Tack energy and switchable adhesion of liquid crystal elastomers

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The mechanical properties of liquid crystal elastomers (LCEs) make them suitable candidates for pressure-sensitive adhesives (PSAs). Using the nematic dumbbell constitutive model, and the block model of PSAs, we study their tack energy and the debonding process as could be measured experimentally in the probe-tack test. To investigate their performance as switchable PSAs we compare the tack energy for the director aligned parallel, and perpendicular to the substrate normal, and for the isotropic state. We find that the tack energy is larger in the parallel alignment than the isotropic case by over a factor of two. The tack energy for the perpendicular alignment can be 50% less than the isotropic case. We propose a mechanism for reversibly switchable adhesion based on the reversibility of the isotropic to nematic transition. Finally we consider the influence of several material parameters that could be used to tune the stress-strain response.

I. INTRODUCTION

Pressure sensitive adhesives (PSAs) are soft materials that adhere to nearly any surface when low pressure is applied. Their effectiveness can be described by the total energy required to separate the adhesive from a surface, known as the tack energy. Experimentally this can be measured in the probe-tack test, where the force required to remove a probe moving at constant velocity from an adhesive film is measured and a stress-deformation curve is produced. An experimentally measured stress-deformation curve produced from a probe-tack test on two materials is shown in fig. 11. For small deformations the force rises rapidly with extension up to a peak force. During this phase cavities form within the adhesive and grow. Following the peak force there is a pronounced plateau in the force which can be upward pointing (P1) if the material strain-hardens. During this phase fibrillation occurs and the force is dominated by the viscoelastic properties of the adhesive rather than the cavities. Ultimately the plateau region ends when the material detaches from the probe. Detachment can happen in the bulk, which is known as cohesive failure and occurs for material P2 in fig. 11. Alternatively detachment can happen in the probe, which is known as adhesive failure and occurs for material P1 in fig. 11.

To achieve a high tack energy the PSA must have a low dynamic modulus (typically 0.1 MPa at 1 Hz) to make conformal contact with the substrate. 2 As the probe is retracted, the adhesive film is drawn into fibrils. The adhesive must be sufficiently soft so the fibrils do not detach at small strain, yet still require some energy to deform 3. PSAs are typically made from high molecular weight polymers that are lightly crosslinked to form viscoelastic solids. Acrylic, styrenic, and siloxane based polymers have been refined for use as PSAs 4. The bulk rheological properties of a PSA are important in determining its tack energy. The optimal stress-strain behaviour is initially strain softening, to aid crack blunting, and eventually becomes strain hardening to stiffen the fibrils, and increase the force required in the latter stages of debonding 3.

Gay et al. have presented a successful theoretical description of PSA debonding based on the growth of bubbles at the substrate/adhesive interface 6. As these bubbles join, they form larger bubbles which are then drawn into fibrils. The main physical processes of homogeneous deformation, nucleation of cavities, followed by fibril formation have been included in a simplified model of the debonding process called the Block model 7, 8. Here the adhesive layer is divided up into N equal rectangular blocks that can undergo a combination of shear and stretching deformation, as well as slipping on the substrate. The force-displacement curves of the block model reproduce the characteristic features seen in probe-tack experiments.

There is considerable interest in being able to turn off the adhesive properties of PSAs using external stimuli such as light, humidity, and temperature. For example methacrylate-functionalized adhesives containing a photoinitiator can show an almost complete loss of adhesion when irradiated under a halogen lamp, as a result of photo-initiated crosslinking raising the elastic modulus 4, 10. The switching here however is only one-
way, the adhesive cannot be returned to a tacky state. Treunor et al. [11] achieved two-way switching by using coumarin-functionalized acrylate adhesives, whereby UV-A radiation was used to switch off adhesion and UV-C radiation was used to (partially) switch it back on. Altering ambient humidity has been used to reversibly modify the surface composition of polymer blends thus changing the adhesive strength [12]; note that here the adhesion is modified by altering the substrate rather than the adhesive itself. There are several other examples of switchable adhesion/wetting based on polymer brush surfaces driven by an external stimulus [13,14]. Liquid Crystal Polymer (LCP) based adhesives which undergo a reversible Smectic-Isotropic transition have been shown to have a transition between a tacky and a non-tacky regime as one cools into the smectic phase [15]. The low temperature smectic phase is harder, and less wetting than the isotropic phase. Kamperman and Synytska [16] provide a review of two mechanisms to achieve switchable adhesion; topography and chemical functionality.

In this paper we propose an application for weakly crosslinked LCPs, called liquid crystal elastomers (LCEs), as anisotropic adhesives whose tack energy can be switched depending on the orientation of the director, and the degree of liquid crystalline order. The mechanism here is based on the change in the bulk rheology of the adhesive.

LCEs are unique materials that couple liquid crystal mesogens to the underlying polymer network. In the high temperature isotropic phase, they behave much like conventional rubbers. When cooled into the nematic phase the orientation of the director is crucial to determining their mechanical behaviour. When stretched parallel to the director they behave like uniaxial solids. On stretching perpendicular to the director they exhibit (semi-)soft elasticity – that is strain increases with little increase in stress. They have a long plateau in their stress-strain curve before undergoing strain hardening to values of the modulus found in isotropic rubbers at low extension. The curve before undergoing strain hardening to values of the modulus found in isotropic rubbers at low extension. They have a long plateau in their stress-strain curve before undergoing strain hardening to values of the modulus found in isotropic rubbers at low extension. However, this equilibrium statistical physics model does not describe the dynamics of the LCE that are essential to model adhesive properties. We will show that the nematic dumbbell model of Maffettone and Marrucci includes the equilibrium behaviour of nematic elastomers, and also provides a description of their dynamics [21]. By using this constitutive model in the block model we describe the behaviour of LCE based viscoelastic adhesives.

II. MODEL SYSTEM

Here we consider an idealised version of the probe-tack test. A thin adhesive layer is placed between two rigid substrates, which are then pulled apart with a constant velocity. The force required to separate the substrates is measured as a function of the displacement between them. We will model the subsequent debonding process in two dimensions by assuming that the adhesive and any deformational flow are confined to the $xy$ plane. The debonding process involves several complex phenomena, but the following dominant effects will be included in our description; large strain deformation of the adhesive, cavity expansion/contraction, slip of the adhesives at the substrate interface. These effects have been incorporated in the Block model developed by Yamaguchi et al. [7], which gives a 2-dimensional description of isotropic adhesives at low Reynolds number. We modify the Block model by utilising simpler shapes and deformations for the blocks, and a material constitutive law that describes LCEs and their associated director reorientation.

