The effect of glycerol on the crazing behaviour of polystyrene in relation to the craze boundary temperature

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Dedicated to Professor Dr. Derk Heikens on the occasion of his 65th birthday

The stress–strain behaviour of polystyrene–glycerol blends has been compared with that of polystyrene–polyethylene blends. The presence of glycerol appears to have a strong inhibiting effect on craze thickening, but does not affect the activation parameters of crazing. It is proposed, tentatively, that this is a result of the cooling action of glycerol at the craze boundaries. Calculations indicate that, at the craze tip, an increase of the craze boundary temperature, facilitating craze thickening, can be expected. Glycerol will be transported into the crazes by the capillary forces, and can thus act as a coolant. As a consequence the rate of craze thickening is slowed down.

(Keywords: craze kinetics; polystyrene; craze boundary temperature; glycerol; craze thickening)

INTRODUCTION

During the past two decades it has become apparent that the strength of glassy thermoplastics is largely determined by the presence of plastic deformation mechanisms, i.e. crazing and shear flow[1]. Generally an increase of the rates of these plastic deformation mechanisms results in a higher impact strength. However, high rates of plastic deformation mechanisms are not always beneficial to the performance of a material. For example, a high rate of crazing adversely affects the fatigue behaviour of glassy thermoplastics. It is clearly advantageous to be able to control the rate by which the plastic deformation mechanisms proceed in order to obtain maximum performance for a given application. In rubber toughened thermoplastics the rate of crazing defined as the rate of craze volume formation per unit volume material can be influenced to a considerable extent by changing the rubber content. However, the result will always be a compromise between impact strength, modulus and fatigue strength. Therefore it is useful to look for other means to control the rate of crazing. It is known that this rate is strongly affected by the presence of certain environments[2]. These environmental effects are usually ascribed to changes in the surface tension[3] and to plasticization of the thermoplastic[4]. The contributions of these mechanisms have been discussed quantitatively by Andrews *et al.*[5,6]. A lower surface tension results in the formation of a more finely divided craze fibril structure but its effect on craze kinetics is of minor importance[2]. Plasticization facilitates the craze fibril drawing process[7] and thus influences the overall rate of the crazing process. However, its effect is usually detrimental to the mechanical properties as destabilization of crazes due to an enhanced rate of craze fibril creep takes place as well[8].

An environment that has an apparent anti-plasticizing effect can be expected to suppress craze formation. Such an effect has been reported by Sauer *et al.*[9,10] for polystyrene (PS) in a glycerol environment. Failure times in fatigue experiments were significantly enhanced by the presence of glycerol as compared with failure times in air.

Apparently the formation and/or growth of surface crazes is suppressed by glycerol and it thus appears that choosing a suitable environment is an effective means to control craze rates. However, in practice it is usually not possible to choose an optimum environment. Therefore, in order to control the rate of crazing attention should be focussed on the internal crazes. In the work described here results will be presented concerning the effects of glycerol dispersed in PS on the rate of internal crazing. For comparison purposes blends of PS and low density polyethylene (LDPE) are used, as LDPE can be considered to be inactive towards PS.

EXPERIMENTAL

In order to study the effect of glycerol on the rate of internal crazing in PS a blend of PS and glycerol was made in a David Bridge 1.1 1 mixer. Blends of PS and an LDPE, Stamylan 1500 from DSM, The Netherlands, were prepared on a Schwabenthan laboratory mill. After crushing and compression moulding into plates tensile specimens according to ASTM D 638 iii were machined. The mechanical properties were evaluated on a thermostatted Zwick 1474 Tensile Tester, equipped with a closed loop control system to obtain truly constant strain rates.

RESULTS

The very low viscosity of glycerol at elevated temperatures gave rise to some leakage from the mixer. Therefore the composition of the PS/glycerol blends could not be calculated directly from the amounts in which the components were added to the mixer. However, the composition of these blends can be determined from the blend modulus. At low volume fractions of the

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dispersed phase and if the modulus of the dispersed phase is much lower than the modulus of the matrix material the blend modulus is dependent only on the modulus of the matrix material and on the volume fraction of the dispersed phase, while it is practically independent of the modulus of the dispersed material[11]. Therefore it was decided to prepare a range of PS/LDPE blends with LDPE contents that varied between 0 and 10%. By comparing the modulus of the PS/glycerol blend with the moduli of these blends the glycerol content can be determined. The results of these modulus measurements are represented in *Figure 1*. From this Figure it can be inferred that the PS/glycerol blend contained 6% glycerol. This result is in good agreement with the average value of 5.6% as obtained from an analysis of optical micrographs of the PS/glycerol blend (*Figure 2*).

