MODELING OF THE PEEL AND TACK VALUES OF PSAS USING PROBE TEST MEASUREMENTS

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Introduction

Pressure-sensitive-adhesives (PSAs) are increasingly popular for fastening applications due to their safe and easy handling. With the increase in the number and variety of applications come more demanding requirements in terms of properties. In order to speed up the optimization of the properties needed for a specific application, it will become more and more important to develop a good test for the quick screening of a large number of materials, in order to select the most promising ones [1].

Initially, the instrumented probe tack test has been developed to gain more physical insight in the mechanisms of debonding of PSAs [2] [3]. Most advances came from the very detailed information obtained from the probe test, which provides an entire stress-strain curve and not a unique value, coupled with an *in situ* observation of the deformation mechanisms of the adhesive layer with a video camera [4] [5].

Despite its advantages, such as speed of execution and reproducibility [6], the probe test is not yet widely accepted in industry where adhesive properties are still typically tested with standardized industry tests closer to applications, such as loop tack, peel or shear tests [7]. It would therefore be economically advantageous to be able to predict the result of a peel test, of a loop tack test or of a shear test from a simple probe test experiment which typically lasts less than a minute. However, the important conceptual advances that the more fundamental investigations brought did not yet result in an easy correlation between the outcome of the probe test (a curve of stress as a function of strain) and a value such as peel force, loop tack or shear.

Here, we explore a different but parallel approach to predict the tack or the peel value from a probe test curve. This approach is based on the assumption that the information about the tack and the peel is contained in the probe test curve, but needs to be extracted with statistical tools. Indeed, the sensitivity of the test to changes in chemical structure and in formulation has been shown in several publications [2]. The methodology we use has been developed to extract the most significant part of the data to build a predictive model of the desired property [8] [9].

Experimental

Probe tests were performed for 26 different materials representative of commercial PSAs based on SIS (Kraton D-1160 and D-1161, from Kraton Polymers) and tackifing resins (Piccotac 95E, Piccotac 212, Foral 85-E, from Eastman Chemical Company). Three to five repeat tests were performed for each material on a TA-XT2 i HR texture analyzer (Stable Microsystems) fitted with a spherical probe having a diameter of 25 mm. The probe was brought in contact with the adhesive layer at a velocity of 10 μm/s, until a compressive force of 1.1 N was achieved. It was kept in contact for 0.5 s at this load, and next removed at a debonding speed of 10 μm/s. The whole force-distance curve (compression and traction) was recorded.

The adhesive films were prepared by transfer coating: a toluene solution of polymer and tackifier was applied on Silicon paper using an automatic bar coater. The drying conditions were as follows: 30 min at room temperature followed by 3 min at 110°C. The dried PSA film (coat-weight 1.18 mil) was then coated with a PET film (Mylar, 23 μm). The laminate was conditioned for 24 h under controlled humidity and temperature (23°C ± 2°C, 50% RH ± 5% RH) before testing.

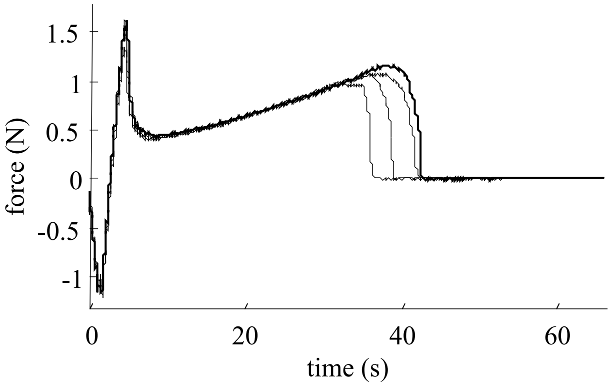

Figure 1. Typical force curves obtained with four probe test repeats; the loop tack test provides a mean value of 21.2 and the peel test a mean value of 15.5.

The peel tests were performed using FINAT FTM 1 conditions: 25 mm x 90 mm strips of PSA were applied on either stainless steel plates or high density polyethylene plates using a 1 kg FINAT standard test roller, and 180° peel were measured after 20 min and 24 hours.

The loop tack tests were performed using FINAT FTM 9 conditions: 25 mm x 210 mm strips of PSA were applied on either stainless steel or high density polyethylene plates.

The outcome of the experimental part of the study was a series of force curves with the corresponding values of the peel force and of the loop tack. Typical force curves obtained with 4 probe test repeats are shown on Figure 1.

