduces by half. In the technical literature this weathering time is sometimes referred to as a 'threshold' value. However, other measures of degradation can also be considered as a threshold value, such as one-third or two-thirds of the initial value. In practice, these threshold values are usually estimated visually.

Here we propose a procedure for estimation of the service life (threshold value) from tensile testing of weathered polymers. The construction of realistic confidence intervals for the service life is also discussed. To our best knowledge, the problem of estimating the confidence intervals (accuracy of the estimations) for the threshold

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value obtained from the tensile testing measurements of aged polymers has not been addressed yet in the literature. The proposed approach is general and also applicable to other degradation processes.

2. Analysis of scatterplot smoothing techniques regarding the application for tensile testing of aged polymers

Typical experimental data from tensile testing of weathered polymers look like a scatter plot. In a smoothed plot, each data point (x_i, y_i) is replaced by the value $(x_i, \hat{y}_i)$ where $\hat{y}_i$ is a smoothed value of y_i determined from all points in the neighborhood of x_i point. Because such a fit produces an estimate of the response that is less variable than the original observed response, such a result is called a smooth, and procedures to obtain such fits are called scatterplot smoothers. Superimposing smoothed values on scatter plots is important since in many cases it is difficult to get an accurate impression of the pattern of dependence of y on x simply by eye. There are two general strategies for fitting a smooth curve: parametric and non-parametric fitting.

The classical procedure for smoothing scatter plots is a parametric fit, for example, to fit polynomials to the data, usually straight lines or quadratics. The problem with a parametric fitting function is that it is neither flexible nor local. What happens on, say, the extreme right of the scatter plot can very much affect the fitted values at the extreme left. That is not acceptable for processing of weathering data, where the form of the curve might change during the weathering experiment because of possible chemical changes in the polymer owing to aging. Moreover, a parametric fit might have difficulty for patterns on scatter plots where some data are missed or following patterns with abrupt changes in the curvature. Additionally, calculated parameters can be completely distorted by outliers, because all points contribute in their calculation. In the field of polymer testing only a few papers are available where regression methods were applied to the subject of polymer aging [3–8]. They usually employ a parametric approach, where a functional form is searched for exploring relationships between measurable variables.

Non-parametric scatterplot smoothers are useful tools for fitting arbitrary smooth functions to a scatter plot of data points. The smoother summarizes the trend of the measured response as a function of the predictor variables. The approach relies on the data to fit a curve to the data points locally. With this technique, the curve at any point depends only on the observations at that point and some specified neighboring points. These techniques are widely used in different scientific fields, for example, in spectroscopy [9], social sciences [10,11], economic sciences [12], neuroscience [13], medicine [14], biology [15], climatology [16], environmental research [17] and anthropology [18]. However, in the field of polymer testing non-parametric approaches have not yet been used. We believe that application of non-parametric smoothers is a more appropriate method for processing of weathering data.

The most uncomplicated non-parametric statistical method is a simple moving average of length r (r is odd), where each y-value is replaced by a smoothed value obtained from the average of the r values, $(r-1)/2$ values preceding y and $(r-1)/2$ values following y. The length of moving average, r, governs the degree of smoothness: the longer the average the smoother the line. The disadvantage of a long moving average is the loss of smoothed values at the beginning and the end of the scatterplot. Another disadvantage, which makes the moving average not suitable for the scatterplots under investigation, is that the method is for evenly spaced x-values, which is often not the case in weathering experiments.

A number of more sophisticated procedures for smoothing scatter plots based on locally weighted regression, frequently called non-parametric regression procedures, have been developed [10,19–27]. In non-parametric smoothing, a weighted function of a data subset provides a local estimate for a region. A window, dependent on a fraction of data used for smoothing at each x point, is placed about each x value; points that are inside the window are weighted so that nearby points get most weight. Because each region receives a smooth estimate, the agglomeration of these estimates captures local variations well without the need for complicated models or additional parameters found in parametric smoothing. Constructing a non-parametric smoother involves (a) specifying the size of the estimation region by defining of the number of neighboring points or as a fixed range of data; (b) defining the weighting function (some examples, which are available in different software packages, include uniform for local constant fitting, Gaussian (normal), triangle, biweight, triweight, tricube and Cauchy); (c) the local parametric family, i.e. the order of the polynomial that is locally fitted to each point; (d) assigning a method of combining the weighted observations. For example, estimates can be computed as means, medians, polynomial regression estimates, or robust estimates. The combinations of estimation window, weighting function, local parametric family and smoothing method results in more than 100 possible non-parametric smoothers. Choosing the more appropriate smoothing procedure is somewhat subjective and will in any case be dependent on the specific data set.

We have tried different weighting functions (b), linear and quadratic local fitting (c) and some of the methods (d) for the data obtained from tensile testing of aged polymers. Actually, most of them provide reasonably good results for the scatter plots under investigation by means of tuning the window (a). We recommend to use *loess*, (or sometimes it is called *lowess*—*lo*cally *we*ighted *s*catter plot *s*moothing) procedure, which employs the tricube weighting function with robust smoothing (a polynomial regression estimate resistant to outliers) [10,19–22,27]. Here are some arguments in favor of our choice. Firstly, the *loess* (*lowess*)