A. Block Model

The initial adhesive layer has height $H_0$ and length $L_0$ (we assume the adhesive is thin, i.e. $L_0 >> H_0$). This layer is divided into $N$ rectangular blocks of equal width $W_0 = L_0/N$, which can undergo slip at the interface with the substrate. Each block is assumed to undergo a stretching deformation along the $y$-direction, no deformation in the $z$-direction, a corresponding volume-conserving contraction in the $x$-direction, and a piece-wise linear simple shear deformation in the $x$-direction as shown in Fig. 2. The motion of the $i$th block is characterised by three parameters: the elongation along the $y$-direction denoted $\lambda$, the shear deformation denoted $\lambda_{xy}$, and the $x$-coordinate of the centre of mass of the block denoted $X_i$.

On stretching the adhesive layer by a factor $\lambda$ in the $y$ direction, each block has a new height $H = \lambda H_0$ and a new width $W = W_0/\lambda$. The shear deformation of a block can be described by dividing it into two sub-blocks of width $W$ and height $H/2$. The lower sub-block shears by $\lambda_{xy}$ while the upper sub-block has the opposite shear $-\lambda_{xy}$ as illustrated in Fig. 2. This deformation is slightly different to that employed by Yamaguchi et al. [7]. They allowed a parabolic deformation in the $x$-direction, which implies a shear which varies continuously with position along the $y$-axis. We anticipate a coupling between shears and the director in our nematic adhesives, and modelling the nematic degrees of freedom is substantially simplified if we assume that the sub-blocks have constant shear and director. We will see later that this change simply modifies the constant prefactor in the equation for the shear of the block. The deformation gradient tensor $\lambda$ for each
FIG. 2. The deformation of an individual block involves an area preserving elongation along the y direction, and a piecewise linear deformation in the xy plane. The z component of the centre of mass of the block is \( X_i \), while the point of contact at the interface between the block and the substrate is \( X_{si} \).

sub-block can be written as

\[
\lambda = \left( \begin{array}{cc} \frac{1}{\lambda} & \pm \lambda x_{xy} \\ \frac{0}{\lambda} & \lambda \end{array} \right), \tag{1}
\]

where the sign of the shear \( \lambda x_{xy} \) depends upon which sub-block is being described.

Let \((X_{si}, 0)\) be the mid-point of the contact between the block and the substrate in the undeformed state, and \((x_{si}, 0)\) the equivalent point in the undeformed state. Then transforming between the undeformed state \((x, y)\) and deformed state \((X, Y)\) using \((dX, dY) = \lambda \cdot (dx, dy)\) and integrating we obtain

\[
X_i(x, y) = \begin{cases} X_{si} + \frac{(x-x_{si})}{\lambda} + \lambda x_{xy} y & y < H_0/2 \\ X_{si} + \frac{(x-x_{si})}{\lambda} + \lambda x_{xy}(H_0 - y) & y \geq H_0/2 \end{cases}
\]

\[
Y(x, y) = \lambda y.
\]

Hence the x-coordinate of the centre of mass of the ith block, is given by

\[
X_i = \int_{y=0}^{y=H_0} \int_{x=x_{si}-W_0/2}^{x=x_{si}+W_0/2} X(x, y) dx dy/(H_0 W_0)
= X_{si} + \lambda x_{xy} \frac{H_0}{4}. \tag{2}
\]

Finally, we will require the elements of the velocity gradient tensor in the deformed configuration \( K_{ij} = \nabla \cdot v_i \). In terms of the deformation gradient tensor \( \lambda \) this is given by \( K = \lambda \cdot \lambda^{-1} \):

\[
K = \begin{pmatrix} -\frac{\lambda}{\lambda} & \frac{\lambda}{\lambda} + \frac{\lambda x_{xy}}{\lambda} \\ 0 & \frac{\lambda}{\lambda} \end{pmatrix}. \tag{3}
\]

**B. Cavity Expansion**

As the separation between substrates \( \lambda H_0 \) increases, there is a corresponding reduction in block width \( W_0/\lambda \).

If the displacement between the centres of the blocks \((X_{i+1} - X_i)\) is not equal to their width, a gap is created between the blocks labelled \( i + 1 \) and \( i \). We treat this gap as a circular cavity with radius \( R_i \) having the same area as the void between the blocks, see Fig. 3. The instantaneous radius of the circular bubble is given by

\[
\pi R_i^2 = H_0 \lambda \left( X_{i+1} - X_i - \frac{W_0}{\lambda} \right). \tag{4}
\]

The Rayleigh-Plesset (RP) equation describes the dynamics of a spherical bubble placed in a Newtonian fluid with viscosity \( \eta \). If \( P_1 \) is the pressure in the fluid at the bubble interface, \( P_{cav,i} \) the pressure in the cavity at the fluid interface and \( \gamma \) the surface tension, then the RP equation is

\[
\frac{dR_i}{dt} = \frac{R_i}{2\eta} \left( P_{cav,i} - P_1 - \frac{\gamma}{R_i} \right). \tag{5}
\]

If the cavities do not contain air then \( P_{cav,i} \) is simply zero. If the cavity includes air, initially at atmospheric pressure \( P_{atm} \) in the undeformed state then \( P_{cav,i} \) is related to the area change in the cavity via

\[
P_{cav,i}(t) = P_{atm} \left( \frac{R_i(t)}{R_i(0)} \right)^2. \tag{6}
\]

This is a highly simplified model of the growth/contraction of the cavities, it ignores both the elasticity and the anisotropy of the viscoelastic adhesive surrounding the cavity. Given the anisotropy of the adhesive it is unlikely bubbles would grow in a uniform circular/spherical way. Nevertheless the model has the correct qualitative features for any model of cavity dynamics and we adopt it for simplicity.
C. Block positions

Equation (4) gives the radii of the $N - 1$ cavities in terms of the positions of $N$ blocks. To invert this equation and hence determine the positions of the $N$ blocks we need an additional constraint. The applied external stretching force is in the $y$ direction, there is no external force in the $x$ direction. The $x$ coordinate of the centre of mass of the $N$ blocks thus does not change with time

$$\sum_{i=1}^{N} X_i(t) = \sum_{i=1}^{N} X_i(t = 0) = 0.$$  

Therefore if we know the cavity radii, we can use equations (1) and (2) to solve for the positions of all $N$ blocks.