Statistical Approach

The proposed procedure is achieved in three steps: a) the choice of the candidate descriptors, i.e. of the variables that potentially contain the information about the tack and the peel; b) the construction of nested models of increasing complexity involving the candidate descriptors, and the selection of the model of minimal necessary complexity given the precision of the peel and tack values; c) the estimation of the model performance.

a. Choice of the candidate descriptors

Since the displacement is the same for each probe test, only the force as a function of the time is useful for the tack or peel prediction. The force measurements being made every 2 ms, we performed a reduction of the dimensionality by drastically reducing the time resolution. A number of descriptors (i.e. of force values) in the interval [50,100] seem appropriate to grasp the information contained in the force curve, see Figure 2. The candidate descriptors are denoted by the $\{\xi_i\}$ for i=1 to n.

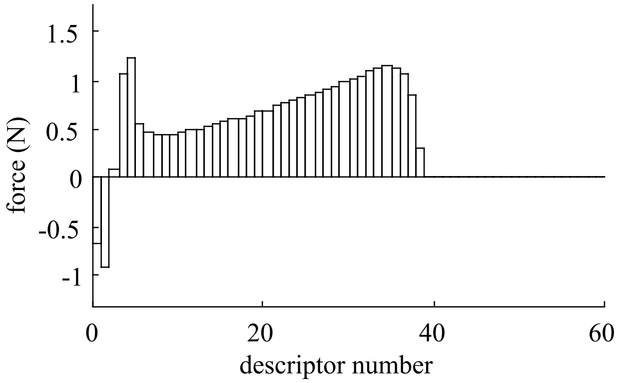

Figure 2. A probe test curve (the thick curve of Figure 1) represented with n=60 force descriptors.

The probe test curves of some adhesives showing a significant variability (see Figure 1), we choose to consider mean values as descriptors, i.e. the mean of the previous descriptor values over at least 3 repeats of the probe test.

b. Model construction and selection

Since the number of candidate descriptors is large (n=60), even a simple affine model involves too many parameters given the number of measurements (N=26 for loop tack, N=24 for peel due to two missing values). Thus, the design of the model heavily relies on the selection of the relevant and non redundant descriptors among the candidates. This can be achieved by constructing nested polynomials involving an increasing number of the most relevant monomials of the descriptors, and by stopping this construction when the variability of the polynomial model becomes of the order of the output (tack or peel) variability. A degree 2 polynomial seems appropriate: it is able to represent linear (monomials ξ_i) and quadratic (monomials ξ_i^2) dependencies, as well as interactions between different parts of the curves (monomials $\xi_i \xi_j$).

More precisely, let us denote by $\mathbf{y}$ the vector of the N desired outputs (tack or peel), and by $\mathbf{x}_i$ the vector of the N values of the i-th monomial. The $\{\mathbf{x}_i\}$ are successively introduced as inputs to the predictive model with parameters $\boldsymbol{\theta}$ according to their decreasing contribution to the explanation of the output $\mathbf{y}$. The monomial with the largest contribution is the one that decreases most the residual sum of squares, and is introduced first. Then, the remaining monomial vectors $\{\mathbf{x}_i\}$ and the output vector $\mathbf{y}$ are orthogonalized with respect to the first monomial using the Gram-Schmidt algorithm [10]. The procedure is repeated in the subspace orthogonal to the first monomial, and so on.

The construction is stopped when the model root mean square error (RMSE) is of the order of the output standard error, using a test for lack of fit [9] [11]. For both loop tack and peel, the measurement standard error depends on the adhesive. However, it is available only for some of them (10 out of 26). Thus, we consider an average standard error estimate, which equals 1.2 N/in for both tack and peel. Since 3 to 5 repeats of the loop tack or peel measurements were performed, we consider a mean number of repeats of 4, and an output standard error of $1.2/\sqrt{4} = 0.6$ N/in. The selected model output is denoted by $f(\boldsymbol{\xi},\boldsymbol{\theta})$.

c. Model performance estimation

The performance of the model is defined as the root of the expectation of its mean square error $E((y - f(\boldsymbol{\xi},\boldsymbol{\theta}))^2)$.