In order to quantify the effect of glycerol on the crazing behaviour a previously developed model was used that describes the stress–strain behaviour of materials that deform by crazing[12,13]. From this model it follows for constant strain-rate experiments that, at yield point,

$$k_ik_g = -\frac{f}{f-1}\frac{\ddot{\sigma}}{E} \qquad (1)$$

Here k_i and k_g are the rate of formation of craze area per unit volume material normal to the stress direction and the rate of craze thickening, respectively. The term $f/(f-1)$ takes into account the density difference between the crazes and the bulk material, where f denotes the reciprocal volume fraction of craze material (fibrils) within a craze. E is the Young's modulus of the blend, which is, at temperatures well below the glass transition temperature of the matrix material, to a good approximation independent of rate and temperature, and $\ddot{\sigma}$ is the second derivative of the stress with respect to time.

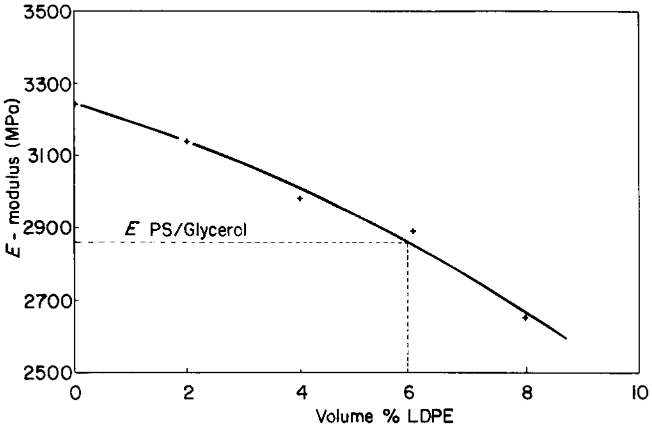

Figure 1 Modulus of PS/LDPE blends of varying compositions and of the PS/glycerol blend

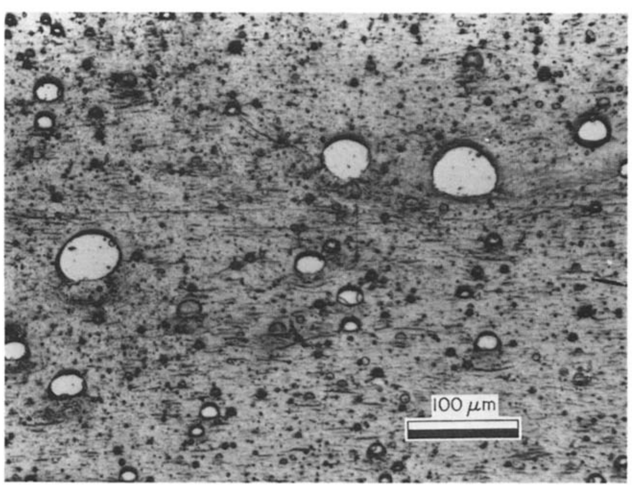

Figure 2 Optical micrograph of a section of the PS/glycerol blend

Using equation (1) the value of the product k_ik_g at the yield stress can be calculated from a stress–strain curve. As the value of the product k_ik_g is very stress dependent a comparison between PS/glycerol blends and PS/LDPE blends is meaningful only if the yield stresses of the blends are equal. It was found that this is the case when the strain rate applied to the PS/LDPE blends is approximately 60 times the strain rate applied to the PS/glycerol blends, as shown in *Figure 3*. This implies that, provided that the curvature of the stress–strain curve at yield stress is the same for both blends, the value of the product k_ik_g for PS/LDPE blends is 3600 times as large as the value of the same product for PS/glycerol blends. From *Figure 3* it can be inferred that the curvature in the stress–strain curve is stronger in the case of PS/LDPE blends, indicating that the factor 3600 is a conservative estimate, and may in fact be considerably higher.

