A continuum-based model capturing size effects in polymer bonds

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Abstract. It is known from applications that the mechanical behaviour of polymer bonds does not only depend on the properties of the polymer itself but also on the substrate. Therefore, the mechanical behaviour, i.e. the stiffness, of a polymer joint becomes thickness dependent. In the present work we describe experiments performed on polymer joints and we develop a continuum-based model which is able to describe the experimentally observed size effects without suggesting the microstructure in detail. The continuum mechanical model is enhanced by a scalar-valued structure parameter which describes all the effects taking place in the boundary layer which arises near the substrate. It is shown that the model parameters can be determined on the basis of simple shear experiments performed on polymer layers of different thickness.

1. Introduction

Polymers form boundary layers if they come into contact with a metallic substrate. In the corresponding boundary layer the properties of the polymer differ from the bulk ones. Therefore, the mechanical features of a polymer joint, i.e. a thin film of polymer between metal substrates, depend on the thickness of the film. In the present paper a system of polyurethane (PUR) on an anodised aluminium substrate is experimentally investigated. This is an example for a typical industrial application of an adhesive joint where polyurethane is used as a commercial glue. At first the bulk properties of the PUR are studied in uniaxial tension experiments. Afterwards polymer joints of different thicknesses are tested under shear. It is found that the stiffness of these joints strongly depends on the thickness of the polymer film between the substrates. This could be expected on the basis of data obtained by Brillouin microscopy [10, 11].

In the next section of the paper we briefly discuss the preparation of the specimens, as well as the set-up of the tension tests and the shear tests. Based on the experimental results it becomes evident that a classical continuum mechanical approach is not able to describe the observed phenomena due to the strong size effect. In the present case the size effect leads to the behaviour smaller is weaker, which is typically not documented in literature. Therefore, we present an extended model based on a dimensionless structure parameter approach. The structure parameter and its related balance equation are introduced to describe all effects taking place in the polymer close to the surface of the substrate where a boundary layer is formed. The continuum-based modelling concept including abstract structure parameters can be formally traced back to an extension of the balance of energy, cf. Capriz [3, 4], Svendsen [15, 16] and...
Steeb & Diebels [5, 13, 14]. An axiomatic way of systematically deriving the relating balance equations with respect to the extended balance of energy was introduced in the work of Green & Rivlin [8] by taking into account invariance arguments.

Further developments of extended continua with microstructure can be found in [3, 4, 6, 15, 16]. The advantage of such an abstract setting is found in the fact that a phenomenological approach does not require an explanation of the physical and chemical processes governing the formation of the boundary layer which are not understood in detail. Finally, the inherent model parameters are determined from the experimental data. Therefore, a stochastic optimisation algorithm is applied based on the ideas of biological evolution [12]. It is found that the model parameters can be determined independently from the starting point of the optimisation procedure. The paper is closed by a short summary and a discussion of the results.

2. Experimental setup and results

The PUR studied in the present paper is based on commercial components obtained from Bayer AG, namely Desmodur® CD, Desmophen® 2060 BD and Desmophen® 1380 BT. For this kind of material the assumption of isotropic material behaviour is established. At room temperature the resulting PUR behaves viscoelastically. In order to determine the bulk properties, tension tests are performed. For the preparation of the required specimens a film of 1.5 mm thickness is manufactured on a silicon surface. Specimens, which are used for the tension tests according to ISO 527-2:1996 Type 5A, are die cut from the film and evaporated with aluminium stripes by physical vapour deposition (PVD), cf. Figure 1. Lighted from behind, these strips give a good contrast for optical deformation measurements.

![Figure 1. Specimen according to ISO 527-2:1996 Type 5A for tension tests.](image)

The tension tests are performed in a custom-made high precision testing device shown in Figure 2 [1, 2].

Even if the specimens show viscoelastic behaviour we focus on the basic elasticity, i.e. we only present and discuss the equilibrium stress-strain curve obtained by quasi-static deformations. Details of the tests including the viscoelastic behaviour are described in [9]. The experimentally obtained average stress-strain curve is shown in Figure 3. The stress $T_{11}$ is the true stress or Cauchy stress in longitudinal direction which is obtained as the ratio of the force with respect to the cross-section in the current configuration. During the experiment the longitudinal and the transversal mean stretch are measured optically. With the assumption of isotropy the stretch in thickness direction is the same as in transverse direction. It was found that the specimens show a nearly incompressible behaviour, i.e. the Jacobian of the deformation gradient is close to one ($\det \mathbf{F} = J = 1$).