D. Stress Tensor

The total stress tensor within each block is made up of two components, the polymer stress arising from forces transmitted by the polymer chains within the adhesive denoted by $\Sigma$, and the isotropic pressure term $-pI$. The total stress tensor $\sigma$ is produced by adding these two components

$$\sigma = -pI + \Sigma.$$  

The constitutive equation obeyed by $\Sigma$ will be discussed in [11]. We assume that the components of the polymer stress tensor are homogenous within each block. This is not so for the pressure contribution. The $i$th block has two free surfaces. At these surfaces the $xx$ component of the total stress tensor is $\sigma_{xx} = -P_i$ and $\sigma_{xx} = -P_{i+1}$. To accommodate this change in the total stress it is clear the term $-pI$ must vary across the block. We will assume this variation is linear.

E. Slippage at the interface

We denote by $\sigma_{si}$ the shear stress at the interface between the $i$th block and the substrate. We assume a simple linear relationship between the position of the interface between the block and the substrate $X_{si}$ and the shear stress $\sigma_{si}$ at the same place

$$\mu \frac{d}{dt} X_{si} = \sigma_{si}.$$  

Recall $X_{si} = X_i - \lambda_{xy,i} H_0 / 4$, thus having previously determined the positions of the blocks $X_i$ we can rewrite this as an equation for the rate of change of the shear strain $\lambda_{xy,i}$.

F. Force Balance

The difference in the pressure on either side of the block $(P_{i+1} - P_i)$ is balanced by the shear stress, leading to a force balance equation

$$(P_{i+1} - P_i) H_0 \lambda = -2\sigma_{si} \frac{W_0}{\lambda}.$$  

Once the shear stress of each block has been calculated, we can use this equation, coupled with the boundary condition $P_1 = P_{\text{atm}}$ to calculate the pressure within each block.

G. Debonding Force

To determine the debonding force $F_y$ (the total force acting on the substrate) we require the pressure, and the $xx$ and $yy$ components of the polymer stress tensor $\Sigma$. The $\sigma_{xx}$ component at the left and right edges of the $i$th block can be used to calculate an approximate value of the average pressure in the block $p$ using the assumption of a linear variation in $p$ through the block

$$\sigma_{xx,i} \Big|_{x_i - W_0/2} = \sum_{x_i - W_0/2}^{p_{i-1}} = -P_i - 1 \quad (11)$$

$$\sigma_{xx,i} \Big|_{x_i + W_0/2} = \sum_{x_i + W_0/2}^{p_i} = -P_i \quad (12)$$

$$\Rightarrow p = p_{x_i - W_0/2} + p_{x_i + W_0/2}$$

$$\approx \sum_{x,i} + \frac{P_i + P_{i-1}}{2}.$$  

The $\sigma_{yy,i}$ component from the $i$th block is thus

$$\sigma_{yy,i} = \Sigma_{yy,i} - \Sigma_{xx,i} = \frac{P_i + P_{i-1}}{2}.$$  

This result contains the normal stress difference of $\Sigma$, hence the addition of an isotropic pressure term to the constitutive model will be absorbed into the pressure $p$ of Eq. (13). The total force $F_y$ can be calculated by summing the force due to atmospheric pressure on the substrates, and that due to each block in the adhesive

$$F_y = \frac{A}{N} \sum_{i=1}^{N} \left( \Sigma_{yy,i} - \Sigma_{xx,i} - \frac{P_i + P_{i+1}}{2} \right) + P_{\text{atm}} A,$$  

where $A$ is the initial contact area. Note Yamaguchi et al. did not use a normal stress difference in [1], however it makes little difference to the results for the parameters and strain ranges used there. Dividing Eq. (15) through by $A$ we obtain the engineering stress in debonding

$$\sigma_{yy}^{\text{eng}} = \frac{F_y}{A} = \left( \Sigma_{yy} - \Sigma_{xx} \right) + (P_{\text{atm}} - \overline{T}),$$  

where $\overline{T}$ represents an average of quantity $T$ over all blocks. To calculate the tack energy $\mathcal{E}_T$ we integrate the debonding force over the distance moved by the upper substrate

$$\mathcal{E}_T = \int_{y' = H_0}^{y' = 0} F_y' dy' = AH_0 \int_{\lambda' = 1}^{\lambda' = \lambda} \sigma(\lambda') d\lambda'.$$  


III. CONSTITUTIVE RELATIONSHIP

To determine the tack energy of the PSA we require the rheological properties of the adhesive layer in [24]. As we are modelling a LCE based PSA, we will use the nematic dumbbell model of Maffetone and Marrucci [21]. We consider a polymer chain made up of $N$ freely hinged nematicogenic rods with individual length $b$. The end-to-end vector for the chain is $\overrightarrow{R}$. Assuming Gaussian fluctuations the quantity of interest is the scaled second moment of the end-to-end vector, that is $\overrightarrow{W} = 3 \langle \overrightarrow{R} \overrightarrow{R} \rangle / Nb^2$. The dynamics of $\overrightarrow{W}$ are governed by

$$\nabla \overrightarrow{W} = \frac{1}{\tau} \overrightarrow{I} - \frac{1}{2\tau} (\overrightarrow{\nabla} - \overrightarrow{W} \cdot \overrightarrow{\ell}^{-1})$$ \hspace{1cm} (18)

and

$$\overrightarrow{\Sigma} = G \overrightarrow{\ell}^{-1} \cdot \overrightarrow{W},$$ \hspace{1cm} (19)

where $\nabla \overrightarrow{W} = d\overrightarrow{W}/dt - \overrightarrow{K} \cdot \overrightarrow{W} - \overrightarrow{W} \cdot \overrightarrow{K}^T$ is the upper convected Maxwell derivative (UCMD) and $\overrightarrow{K}$ is the velocity gradient tensor in Eq. (3). The inverse chain shape tensor $\overrightarrow{\ell}^{-1}$ is given by

$$\overrightarrow{\ell}^{-1} = \frac{1}{(1-S)} \left( \overrightarrow{I} - \frac{3S}{1+2S} \overrightarrow{n} \overrightarrow{n} \right),$$ \hspace{1cm} (20)

in which the nematic director $\overrightarrow{n}$ describes the average orientation of the nematogenic units and the order parameter $S$ which describes the degree of alignment along the director ($S = 1$ corresponds to perfect ordering, while $S = 0$ corresponds to an isotropic phase). The polymer stress $\overrightarrow{\Sigma}$ is that arising from the polymer chains within the material. The time-scale $\tau$ is related to the diffusivity of the chain ends $D$ via $\tau = Nb^2/6D$, while the modulus $G = c k_B T$, (21)

where $c$ is the number of chains per unit volume.