It is of interest to specify the origins of the reduction of k_ik_g that is caused by glycerol. From earlier research[13] it appeared that the rates of craze surface formation, k_i, and craze thickening, k_g, are well described by the Eyring activated flow equation[14]

$$k_{i,g} = A_{i,g}\exp\frac{-\Delta H^*_{i,g}}{kT}\exp\frac{\gamma_{i,g}V^*_{i,g}\sigma}{4kT} \qquad (2)$$

In equation (2) A, ΔH^* and V^* are the pre-exponential factor, the activation enthalpy and the activation volume, respectively. The term γ denotes the stress–concentration factor, and the subscripts i and g refer to craze surface formation and thickening.

The stress–strain properties of a material that undergoes crazing are directly related to k_i and k_g. By using the same model that gave rise to equation (1) it can be shown[15] that

$$\sigma_y = \frac{8kT}{\gamma_iV_i^*+\gamma_gV_g^*}\ln\dot{\varepsilon} + 4\frac{\Delta H_i^*+\Delta H_g^*}{\gamma_iV_i^*+\gamma_gV_g^*} + \frac{4kT}{\gamma_iV_i^*+\gamma_gV_g^*}\left\{c+\ln\frac{\gamma_gV_g^*}{4kT}-\ln A_iA_g\right\} \qquad (3)$$

Here σ_y is the yield stress, $\dot{\varepsilon}$ is the strain rate and c is a constant. Equation (3) predicts a linear relationship between the yield stress and the strain rate and between the yield stress and the temperature as the temperature effect on the term $\ln\frac{\gamma_gV_g^*}{4kT}$ is relatively small. Thus equation (3) provides a convenient means to determine the craze activation parameters $\gamma_iV_i^*+\gamma_gV_g^*$ and $\Delta H_i^* + \Delta H_g^*$.

The predicted linear relationships have indeed been found, as shown in *Figures 4* and *5*. From the respective slopes the terms $\gamma_iV_i^*+\gamma_gV_g^*$, $\Delta H_i^*+\Delta H_g^*$ and the bracketed quantity $c+\ln\frac{\gamma_gV_g^*}{4kT}-\ln A_iA_g$ were calculated. Results are given in *Table 1*.

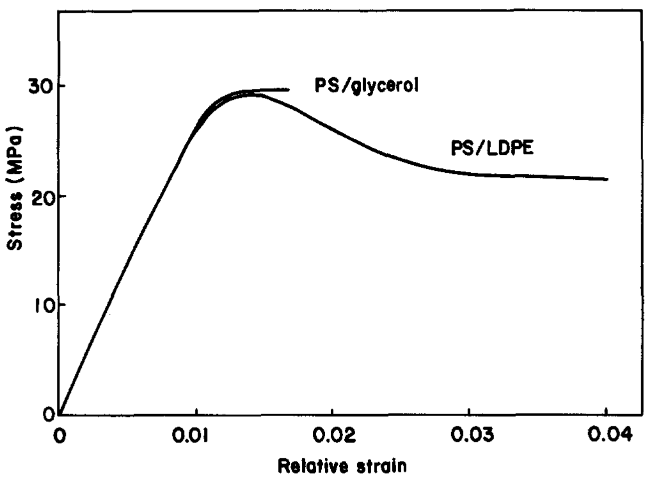

Figure 3 Stress–strain curves of a PS/glycerol blend and a PS/LDPE blend of equal composition. The strain rates are 1.7×10^{-4} and $1.1\times10^{-2}\ \mathrm{s}^{-1}$, respectively

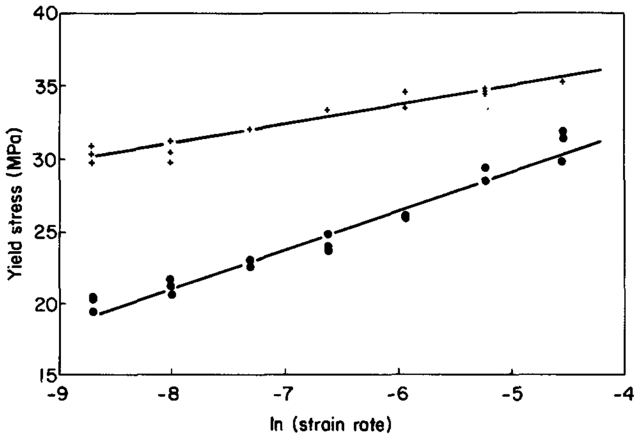

Figure 4 Strain rate dependence of the yield stress of a PS/LDPE blend (●) and a PS/glycerol blends (+) of equal composition (94/6 vol%). T is 296 K, strain rate in s^{-1}

DISCUSSION

The data given in *Table 1* are remarkable in that the values of the crazing activation parameters are almost exactly a factor 2 higher for PS/glycerol blends than for the PS/LDPE blends. This suggests that the differences have a common origin, which is not necessarily associated with the true craze activation parameters. Equation (3) is based on the supposition that craze thickening is a continuous process. The results in *Table 1* can be made plausible by assuming a different mechanism.