The specimens tested in tension do not possess an interphase according to the manufacturing process. Therefore, the experimental data are used to adjust the model parameters governing the bulk behaviour. The boundary layer is activated if the PUR is polymerised on anodised aluminium substrates. Two blocks of aluminium are separated by spacers of thickness 100 $\mu$m, 200 $\mu$m, 300 $\mu$m, 500 $\mu$m and 1000 $\mu$m while the gap is filled with PUR. The resulting bonds are tested under shear loading in a GIESA RS10 device. Figure 4 shows a photo and
Figure 2. High precision testing device according to [1, 2].

Figure 3. Experimental average data of true Cauchy stress $T_{11}$ vs. deformation $B_{11}$ and Neo-Hookean fit.

a principle sketch of the specimen under shear loading. Therefore, we used an as small as necessary deformation rate not to affect viscoelasticity. The influence of the boundary layer due to the viscoelastic material behaviour of a polymeric joint is not part of this paper and will be investigated in further experiments.

The results of the shear tests are collected from different realisations. Figure 5 shows the effective shear stress $\tau = F/A$ which is plotted over the effective shear strain $\gamma = u/h$. This results are called effective because they are computed from macroscopically measured quantities, i. e. from the shear force $F$, the cross-section $A = \text{const.}$, the displacement $u$ of the two aluminium blocks and the film thickness $h = \text{const}$. The deformation is recorded for a shearing strain of $0 \leq \gamma \leq 0.5$ corresponding to a maximum shear angle of $22.5^\circ$. Even if the shear deformation is finite the obtained curves are straight lines. But as can be seen from Figure 5 (left) the slope of the lines depends on the film thickness leading to a pronounced size effect in the form
smaller is weaker. This can be verified very well if the effective shear modulus $\mu_{\text{eff}}$ is computed according to $\tau = \mu_{\text{eff}} \gamma$. In Figure 5 (right) it is shown that the effective modulus decreases to 58% of the value of the bulk if the film thickness is decreased.

3. Model equations
In this section we briefly review the governing equations of our extended model. Modelling details and the underlying thermodynamic framework can be found in [13, 14]. In order to include a size effect into the model an extension in form of a structure parameter is chosen. The advantage of this extension of the classical continuum mechanical setting will be found in the fact that stiff and weak boundary layers can be modelled depending on the choice of the
boundary conditions.
The primary variables of the model are the displacement \( \mathbf{u}(\mathbf{x}, t) \) and the structure parameter \( \kappa(\mathbf{x}, t) \). For both quantities balance equations are postulated, i. e. the balance of momentum

\[
\text{div} \mathbf{T} = 0 \tag{1}
\]

and the additional balance equation

\[
\text{div} \mathbf{S} + \hat{\kappa} = 0. \tag{2}
\]

For simplicity we restrict ourselves to the quasi-static limit without considering supply terms. Note that equation (2) possesses the same structure as the balance of equilibrated forces introduced by Goodman and Cowin [7]. The axiomatic derivation of such additional balances is discussed in detail for affine microdeformations by Capriz [3, 4], Svendsen [15, 16] and without a kinematical interpretation by Steeb & Diebels [13, 14] and Diebels et al. [5].

The symbols introduced in (1) and (2) are the Cauchy stress tensor \( \mathbf{T} \), the flux \( \mathbf{S} \) related to \( \kappa \) and a production term \( \hat{\kappa} \).

If we restrict further investigations to the equilibrium behaviour of the PUR, i. e. to the elastic deformation obtained at small deformation rates, it is sufficient to choose the following set of process variables

\[
\mathcal{S} = \{ \mathbf{B}, \kappa, \text{grad} \kappa \}. \tag{3}
\]

In (3) \( \mathbf{B} \) is the left Cauchy-Green deformation tensor which can be computed from the deformation gradient \( \mathbf{F} \) according to

\[
\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T, \quad \mathbf{F} = \mathbf{I} + \text{Grad} \mathbf{u}. \tag{4}
\]

Here we introduced the identity tensor \( \mathbf{I} \), and \( \text{grad}(\bullet) \) is the gradient operator with respect to the position vector \( \mathbf{x} \) of the current configuration, whereas \( \text{Grad}(\bullet) \) is the gradient operator with respect to the position vector \( \mathbf{X} \) of the reference configuration. The two position vectors are linked by the displacement field \( \mathbf{u} = \mathbf{x} - \mathbf{X} \). The superscript \( (\bullet)^T \) refers to the transposed tensor whereas a single dot represents a single contraction between the basis vectors of the tensor bases.