This Gaussian model does not include effects of finite chain extensibility, or entanglements. However Gaussian models have been shown to provide a good description of the mechanical behaviour of liquid crystalline elastomers [19].

A. Isotropic Limit

Yamaguchi et al. first described the block model using the constitutive equation of an isotropic Maxwell fluid for the polymer stress. Here we demonstrate the isotropic limit of Eqs. (18) and (19) produce the same constitutive equation.

To obtain the isotropic limit, we set $S = 0$ in Eq. (18) and (19). This gives

$$\nabla \overrightarrow{W} = \frac{1}{\tau} \overrightarrow{I} - \frac{1}{\tau} \overrightarrow{W},$$ \hspace{1cm} (22)

$$\overrightarrow{\Sigma} = G \overrightarrow{\ell}^{-1} \cdot \overrightarrow{W},$$ \hspace{1cm} (23)

Substituting for $\overrightarrow{W}$ in equation (22) in terms of $\overrightarrow{\Sigma}$

$$\nabla \overrightarrow{\Sigma} = G \overrightarrow{\ell}^{-1}$$ \hspace{1cm} (24)

Any isotropic stress can be added to the definition of $\overrightarrow{\Sigma}$, as it can be absorbed into the pressure term in Eq. (22). It is convenient to subtract $G \overrightarrow{I}$ from the stress $\overrightarrow{\Sigma}' = \overrightarrow{\Sigma} - G \overrightarrow{I}$. This subtraction is useful since $\overrightarrow{\Sigma}'$ is zero in the undeformed state.

$$\nabla \overrightarrow{\Sigma}' + \frac{\overrightarrow{\Sigma}'}{\tau} = 2GD,$$ \hspace{1cm} (25)

where $D = \left( \overrightarrow{K} + \overrightarrow{K}^T \right) / 2$ is the symmetric part of the velocity gradient tensor. This is identical to the constitutive relationship used by Yamaguchi et al. [1].

B. Director dynamics

To complete our description of the dynamics of the polymer stress we must also describe the behaviour of the nematic director with time. In general this is a complicated task involving the coupling of the director to the flow field. Maffetone and Marrucci [21] identify two simplified regimes

1. Weak external field. In this case the polymer stress tensor is required to be symmetric. To achieve this in Eq. (18) the director $\overrightarrow{n}$ must be one of the eigenvectors of $\overrightarrow{W}$. Since in static equilibrium we require the polymer stress to be isotropic, $\overrightarrow{W}_{eq}$ must be equal to $\overrightarrow{\ell}$, from which we can identify $\overrightarrow{n}$ as the eigenvector corresponding to the largest eigenvalue of $\overrightarrow{W}$.

2. Strong external field. In this case the torques arising from coupling to the flow field are insufficient to move $\overrightarrow{n}$ from the direction imposed by the external field. The polymer stress will not be symmetric in this case.

We model the first of these limits, where the director responds much faster than the polymers. We leave the more complicated task of generalised director dynamics to future work.

C. Quasi-Static Limit

There are consistent theoretical descriptions of nematic elastomers derived phenomenologically from continuum mechanics [24], and from a microscopic equilibrium statistical physics model [19]. These models both contain the Goldstone modes predicted in Nematic elastomers using symmetry arguments [22], known as soft modes. The microscopic model produces the following trace formula for the free energy density $F$

$$F = \frac{1}{2} G \overrightarrow{Tr} \left[ \overrightarrow{\lambda} \cdot \overrightarrow{\ell_0} \cdot \overrightarrow{\lambda}^T \cdot \overrightarrow{\ell}^{-1} \right],$$ \hspace{1cm} (26)

where $G$ is the shear modulus of the rubber defined in Eq. (21), $\overrightarrow{\ell_0}$ is the initial chain shape distribution, and it
is assumed that \( \det[\lambda] = 1 \). The soft modes permitted by this free energy have the following explicit form

\[
\lambda = \ell^T \cdot Q \cdot \ell_0 \cdot \ell^T, \tag{27}
\]

where \( Q \) is an orthogonal tensor. They arise because states which are related to each other by a simple rotation of the chain shape distribution tensor \( \ell \) have the same energy. The true stress can be derived from Eq. (26) by differentiating \( F \) with respect to \( \lambda \), then post-multiplying by \( \lambda^T \), producing a polymer stress component

\[
\Sigma = G \ell^{-1} \cdot \lambda \cdot \ell_0 \cdot \lambda^T. \tag{28}
\]

Eqs. (18) and (19) also permit soft mode solutions. Motivated by Eq. (28) we substitute \( W = \lambda \cdot \ell_0 \cdot \lambda^T \), into Eq. (18) and observe that the UCMD is identically zero, leaving

\[
0 = \frac{1}{\tau} \left( \ell^{-1} \cdot \lambda \cdot \ell_0 \cdot \lambda^T + \lambda \cdot \ell_0 \cdot \lambda^T \cdot \ell^{-1} \right), \tag{29}
\]

This equation holds provided that \( \lambda \) obeys Eq. (27). The stress tensor associated with these modes is simply \( \Sigma = G \ell \). The normal stress difference \( \Sigma_{yy} = \Sigma_{xx} = 0 \), and thus these modes would not contribute directly to the debonding force of Eq. (16) (they contribute indirectly in so much as the pressure difference across the block is determined by the shear stress associated with the mode). In typical experiments on nematic elastomers stretching perpendicular to the nematic director produces a soft response as the director rotates towards the stretch direction. Stretching parallel to the director produces a hard elastic response. We thus have reason to suspect that the debonding force could be substantially different for parallel and perpendicular geometries.