If the presence of glycerol in some way inhibits continuous craze thickening after a short period Δt following craze area formation then the relative volume increase of the sample with a volume V_0 due to crazing is given by

$$\Delta V/V_0=\Delta t\cdot\int_0^t k_i k_g\,\mathrm{d}\tau \qquad (4)$$

As shear flow does not take place the cross-sectional area is to a good approximation constant, so $\Delta V/V_0$ equals the craze strain. The craze strain is given by:

$$\left(\varepsilon-\frac{\sigma}{E}\right)\frac{f}{f-1} \qquad (5)$$

where the term $\frac{f}{f-1}$ again takes into account the density difference between the bulk material and the crazes.

Equations (2), (4) and (5) can be combined to obtain

$$\Delta t\int_0^t A_i A_g \exp\frac{-\Delta H_i^*-\Delta H_g^*}{kT}\exp\frac{\gamma_i V_i^*\sigma+\gamma_g V_g^*\sigma}{4kT}\,\mathrm{d}\tau =\left(\varepsilon-\frac{\sigma}{E}\right)\frac{f}{f-1} \qquad (6)$$

Equation (6) describes the stress–strain behaviour. It is of interest to note that this equation does not predict a stress decrease after yielding, while if craze thickening is assumed to proceed continuously a stress decrease is predicted. This is in accordance with experimental findings in which PS/glycerol blends do not show a stress decrease while PS/LDPE blends show a pronounced stress decrease (*Figure 3*).

Differentiating equation (6) with respect to time and setting $\frac{\mathrm{d}\sigma}{\mathrm{d}t}=0$ results in the following expression for the yield stress at constant strain rate:

$$\sigma_y=\frac{4kT}{\gamma_i V_i^*+\gamma_g V_g^*}\ln\dot{\varepsilon}+4\frac{\Delta H_i^*+\Delta H_g^*}{\gamma_i V_i^*+\gamma_g V_g^*} +\frac{4kT}{\gamma_i V_i^*+\gamma_g V_g^*}\left(-\ln\left(\Delta t\frac{f-1}{f}\right)-\ln A_i A_g\right) \qquad (7)$$

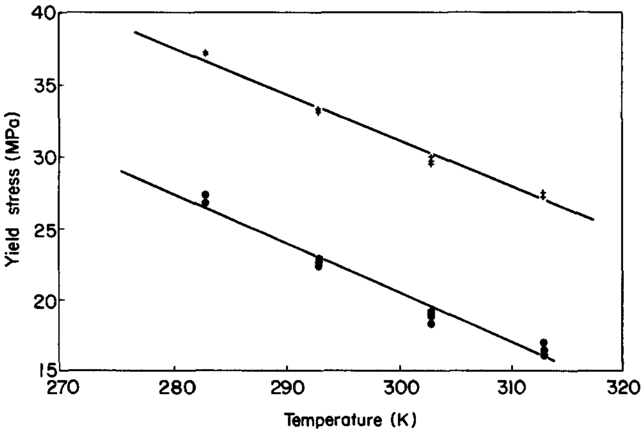

Figure 5 Temperature dependence of the yield stress of a PS/LDPE blend (●) and a PS/glycerol blend (+) of equal composition (94/6 vol%). Strain rate is $1.7\times10^{-4}\ \mathrm{s}^{-1}$

Table 1 Terms from respective slopes of *Figures 4* and *5*

	PS/LDPE	PS/glycerol
$\gamma_i V_i^*+\gamma_g V_g^*$ (nm^3)	12.3	25
$\Delta H_i^*+\Delta H_g^*$ (kJ mol^{-1})	230	480
$c+\ln\frac{\gamma_g V_g^*}{4kT}-\ln A_i A_g$	−60	−130

Equation (7) again allows the determination of the craze activation parameters from plots of σ_y vs. $\ln \dot{\varepsilon}$ and σ_y vs. T. For PS/glycerol blends the sum $\gamma_i V_i^* + \gamma_g V_g^*$ can be calculated to be 12.5 nm^3, $\Delta H_i^* + \Delta H_g^*$ is 240 kJ mol^{-1} and $-\ln\left(\Delta t \frac{f-1}{f}\right) - \ln A_i A_g$ is -65.