It can be shown by thermodynamic investigations [13] that the Cauchy stress tensor \( \mathbf{T} \), the flux \( \mathbf{S} \) and the production \( \hat{\kappa} \) can be derived from a postulated free Helmholtz energy function \( \Psi = \hat{\Psi}(\mathbf{B}, \kappa, \text{grad} \kappa) \). Without going into detail, the following representations are found:

\[
\mathbf{T} = 2 \rho \mathbf{B} \frac{\partial \hat{\Psi}}{\partial \mathbf{B}}, \quad \mathbf{S} = \frac{\partial \hat{\Psi}}{\partial \text{grad} \kappa}, \quad \hat{\kappa} = - \rho \frac{\partial \hat{\Psi}}{\partial \kappa}. \tag{5}
\]

Note in passing that these equations are valid only if reversible processes are investigated. In the present case only the basic elasticity of the PUR is described by the presented equations. If the viscoelastic behaviour of the bulk should be taken into account the model has to be enhanced by internal degrees of freedom, i. e. inelastic strains in the sense of internal variables have to be included. An identification of the viscoelastic properties of the PUR and an appropriate model are discussed in [9].

The balance equations (1) and (2) as well as the constitutive equations (5) lead to a set of coupled equations for the displacement field \( \mathbf{u} \) and for the structure parameter \( \kappa \). Due to the experimentally verified fact that the bulk behaviour of the investigated PUR can be described by a Neo-Hooke model [9] we choose the following additive split of the free energy function

\[
\rho_0 \Psi = \Psi_{\text{iso}}(\mathbf{I}_B) + \Psi_{\text{vol}}(J) + \Psi_{\text{struct}}(\kappa, \text{grad} \kappa) + \Psi_{\text{couple}}(\kappa, \mathbf{I}_B). \tag{6}
\]
The first term of (6) represents the standard free energy term of the incompressible Neo-Hooke material

$$\Psi_{\text{iso}} = \frac{1}{2} \mu (\bar{I}_B - 3), \quad (7)$$

where $\bar{I}_B$ is the first principle invariant of the isochoric left Cauchy-Green deformation tensor $B_{iso} = J^{-2/3} B$ and $\mu$ represents the shear modulus. The second term is a volumetric extension term formulated in the Jacobian $J = \det F = \sqrt{\det B}$, e. g.

$$\Psi_{\text{vol}} = \frac{1}{4} K \left( (J - 1)^2 + (\ln J)^2 \right). \quad (8)$$

The bulk modulus $K$ will be chosen much larger than the shear modulus $\mu$ and acts like a penalty term. Therefore, the model behaves nearly incompressible without introducing an additional Lagrangian multiplier to ensure the incompressibility constraint. The third term is chosen as simple as possible, i. e. a quadratic form in $\kappa$ and grad $\kappa$ is chosen

$$\Psi_{\text{struct}} = \frac{1}{2} \alpha \kappa^2 + \frac{1}{2} \mu L^2 (\text{grad} \kappa)^2. \quad (9)$$

The additional material parameters are $\alpha$ and $\mu L^2$. For dimensional reasons the internal length $L$ is introduced in (9). Finally, the coupling part of the free energy is chosen as

$$\Psi_{\text{couple}} = \phi \kappa (\bar{I}_B - 3) \quad (10)$$

introducing a further model parameter $\phi$.