### IV. NUMERICAL METHOD

To solve our set of differential equations we implement a mixed implicit/explicit finite difference scheme to step forwards in time. To improve computational accuracy we reduce the number of free parameters by combining those with equivalent effects. The numerical results are in agreement with the analytic single block results and the semi-analytic two block case with \( \tau \rightarrow \infty \). They are consistent with the isotropic results of Yamaguchi et al. [7].

#### A. Initial Condition

The initial condition has \( N \) blocks all of which have \( \lambda = 1 \) and \( \lambda_{xy,i} = 0 \). There are \( N - 1 \) cavities with initial radius \( R_i = R_0 \exp(\chi_i) \) where \( \chi_i \) is assigned from a normal distribution with \( \langle \chi \rangle = 0 \) and \( \langle \chi^2 \rangle = 1 \) and \( R_0 \) is a characteristic size. The initial positions \( X_i(t = 0) \) can then be determined by solving Eqs. (4) and (7).

The pressures at the block interfaces are initially set to atmospheric pressure, thus \( P_i = P_{atm} \). We assume that the cavities form at the substrate/adhesive interface and are initially filled with air, and thus we also set the cavity pressure equal to atmospheric pressure, \( P_{cav,i} = P_{atm} \) [28]. Experimentally, the cavities are sometimes found to be filled with vacuum even if the cavities formed at the substrate/adhesive interface [27]. Yamaguchi et al. found the presence or absence of air within the cavities made very little difference to the resulting tack curves [1]. We divide the time \( t \) into units \( \delta t \) and advance the equation set using a mixed explicit/implicit scheme. We introduce a superscript to quantities to indicate at which time-step they are evaluated, i.e. \( \lambda^{(n)} \) is evaluated at the \( n \)th time step when \( t = n\delta t \).

#### B. Time Stepping

1. We increment the strain explicitly

\[
\lambda^{(n+1)} = \lambda^{(n)} + \lambda \delta t.
\]

2. We update the cavity radius semi-implicitly

\[
R_i^{(n+1)} = \frac{2\eta R_i^{(n)} - \gamma \delta t}{2\eta + \delta t(P_i^{(n)} - P_{cav,i}^{(n)})}.
\]

3. Using the new values of the cavity radii we obtain the cavity pressure

\[
P_{cav,i}^{(n+1)} = P_{cav,i}^{(n)} \left( \frac{R_i^{(n+1)}}{R_i^{(n)}} \right)^2.
\]

4. With the new values for the strain \( \lambda^{(n+1)} \) and cavity radii \( \{ R_i^{(n+1)} \} \) we solve Eqs. (11) and (7) for the new positions of the blocks \( \{ X_i^{(n+1)} \} \).

5. Using \( X_{si} = X_i - \lambda_{xy,i} H_0 / 4 \) we update \( \lambda_{xy,i} \) from Eq. (9)

\[
\lambda_{xy,i}^{(n+1)} = \lambda_{xy,i}^{(n)} + \frac{4}{H_0} \left[ (X_i^{(n+1)} - X_i^{(n)}) - \frac{\sigma_{si}}{\mu} \delta t \right].
\]

This equation replaces the curvature of the blocks used by Yamaguchi et al. It describes the same physical process of block shear, though it differs by a geometrical factor.

6. With the shear strains \( \{ \lambda_{xy}^{(n+1)} \} \) and \( \lambda^{(n+1)} \) we calculate the elements of the deformation gradient tensor

\[
K_{yy} = \frac{\lambda}{\lambda^{(n+1)}}, \quad K_{xx} = -K_{yy}, \quad K_{xy,i} = \frac{K_{yy}}{\lambda^{(n+1)}} \left( \frac{\lambda_{xy,i}^{(n+1)} - \lambda_{xy,i}^{(n)}}{\lambda^{(n+1)} \delta t} \right), \quad K_{yx} = 0.
\]
7. We now update elements of $W$ using a mixed explicit/implicit scheme

$$\begin{align*}
W_{yy}^{(n+1)} &= \frac{{W_{yy}^{(n)} + \frac{\delta t}{4} - \alpha \frac{\delta t}{2} n_x^{(n)} n_y^{(n)} W_{xy}^{(n)}}}{1 - 2K_{yy}\delta t + \frac{\delta t}{1 - S} + \alpha n_y^{(n)} n_y^{(n)}}, \\
W_{xy}^{(n+1)} &= \frac{1}{1 + \frac{\delta t}{2(1 - S)} \left[ 1 + \left( \frac{1}{\tau} + 1 \right) n_x^{(n)} n_x^{(n)} \right]} \times \left( W_{xy}^{(n)} - \alpha \delta t n_x^{(n)} n_y^{(n)} (W_{xx}^{(n)} + W_{yy}^{(n+1)}) \right) - \frac{\delta t K_{xy} W_{yy}^{(n+1)}}{2(1 - S)} \\
W_{xx}^{(n+1)} &= \frac{1}{1 + 2K_{yy}\delta t + \frac{\delta t}{1 - S} + \alpha n_y^{(n)} n_y^{(n)} + \alpha \delta t n_x^{(n)} n_{xy}^{(n+1)} W_{xy}^{(n+1)}} \times \left( W_{xx}^{(n)} + \frac{\delta t}{3} - \alpha \delta t n_x^{(n)} n_y^{(n)} W_{xy}^{(n+1)} \right) - \alpha \delta t K_{xy} W_{yy}^{(n+1)} \\
\end{align*}$$

where $\alpha = -\frac{3S}{25+1}$. 