The values of the activation parameters of PS/glycerol blends are now very close to those calculated for PS/LDPE blends.

Apparently the anomalous effect of glycerol on the stress–strain behaviour of polystyrene and on the activation parameters for crazing can be explained by an inhibiting action of glycerol on the craze thickening mechanism. However, the mechanism of this action does not affect the activation parameters.

Warty *et al.*[9] suggested that the increased fatigue lifetime of polystyrene in a glycerol environment is due to either an increase of the surface energy or to the reduction of stress concentrations. The latter suggestion is not likely to be applicable to the case of PS/glycerol blends. The first suggestion does not apply either as the contact angle between polystyrene and glycerol is less than 90°.[16]

An altogether different possibility to explain the inhibiting effect of glycerol on the craze thickening mechanism concerns the craze temperature. Craze thickening takes place by a surface drawing process[17]. This process generates heat which, combined with the low heat conductivity of polystyrene and the absence of heat conduction within a craze, may give rise to a temperature increase. This temperature rise results in a higher rate of the surface drawing process until a temperature equilibrium is reached when the amount of heat dissipated by the plastic flow process is compensated by the heat conduction and transport of heated material from the bulk into the craze. The transport of glycerol into the crazes by the capillary forces will result in a marked increase of the heat conductivity within the crazes. Furthermore, as the heat capacity of glycerol is not small, it is an effective heat sink. Thus the presence of glycerol will produce a delay in the attainment of the equilibrium temperature. The craze boundary temperature will be lower than the corresponding temperature in non-glycerol containing crazes, which gives rise to a reduced rate of craze thickening. How much this rate is reduced depends on the temperature differences involved and on the activation enthalpy of the craze thickening process.

The temperature at the craze boundary can be calculated as follows. Consider an isolated craze with an area that is large enough to neglect end effects, allowing a one dimensional analysis. If the rate of craze thickening under a constant applied stress is denoted as $2v$ then it follows that the rate of sample length increase is $2v(1-1/f)$. The work done per unit craze area and per unit time is equal to $2\sigma v(1-1/f)$. It now is assumed that this work is converted into heat at the craze boundaries. The relevant heat transfer equation for this system is:

$$\left(\frac{\partial T}{\partial t}\right)_z = a\left(\frac{\partial^2 T}{\partial z^2}\right)_t + v/f\left(\frac{\partial T}{\partial z}\right)_t \tag{8}$$

Here z is a coordinate normal to the craze surface with its origin at the craze boundary. The constant a is the thermal diffusivity defined by $\lambda/\rho c$, where λ denotes the thermal conductivity and ρ, c are the density and specific heat, respectively. The second term on the right hand side is an additional term which takes into account the movement of the craze boundary relative to the surrounding material. The heat generated at the craze boundary provides a first boundary condition:

$$\frac{\partial}{\partial z}T(0,t) = -\frac{\sigma v}{\lambda}(1-1/f) \tag{9}$$

Further appropriate boundary conditions are:

$$T(z,0) = T_0 \tag{10}$$

$$T(\infty,t) = T_0 \tag{11}$$

Solving equation (8) using these boundary conditions results in:

$$\begin{aligned} T(z,t) = \frac{\sigma v}{\lambda}(1-1/f)\sqrt{a}\,e^{-(hx+h^2t)}\Big\{ &\sqrt{t/\pi}\,e^{-x^2/4t} \\ &+ \frac{1}{4h}e^{-hx+h^2t}\operatorname{erf}c(x/2\sqrt{t} - h\sqrt{t}) \\ &- \frac{1}{4h}(4h^2t + 2hx + 1)e^{hx+h^2t}\operatorname{erf}c(x/2\sqrt{t} + h\sqrt{t})\Big\} + T_0 \end{aligned} \tag{12}$$

where $h = v/2f\sqrt{a}$

and $x = z/\sqrt{a}$.