Evaluating (6) – (10) according to (5) yields the constitutive relations for the Cauchy stress tensor $T$, the flux vector $S$ and the scalar production term $\hat{\kappa}$ in the following form

$$T = J^{-1} \left( \frac{1}{2} K (J^2 - J + \ln J) I + (\mu + 2 \phi \kappa) B_{iso} \right),$$

$$S = J^{-1} \mu L^2 \text{grad} \kappa,$$

$$\hat{\kappa} = -J^{-1}(\alpha \kappa + \phi (\bar{I}_B - 3)). \quad (11)$$

The balance of momentum (1) and the balance equation for the structure parameter (2) can be solved numerically by a coupled multifield Galerkin finite element method [13] in combination with the constitutive relations (11) if boundary conditions are given. In the present case, we prescribe the usual Dirichlet and Neumann data for the displacement field $u$ according to the situation corresponding to the experimental test. For the structure parameter it is assumed that free boundaries with normal $n$ lead to a vanishing flux in the form $S \cdot n = 0$ while Dirichlet data in the form $\bar{\kappa} = 1$ or $\bar{\kappa} = -1$ are prescribed if either stiff or weak boundary layers are observed in the experiment. Therefore, the dimensionless value $\bar{\kappa}$ characterises the properties of the adhesive bond between the polymer and the substrate and its influence on the boundary layer. The assumption of the values of the Dirichlet boundary conditions of the scalar structure parameter is arbitrary. If we chose other values the additional parameters of the model would have been identified as other values. We intend to use modified values for the boundary conditions of the structure parameter when using certain substrates or other treated surfaces. Note again, that the phenomenological approach does not require a detailed explanation of the physical and chemical processes taking place in the boundary layer.

4. Parameter identification

The model presented in the previous section is adapted to the experimental data given above in section 2. The strategy of the identification is a two-step procedure: First, the bulk parameters $\mu$ and $K \gg \mu$ are determined from tension tests. Second, the additional parameters $\alpha$, $L^2$ and
related to the structure parameter are determined. Therefore, the size effect observed in shear experiments is utilised.

A flexible tool for the identification is found in a genetic algorithm [12]. Starting point is a generation of $N$ sets of parameters $\mathcal{P}_i = \{\alpha_i, L^2_i, \phi_i\}$ which are chosen arbitrarily. These are called the parents. For each of the parents the model is evaluated according to the boundary value problem which corresponds to the performed experiment. An objective function $Q$ is defined as the sum of the squares of differences between measured data $f_{\text{exp}}$ and computed data $f_{\text{model}}$, respectively,

$$Q = \sum_i (f_{\text{exp}} - f_{\text{model}}(\mathcal{P}_i))^2.$$  \hspace{1cm} (12)

Our goal is to minimise the objective function $Q$ with respect to the model parameters $\mathcal{P}$. Therefore, a certain number $M$ of the $N$ parents is chosen leading to the smallest values of $Q$. From these parents a new set of parameters is generated called children. The children are generated according to principles of evolution, i.e. parameters of different parents are recombined, some of the parameters are slightly changed, some are chosen arbitrarily by a random number generation. If $N$ children are generated these children form the next generation and the algorithm starts again. The procedure is continued until the objective function reaches its global minimum.

Application of this strategy to the tension test determines the bulk shear modulus $\mu$ from the data obtained in the tension tests. During this identification procedure $\kappa = 0$ is chosen for the whole domain, which means (in terms of a physical interpretation) that no boundary layer is present. In the present case the shear modulus is identified to $\mu = 1.361 \text{ N/mm}^2$. Numerical simulations of the tension test are shown in Figure 3 (right).

In the next step the shear experiments on different layer thicknesses are used to identify the remaining parameters. First of all, the boundary layer thickness is determined and the internal length $L$ is interpreted as the boundary layer thickness. The Brillouin data measured by Krüger et al. [10] and Sanctuary et al. [11] are investigated leading to $L \approx 100 \text{ µm}$. The remaining parameters $\alpha$ and $\phi$ are determined from the data shown in Figure 5. The objective function is formulated in the effective moduli $\mu_{\text{eff}}$ obtained from the experimental data and from the computations respectively. Note that the effective moduli are not material parameters of the presented model but they are computed from the global solution behaviour of a boundary value problem.

After 50 generations the values $\alpha = 4.88 \text{ N/mm}^2$ and $\phi = 0.33 \text{ N/mm}^2$ are obtained by the evolution strategy leading to the effective moduli as functions of the film thickness as shown in Figure 6. Further investigation is necessary to improve the values of the bulk material parameters.

5. Discussion

It is known from literature that polymers form interphases if they are applied to substrates. In the present contribution we investigated a commercial polyurethane system from Bayer AG which was applied to an aluminium substrate. In the experimental investigation a strong size effect was found: The effective shear modulus of a polymer film between two Al blocks decreased with the film thickness. In general, size effects are reported in the form smaller is stiffer but the presented system showed the opposite effect smaller is weaker.