8. Determine the director by finding the eigenvector of $W^{(n+1)}$ corresponding to the largest eigenvalue.

9. Calculate the updated polymer stress $\Sigma^{(n+1)}$ from Eq. (19).

10. Calculate the new pressure field $\{p_i^{(n+1)}\}$ from Eq. (10) with the boundary condition $p_1 = P_{\text{atm}}$.

11. Repeat to advance to the next time step.

**V. RESULTS AND DISCUSSION**

A typical set of simulation parameters are shown in Table III. Most of the values are those used by Yamaguchi and Doi. According to the Maier-Saupe theory of the isotropic-nematic phase transition, the order parameter at the first order jump to the nematic phase is $S = 0.42$. The orientational order parameter associated with the polymer backbone is usually a fraction of this bare nematic order parameter, which motivates our choice of $S = 0.3$. We should note however that much higher values of the order parameter have been reported for the backbone order parameter in LCEs, particularly for main-chain systems where $S = 0.9$ has been observed.

The value of $\tau$ adopted here is lower than that used by Yamaguchi et al. but is consistent with creep flow measurements on adhesives manufactured from acrylic polymers.

In Fig. III(a) we show how the debonding stress $\sigma_{yy}^{\text{eng}}$ varies with the deformation $\lambda$ (notice the logarithmic scale on the $x$-axis) for three cases: (i) the adhesive is isotropic, (ii) the adhesive is nematic with the director initially parallel to the stretch direction and (iii) the adhesive is nematic with the initial director perpendicular to the stretch direction. Each case has the same initial random seed for cavity formation. The three cases show the typical behaviour of a PSA. We show the behaviour up to a very large deformation of $\lambda = 20$. Whilst such large deformations can be achieved experimentally using soft, weakly crosslinked polymers, the Gaussian model used here does not provide a good description of these large deformations, or the detachment of the adhesive. However, it does provide a qualitative model of the subsequent behaviour that may be achieved at lower strains in more precise models. We can identify 4 separate behaviours within the plot:

1. A steep initial rise in the debonding stress until $\lambda \sim 1.05$.
2. A decrease in the debonding stress until $\lambda \sim 2$.
3. An increase in the debonding stress until $\lambda \sim 5$ for the isotropic case and $\lambda \sim 10$ for nematic cases.
4. A decrease in the debonding stress for larger strains.

We explain the main processes occurring during each of these stages. Fig. III(a) shows the local debonding stress

$$\sigma_{\text{loc}} = \left[ \Sigma_{yy,i} - \Sigma_{xx,i} + P_{\text{atm}} - \frac{p_1 + p_{i+1}}{2} \right] / P_{\text{atm}},$$

the shear strain $\lambda_{xy}$ and the angle $\theta$ that the director makes with the $y$-axis as a function of position in the adhesive for $\lambda = 1.02$. The local debonding stress is small near the edges ($x \sim 0.5$) of the adhesive and rises rapidly towards the centre ($x \sim 0$). Investigating separately the pressure and polymer stress contributions to the local debonding stress reveals the pressure to be the predominant cause of the initial rise in the debonding stress. As each block expands along the $y$-direction it must also contract along the $x$-direction. This contraction results in large shear strains and concomitantly large

| Parameter (symbol) | Value |
|-------------------|-------|
| Atmospheric Pressure ($P_{\text{atm}}$) | $10^5$ Pa |
| Shear Modulus ($G$) | $10^5$ Pa |
| Relaxation Time ($\tau$) | 30 s |
| Viscosity ($\eta = G\tau$) | $3 \times 10^6$ Pa s |
| Strain Rate ($\lambda$) | 0.1 s$^{-1}$ |
| Surface Tension ($\gamma$) | $3 \times 10^{-2}$ J m$^{-2}$ |
| Friction Coefficient ($\mu$) | $2 \times 10^9$ Pa s m$^{-1}$ |
| Typical Cavity Radius ($R_0$) | $10^{-6}$ m |
| Initial Height ($H_0$) | $10^{-4}$ m |
| Length ($L_0$) | $5 \times 10^{-3}$ m |
| Order Parameter ($S$) | 0.3 (0 if isotropic) |
| Number of Blocks ($N$) | 100 |

| TABLE I. Model Parameters |
The debonding stress $\sigma_{\text{eng}}$ as a function of the deformation $\lambda$ for the parallel, isotropic and perpendicular arrangements.

The debonding stress $\sigma_{\text{loc}}$ in units of $P_{\text{atm}}$, the shear $\lambda_{xy}$ and the angle the director makes with the $y$-axis as functions of position within the adhesive $x$ are shown in (a) for $\lambda = 1.02$, (b) for $\lambda = 1.2$ and (c) for $\lambda = 3$. The angle $\theta$ is largely close to $\theta = \pm 90^\circ$ for the perpendicular case - i.e. at $\lambda = 1.02$ the director has not rotated much away from its initial orientation, apart from close to the edges $x \sim \pm 0.5$. In the parallel case there is evident director reorientation, particularly near the edges of the block $x \sim \pm 0.5$ where the director is at $\theta = \mp 45^\circ$ despite initially being close to $\theta = 0$ - i.e. towards the edges of the block, where the shears are greatest in magnitude, the director has reoriented to accommodate the shear.

Fig. 4(b) shows how $\sigma_{\text{loc}}$, $\lambda_{xy}$ and $\theta$ vary with position $x$ for $\lambda = 1.2$. Comparing with (a) we can see that $\sigma_{\text{loc}}$ has become substantially more negative for the perpendicular case while the parallel and isotropic results look broadly similar to the situation in (a). The shear strains for the isotropic and parallel situation are similar in magnitude to (a), but we can now see kinks which correspond to cavities within the adhesive. The shear strains for the perpendicular case are larger, both when compared with (a) and when compared with the parallel/isotropic cases in (b). The angle $\theta$ is close to $\pm 90^\circ$ for the perpendicular case while for the parallel case the angle remains close to $0^\circ$ around $x = 0$ but becomes $\pm 50^\circ$ towards the edges $x = \pm 0.5$. Fig. 4 shows a representa-
strictly positive for all positions. It is also interesting to look at the large central cavity for both the perpendicular and parallel alignments. We notice in the perpendicular case that the blocks on either side of the cavity are sheared in the same sense, while in the parallel case the blocks are sheared in opposite senses. This can also be seen in the plot of \( \lambda_{xy} \) in Fig. 4(b), the kink in the curves around \( x \sim 0.05 \) involves a change in sign for the parallel alignment, while there is no change in sign for the perpendicular alignment.