Since the data set is small, we provide a leave-one-out (LOO) cross validation estimate. The LOO estimate for a model obtained with N adhesives is defined as follows: the k-th LOO error is the error for the k-th adhesive made by the model obtained when the k-th adhesive is left out from the data set, and the LOO estimate is the root of the mean of the N squared LOO errors. They can be computed economically as functions of the residuals of the model obtained on the whole data set [8] [9]. The calibration RMSE obtained on the whole data set is denoted by $RMSE_{cal}$, and that of LOO by $RMSE_{LOO}$.

We also provide the RMSE obtained when estimating the parameters of the model on a training set of 20 adhesives for tack and 18 adhesives for peel, and testing the model on an independent test set of 6 adhesives corresponding to different materials. The RMSE on the training set is denoted by $RMSE_{train}$, and that on the test set by $RMSE_{test}$.

Results and Discussion

The above procedure is applied separately to the prediction of the loop tack and of the peel. In practice, due to the too small size of the data set, the models obtained with the test for lack of fit possess a $RMSE_{LOO}$ or a $RMSE_{test}$ that is large as compared to the $RMSE_{cal}$ or to the $RMSE_{train}$. Thus, we retained models with a few monomials less than those selected with the test, but for which the discrepancy between the different RMSEs is smaller. In other words, we pay for reducing the model variability (variance) by accepting a lack of fit (bias). The performance of the tack and peel models of degree 2 is summarized in Table 1.

In order to quantify the significance of the force descriptors involve in a model, we define the sensitivity of its output with respect to each force descriptor as:

$$\delta_j = \frac{1}{N} \sum_{k=1}^{N} \left| \frac{\partial f(\boldsymbol{\xi}, \boldsymbol{\theta})}{\partial \xi_j} \right|_k = \frac{1}{N} \sum_{k=1}^{N} \left| \sum_{i=1}^{q} \theta_i \frac{\partial m_i}{\partial \xi_j} \right|_k \quad \text{for j=1 to n}$$

where N denotes the size of the data set, n is the number of descriptors, q is the number of selected monomials, m_i is the i-th selected monomial, and θ_i is the corresponding parameter. The sensitivities are shown in Figure 3. The tack model possesses 9 monomials involving 14 descriptors, and the peel model possesses 7 monomials involving 11 descriptors. The tack model needs descriptors located at the end of the curves, i.e. descriptors whose variability is generally high, whereas the peel model does not.

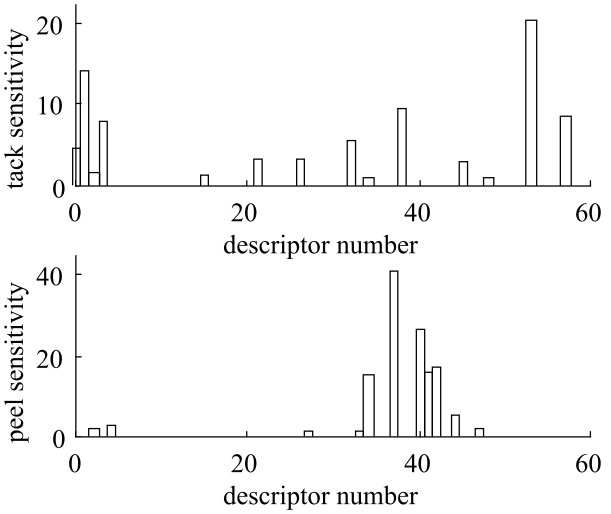

Figure 3. Sensitivities of the tack and peel models to the force descriptors.

Table 1 shows that the peel model achieves a mean error twice as large as the peel standard error, with a reasonable number of parameters as compared to the available number of adhesives. The tack model is more biased, with a mean error three times as large as the loop tack standard error, and with too large a number of parameters. The loop tack seems more difficult to predict, both because it is more nonlinear (since more parameters are needed), and because it involves descriptors located at the end of the curves (which are more variable).

Conclusions

The above results confirm that the information about the tack and the peel is indeed contained in the force signal obtained with a probe test, and that the proposed procedure is likely to provide predictive models of these properties. We expect further improvements from a reliable estimation of the measurement variability for each adhesive, which will allow a correct weighting of the data points, and from the use of a larger, more representative data set.

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Table 1. Summary of the modeling results.

output property	nb monomials /descriptors	nb of PSAs for training/test	$\frac{s}{\sqrt{4}}$	$RMSE_{cal}$	$RMSE_{LOO}$	$RMSE_{train}$	$RMSE_{test}$
tack	9/14	20/6	0.6	1.4	2.2	1.3	2.0
peel	7/11	18/6	0.6	0.9	1.1	0.8	1.3