In order to include this effect into a model an extended continuum formulation is presented. The microstructural effects are described phenomenologically by introducing an additional structure parameter $\kappa$ and its related balance equation. The model allows descriptions of both types of size effects depending on the choice of the boundary data for the structure parameter. In the present work it is shown that the model parameters can be determined from macroscopic experimental
Figure 6. Effective shear moduli $\mu_{eff}$ obtained from measurements and from the model (left) and comparison of simulated and experimental stress-deformation curves (right).

investigations if the internal length is assumed to be known. The required information to determine $L$ can be taken e. g. from Brillouin microscopy.

In summary, it can be seen that the model is able to describe the material behaviour qualitatively and quantitatively. The effective shear modulus of a bond of certain thickness is the output of the model but not a model parameter. Therefore, it can be expected that the model performs well if other boundary value problems than shear tests are investigated and if the model is used as a predictive tool.

The next step has to take into account the viscoelastic properties of the investigated PUR and the influence of the time-dependent effects on the formation of the boundary layer.

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Literature

[1] Batal, J. [2002]. Möglichkeiten zur Messung der Haftkraft einer strukturierten Polymeroberfläche. Studienarbeit, Universität des Saarlandes.
[2] Batal, J. [2004]. Haftkraftmessung an biomimetisch strukturierten Polymeroberflächen. Diplomarbeit, Universität des Saarlandes.
[3] Capriz, G. [1980]. Continua with Microstructures, volume 35 of Springer Tracts in Natural Philosophy. Springer, New York.
[4] Capriz, G., P. Podio-Guidugli & W. Williams [1982]. ‘On balance equations for materials with affine structure.’ Meccanica, 17, pp. 80–84.
[5] Diebels, S., H. Steeb & W. Possart [2005]. ‘Effects of the interphase on the mechanical behaviour of thin adhesive films – a modeling approach.’ In Adhesion – Current Research and Applications, edited by W. Possart, pp. 319–335. John Wiley & Sons, Chichester.
[6] Eringen, C. [1999]. Microcontinuum Field Theories, Vol. I: Foundations and Solids. Springer-Verlag, Berlin.
[7] Goodman, M. A. & S. C. Cowin [1972]. ‘A continuum theory for granular materials.’ Arch. Rat. Mech. Anal., 44, pp. 249–266.
[8] Green, A. E. & R. S. Rivlin [1964]. ‘On Cauchy’s equations of motion.’ Z. Angew. Math. Phys., 15, pp. 290–292.
[9] JOHLITZ, M., H. STEEB, S. DIEBELS, A. CHATZOURIDOU, J. BATAL & W. POSSART [2006]. ‘Experimental and theoretical investigation of nonlinear viscoelastic polyurethane systems.’ J. Mat. Sci., accepted for publication.

[10] KRÜGER, J. K., W. POSSART, R. BACTAVACHALOU, U. MÜLLER, T. BRITZ, R. SANTUARY & P. ALNOT [2004]. ‘Gradient of the mechanical modulus in glass-epoxy-metal joints as measured by Brillouin microscopy.’ J. Adhesion, 80, pp. 585–599.

[11] SANCTUARY, R., R. BACTAVATCHALOU, U. MÜLLER, W. POSSART, P. ALNOT & J. KRÜGER [2003]. ‘Acoustic profilometry within polymers as performed by Brillouin microscopy.’ J. Physics D: Appl. Phys., 36, pp. 2738–2742.

[12] SCHWEFEL, H. P. [1995]. ‘Evolution and optimum seeking.’ John Wiley & Sons, New York.

[13] STEEB, H. & S. DIEBELS [2004]. ‘Modeling thin films applying an extended continuum theory based on a scalar-valued order parameter – Part I: Isothermal case.’ Int. J. Solids Structures, 41, pp. 5071–5085.

[14] STEEB, H. & S. DIEBELS [2005]. ‘Continua with affine microstructure: Theoretical aspects and application.’ Proc. Appl. Math. Mech., 5, pp. 319–320.

[15] SVENSDEN, B. [1999]. ‘On the thermodynamics of thermoelastic materials with additional scalar degrees of freedom.’ Continuum Mech. Therm., 4, pp. 247–262.

[16] SVENSDEN, B. [2001]. ‘On the continuum modeling of materials with kinematic structure.’ Acta Mech., 152, pp. 49–80.