Up until this stage the main contributor to the debonding stress has been the pressure. As the blocks continue to elongate however we anticipate the polymer stress contribution will become more and more important - for a simple neo-Hookean material we would expect these terms to scale quadratically with \( \lambda \). The rise in the debonding stress after \( \lambda \sim 2 \) is principally due to the polymeric terms in the stress tensor increasing. Fig. 4(c) shows \( \sigma_{loc} \), \( \lambda_{xy} \) and \( \theta \) as a function of \( x \) for \( \lambda = 3 \). We see now that \( \sigma_{loc} \) is somewhat more uniform as a function of position for all three cases. The debonding stress is largest for the parallel alignment and lowest for the perpendicular arrangement. The debonding stress is strictly positive for all positions. It is also interesting to note that the \( x \)-range of the plot is substantially reduced at this strain, indicating that the blocks have slipped. For both the parallel and the perpendicular cases we see \( \theta \sim 0 \) for all blocks, i.e. the director has largely aligned with the stretch direction for all blocks. The shears \( \lambda_{xy} \) are smaller in magnitude than those presented in (b), we notice however they remain larger in magnitude for the perpendicular alignment than for the parallel/isotropic.

Above \( \lambda \sim 5 \) for the isotropic and \( \lambda \sim 10 \) for the nematic we see a reduction in the debonding stress. This is due to the stress relaxation inherent in the constitutive model of Eq. (18). We expect the polymer stress to relax over a time-scale set by \( \tau = 30s \) for the isotropic situation. In the nematic case two time-scales appear \( \tau(1 - S) = 21s \) and \( \tau(1 + 2S) = 48s \). The decay time we observe for the perpendicular and parallel alignments is set by this larger timescale \( \tau(1 + 2S) \). At these larger strains the director for each block is aligned along the \( y \)-axis and each block has essentially the same value for the local debonding stress \( \sigma_{loc} \).

![Fig. 5. A representation of the blocks for the perpendicular (a) and parallel (b) alignments. Some cavities are visible within the adhesive layer. The three large circles show close ups on the relevant location in the adhesive. The arrows show the director orientation.](image)

![Fig. 6. a) The tack energy \( E_T \) as a function of strain for the isotropic, parallel and perpendicular cases. b) The relative tack of the parallel and perpendicular alignment compared to the isotropic case.](image)
perpendicular geometry) and by changing the order parameter (i.e. switching between the isotropic and nematic phases). The latter transition is relatively simple to achieve either by altering the temperature or by using photo-active nematics \( n \), whilst the former might be achievable by mechanically stretching the adhesive layer. The difference in tack energy is not so large for small deformations, however it can become appreciable for larger deformations. In Fig. 6 (a) we show the tack energy ratio between the parallel:isotropic and perpendicular:isotropic as a function of the deformation \( \lambda \). For the parallel:isotropic plot the ratio is close to unity deformations up to \( \lambda \approx 3 \), after which we see a gradual increase in the relative tack up to a value of 2.3 by \( \lambda = 20 \). The curve for the perpendicular:isotropic ratio is slightly more complicated. Initially the relative tack is below unity up until deformations of around \( \lambda \approx 14 \), beyond which the relative tack continues to increase above unity. The detachment process is not modelled here so we will assume detachment occurs at a strain of \( \lambda = 10 \), which is consistent with previous work [27]. For large strain the precise choice of this detachment does not change our conclusions. For \( \lambda = 10 \) the ratio of the tack energies is 1.55:1:0.86 for para:iso:perp.

As can be seen in Table II there are a large number of parameters in our model which we might adjust in order to maximise the difference in tack between the isotropic and nematic states. We now consider how changing several of these parameters changes the force extension curves and resultant tack.

A. Varying \( \tau \)

The time constant \( \tau \) is the fundamental time-scale over which stress is relaxed away. In the nematic case we in fact have two time-scales \( \tau_\parallel = \tau (1 - S) \) for the relaxation of stress perpendicular to the director and \( \tau_\perp = \tau (1 + 2S) \) for the relaxation of stress parallel to the director. Nevertheless the average of these time-scales is still \( \tau \) \( (\tau = (\tau_\parallel + 2\tau_\perp)/3) \). The time-scale \( \tau \) is also related directly to the viscosity \( \eta \) which appears in our dynamical equation for the cavity radius (see Eq. (6)) via \( \eta = G\tau \). Altering \( \tau \) can thus be expected to alter both the small strain regions of the tack curve where the debonding force is largely determined by the cavities, and at larger strains where the debonding force is largely due to the elastic deformation of fibrils. Fig. 7 shows the force extension curves for three different values of \( \tau \). All other parameters are as listed in Table II. We can see that the effect of increasing \( \tau \) is to increase the heights of the two peaks which occur in the plot and to move the peaks to larger deformations. Therefore a larger \( \tau \) tends to produce a greater tack energy. Of more interest here however perhaps is the relative tack. For \( \lambda = 10 \) the tack energies are in the ratio 1.57:1:1.11 \( (\parallel:iso:\perp) \) for \( \tau = 10s \), 1.67:1:1 for \( \tau = 20s \) and 1.55:1:0.86 for \( \tau = 30s \). The relative tack values are summarised in Table II.

B. Varying \( S \)

Figure 7 shows the effect of varying the nematic order parameter \( S \) has on the debonding stress as a function of the deformation \( \lambda \). All other parameters in these plots are as listed in Table II. For deformations less than \( \lambda \sim 2 \) there is very little difference the curves for the parallel alignment and for the isotropic adhesive. The perpendicular alignment is quite strongly influenced by the order parameter. Increasing the order parameter leads to a reduction in the height of the first peak in the debonding stress. The deformation at which the peak occurs also becomes larger with increasing order parameter. At larger deformations both the parallel and perpendicular alignments are affected by changes in the order parameter. Increasing the order parameter results in the second peak in the debonding curves occurring at a larger deformation and a larger debonding stress, this can be understood by considering the time-scale for stress relaxation parallel to the director \( \tau_\parallel = \tau (1 + 2S) \). At larger values of \( S \) this time-scale is longer, so elastic stresses build up for a longer time for increasing \( S \). For \( \lambda = 10 \) the tack energies are in the ratio 1.55:1:0.86 for \( S = 0.3 \), 1.84:1:0.65 for \( S = 0.5 \) and 2.07:1:0.41 for \( S = 0.7 \). Hence there...
FIG. 8. Variation of the debonding stress with increasing deformation for several values of $S$. Other parameters are as in Table I.

is a reversible change in the tack energy by more than a factor of 2 for $S = 0.7$ between the parallel and the isotropic states and between the isotropic and perpendicular states. The relative tack values are summarised in Table II.