For the craze boundary temperature ($z=0$) equation (12) reduces to:

$$\begin{aligned} T(0,t) = \frac{\sigma v(1-1/f)}{\lambda}\sqrt{a}\big[&e^{-h^2t}\sqrt{t/\pi} + 1/2h \\ &-(ht + 1/2h)\operatorname{erf}c(h\sqrt{t})\big] + T_0 \end{aligned} \tag{13}$$

The equilibrium craze boundary temperature can be determined from equation (13):

$$T(0,\infty) = \frac{\sigma(f-1)}{\rho c} + T_0 \tag{14}$$

By inserting appropriate values for the constants ($\rho_{ps} = 1040\,\mathrm{kg\,m^{-3}}$, $c_{ps} = 1200\,\mathrm{J\,kg^{-1}\,K^{-1}}$, $f = 4$[17,18] and $\lambda = 0.13\,\mathrm{J\,ms^{-1}\,K^{-1}}$) it becomes clear that the temperature increase can be quite high. For instance, the equilibrium craze boundary temperature increase at 20 MPa is 50 K.

On series expansion equation (13) reduces to:

$$T(0,t) = \frac{2}{\sqrt{\pi}}\frac{\sigma v}{\lambda}(1-1/f)\sqrt{at} + T_0 \tag{15a}$$

or

$$T(0,t) = \sqrt{\frac{a}{\pi t}}\frac{\sigma}{\lambda}(1-1/f)D + T_0 \tag{15b}$$

if

$$v\sqrt{t/a}/2f \ll 1$$

where D is the craze thickness.

In order to calculate the craze boundary temperature it is necessary to know the rate of craze thickening, $2v$. This rate has been estimated for PS/LDPE 94/6 wt% blends by determining the number of crazes per unit length. This can be combined with the associated plastic strain, which is the strain due to crazes, and the time to reach this strain to calculate $2v$ by assuming that v is constant and that all crazes were initiated at the onset of the plastic strain. The number of crazes is $80\,000\,\mathrm{m}^{-1}$ at a plastic strain of 0.014, giving an average craze thickness of 0.18 μm. As the strain rate was $8.3\times10^{-4}\,\mathrm{s}^{-1}$, the time to reach this thickness is 17 s, so v is $5\times10^{-9}\,\mathrm{m\,s}^{-1}$.

Using this value the calculated craze boundary temperature increase is 0.001 K. A decrease in the rate of craze thickening by half an order of magnitude would probably account for the effect of glycerol on the crazing behaviour. As the activation enthalpy of the rate of craze thickening is $110\,\mathrm{kJ\,mol}^{-1}$[19] this corresponds to a temperature change of 8 K. Evidently, the assumption of a constant rate of craze thickening does not result in a temperature increase at the craze boundary that is high enough to account for the inhibiting effect of glycerol on craze thickening. However, while the overall rate of craze thickening is low, it can still be high locally, and thus account for the effects observed. The presence of a midrib in PS crazes may be interpreted as an indication of a high rate of craze thickening at the craze tip. Using a value of 0.1 μm for the thickness of the midrib[17] it can be calculated from equation (15b) that the midrib formation time must be 0.1 μs in order to result in an 8 K temperature change at a craze tip stress of 20 MPa. Unfortunately knowledge concerning midrib formation is limited so it is difficult to determine how realistic the assumption of this growth time is. However, an evident implication is that the tip of a growing craze must be blunt and there is support for this as craze tip blunting is one of the features of the meniscus instability mechanism for craze growth proposed by Argon and Salama[20].

So far attention has been paid only to the craze boundary temperature. However, it is conceivable that a significant temperature increase of the craze fibrils takes place, that may promote the fibril drawing process. Donald *et al.*[21] drew attention to the correlation between the extension ratio of the craze fibrils and the theoretical maximum extension ratio of the polymer calculated by assuming that the entanglement points are fixed. This suggests a tentative calculation of the temperature increase associated with the extension ratio based on simple network theory. Assuming adiabatic unidirectional extension, which is reasonable in the case of PS/LDPE blends, the temperature rise is given by:

$$\Delta T=\frac{G}{2c\rho}\left(\lambda^2+\frac{2}{\lambda}-3\right) \qquad (16)$$

where G is the shear modulus and λ is the extension ratio ($1/f$). For G it is appropriate to use the plateau modulus, which is 2×10^5 Pa at 140°C[22]. At the craze tip $\lambda\simeq8$[17] resulting in a fibril temperature rise of 5 K, which can account for the effect of glycerol on craze kinetics.

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