C. Varying $G$

Figure 9 shows the effect that varying the elastic modulus $G$ has on the debonding stress as a function of the deformation $\lambda$. All other parameters in these plots are as listed in Table I. Note the axes have the same scale on all three plots. It is apparent that increasing $G$ increases the magnitude of the debonding stress. The deformation at which the second peak occurs is the same in all three plots, the associated debonding stress at the second peak scales proportionally with $G$. The debonding stress at the first peak is larger for larger values of $G$, however the debonding stress at the first peak is not proportional to $G$ - the debonding stress at the first peak in fig. II(c) is roughly three times greater than in fig. II(a) while $G$ changes by a factor of 10 between the plots.

It is apparent that increasing $G$ leads to greater values for the absolute tack. The tack values for $\lambda = 10$ are in the ratio 1.49:1:0.86 ($\parallel$:iso:$\perp$) for $G = 3 \times 10^4$Pa, 1.55:1:0.86 for $G = 1 \times 10^5$Pa and 1.61:1:0.86 for $G = 3 \times 10^5$Pa. It is interesting to note that the relative tack for switching between the isotropic and the perpendicular states is identical for the three values of $G$ listed, this is a peculiarity of our choice to quote results for $\lambda = 10$.

The relative tack values are summarised in Table II.

D. Varying $\dot{\lambda}$

We have previously considered the effect of changing $\tau$, $S$ and $G$. These are material parameters of the adhesive that can be changed by altering the material chemistry or the chain architecture (chain length, entanglement, molecular weight, chain branching, etc). We can also consider changing experimental parameters such as the strain rate $\dot{\lambda}$. Figure 10 shows the debonding stress as a function of the deformation $\lambda$ for several values of $\dot{\lambda}$. All other parameters are as listed in table I. As can be seen, changing $\dot{\lambda}$ has quite a large effect on the form of the curves. For $\dot{\lambda} = 0.01$ s$^{-1}$ as shown in fig. 10(a) there appears to be no second peak in the curves for the parallel
and isotropic adhesives, a second peak is just visible in the curve for the perpendicular alignment. This form of the debonding curve is typical of "liquid-like" debonding and is called cohesive debonding. In the current case since the Deborah number $De = \lambda \tau = 0.3$ is less than unity the elastic stresses are able to relax away over the time-scale associated with the increase in deformation and we are left with a viscous liquid type debonding curve. Increasing the strain rate to $\dot{\lambda} = 0.05 s^{-1}$ produces quite a big difference in the curves. The overall magnitude of the stresses has increased, and we can now clearly see secondary peaks in the debonding stress. The shape of this debonding curve is typical of materials intermediate between a brittle solid and a viscous liquid, and is known as adhesive debonding. Increasing the strain rate further to $\dot{\lambda} = 0.1 s^{-1}$ and we see the general form of the curve is the same as in fig. 10(b), but the overall magnitude of the stresses has increased, and the deformation at which the second peak occurs is larger - the deformation corresponding to a relaxation time $\tau$ is larger for larger strain rates. These observations are consistent with experimental results on isotropic adhesives [32]. It is clear that we obtain larger absolute tack values for larger strain rates. Comparing the relative tack values at $\lambda = 10$ we obtain 1.23:1:1.03 for $\dot{\lambda} = 0.01 s^{-1}$ ($\parallel$:iso, $\perp$:iso), 1.72:1:1.09 for $\dot{\lambda} = 0.05 s^{-1}$ and 1.55:1:0.86 for $\dot{\lambda} = 0.1 s^{-1}$. The relative tack values are summarised in Table II.

VI. CONCLUSIONS

In this paper we have employed a modified version of the block model of Yamaguchi et al. [7] and the nematic dumbbell constitutive equation of Maffetone and Marucci [21] to model the adhesive debonding of nematic elastomer adhesives. These models include several approximations and simplifying assumptions in their description of adhesive debonding:

1. The flow of films is assumed to be a superposition of slippage and a piecewise linear deformation of the block,
2. The cavities are assumed to be described by gaps between adjacent blocks,
3. The cavity dynamics are modelled by the Rayleigh-Plesset equation,
4. The slip velocity at the substrates is assumed to be a linear function of the shear stress,
5. The nematic director reorients very quickly compared to the polymer relaxation time,
6. The polymers can be described as Gaussian chains,
7. The adhesive cannot debond from the surface or rupture.

Despite these simplifications the main physical processes which occur during debonding are captured and the overall result of our modelling, i.e. demonstrating a reversible difference between the tack energy as a result of the nematic to isotropic transition is valid qualitatively.

| $\tau$ (s) | $\parallel$:iso | $\perp$:iso |
|-----------|----------------|------------|
| 10        | 1.57           | 1.11       |
| 20        | 1.67           | 1          |
| 30        | 1.55           | 0.86       |

| $S$      | $\parallel$:iso | $\perp$:iso |
|----------|----------------|------------|
| 0.3      | 1.55           | 0.86       |
| 0.7      | 2.07           | 0.41       |

| $G \times 10^5$Pa | $\parallel$:iso | $\perp$:iso |
|-------------------|----------------|------------|
| 0.3               | 1.49           | 0.86       |
| 3                 | 1.61           | 0.86       |

TABLE II. The relative tack values at a deformation of $\lambda = 10$ for parallel:isotropic and perpendicular:isotropic for various parameters.
Within these modelling assumptions we have shown that there can be substantial differences in the tack energy when comparing an isotropic and a nematic adhesive which are due to the difference in their rheology. For example with a nematic order parameter of $S = 0.7$ we were able to achieve a relative tack energy at $\lambda = 10$ of $2.07:1$ between the parallel aligned nematic and the isotropic and $0.41:1$ between the perpendicular aligned nematic and the isotropic (and thus a ratio of $5.05:1$ between the parallel and perpendicular alignments). Given the ease with which one can reversibly cycle between an isotropic and nematic phase this work gives impetus to the experimental investigation of this mechanism of switching adhesives on and off.

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