MECHANICAL STRENGTH OF INTERFACES IN THERMOPLASTIC POLYMERS

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ABSTRACT

In this lecture a brief review is given first on the mechanical problems, which derive from the existence and the large variety of interfaces in thermoplastic polymers, taking into account their specific organization and the particularities of the geometry of stress and strain. The fracture mechanics methods used to determine interfacial "strength" are indicated. Subsequently the molecular conditions required for stress transfer at polymer interfaces are investigated. It is concluded from crack healing and scattering experiments that for unfilled amorphous polymers (PMMA, PS) the strength increases in proportion to the curvilinear depth of interpenetration of chains and the number of newly formed entanglements, which is the main source of the build-up of interfacial strength between identical or compatible polymers. From the many techniques to heat a joint and melt the polymer in the interfacial region of semi-crystalline polymers only the quite recent developments of non-isothermal fusion welding [1] are discussed. For polyethylene and polypropylene (PE, PP) optimum weld strengths are obtained with this technique due to the good interfacial wetting and the efficient stress transfer by crystalline lamellae newly formed across the former interface. In welding of glass fibre reinforced thermoplastics particular attention has to be paid to the behaviour of the fibres in the weld zone. The presence of glass fibres is likely to (i) influence the interdiffusion of molecules, (ii) speed up crystallization by nucleation, and (iii) weaken the weld-line by adverse orientation of the fibres. A study by laser extensometry [2] of the local strains in the weld-zones of these materials yields particularly pertinent information on damage development in space and time. From these considerations conclusions could be drawn with respect to the design and execution of joints, their resistance under thermo-mechanical and environmental solicitation and the testing procedure.

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Introduction

Interfaces in modern materials are frequent; for more than 100 years the properties of homogeneous, continuous polymer matrices are improved through modification and/or combination with other materials forming a distinct phase. Thus elastomeric or other polymeric modifier particles, fibre reinforcements, particulate charges or mineral coatings are used to improve respectively the strength, toughness or barrier properties of the base polymer. In fact most presentations in this Meeting deal with composite systems.

Interfaces separate two dissimilar materials, but they are also formed as phase boundaries in semi-crystalline polymers or at the joints between identical or compatible polymers brought into contact during welding. In all these cases the term interface is used, although it would be more appropriate to speak of an interphase, since the physical organization (degree of orientation, mechanical interpenetration, effect on morphology) and chemical composition across an interface (through molecular interdiffusion) frequently change only gradually – not to speak of the presence of a real third phase due to prior treatment of the surfaces brought into contact, added impurities or traces of degradation. However, the influence of third phases, especially that of classical adhesives such as rubber cement or reactive resins, will not be discussed here. For a thorough discussion of the physical origins of interfacial adhesive forces, their molecular origins and experimental determination the reader is referred to the competent literature (see e.g. Wu [1], Wool [2] or Jones and Richards [3]).

In this contribution we study the mechanical aspects deriving from the presence of interfaces in a loaded sample and investigate more closely three particular examples: the stress transmission through interdiffused chain molecules at amorphous polymer-polymer interfaces, the micro-mechanics and toughness of semi-crystalline thermoplastics and the characterization of weld-lines in fibre-reinforced polyamides. To determine the strength of a plane interface between stiff solid (glassy) polymers fracture mechanics concepts are most appropriate. From the very beginning of such studies compact tension (CT) and (asymmetric) double cantilever beam (DCB) specimens have been used for this purpose (see refs. [4-7]). Both geometries permit to initiate a crack at the welded interface and to separate the interconnected surfaces. The resistance to crack propagation, which is expressed by the critical stress intensity factor $K_c$, or by the critical energy release rate (often simply called fracture energy) $G_c$, can be taken as a measure of interfacial strength.

For the CT specimens $K_c$ is generally obtained from the measurement of applied load $F$ and crack length $a$ at peak load according to the relation:

$$K_c = f(a/W) \frac{F_{\text{max}}}{B\sqrt{W}},$$

(Eq. 1)

where $f(a/W)$ is a tabulated correction function (ISO/DIS [4]).
Strength of amorphous interfaces after crack healing

Essential basic information on stress transmission through individual chain molecules has been obtained by crack healing studies, which have started more than 20 years ago (Kausch et al. [8, 9], Wool [2]); together with later techniques permitting the tracing of a molecule on its path across an interface (comprehensively reviewed by Creton [7]) have led to a very clear picture of the molecular origin of interfacial strength (Fig. 1).

![Quality of interdiffused chains and strength limiting mechanisms](image)

Figure 1: Quality of interdiffused chains and strength limiting mechanisms

It is helpful to recall that the interfacial strength between flat surfaces of two identical or compatible glassy polymers - brought into intimate contact at a temperature $T > T_g$ - is gradually built up (in isothermal condition and over a period of between some minutes to some hours) by chain diffusion through reptational motion; strength is quantified by the $G_c$, or $K_c$ necessary to drive a crack parallel to the interface so as to separate the two surfaces welded together during healing (Fig. 1). The forces transmitted across the gradually opening former interface are the higher the more numerous the intersecting chain backbones and the deeper their penetration into the opposite matrix. Kausch et al. [8, 9] have established that the strength $K_c$ of broken CT specimens increased with the time $t_h$ allowed for healing according to $(t_h)^{1/4}$. To explain this scaling they have postulated that the average curvilinear displacement ($<\Delta l^2>_{1/2} = (2D t_h)^{1/2}$) of the chains is proportional to the number of newly formed entanglements, $n(t_h)$, which subsequently determine the energy release rate $G_c$. This leads to:

$$<\Delta l^2>_{1/2} \sim (2D t_h)^{1/2} \sim n(t_h) \sim (G_c)^{1/2} \sim (t_h)^{1/4}.$$  

Eq. (2)

This fundamental relationship has been consistently confirmed in later studies of crack healing (see e.g. [10, 11]). The molecular micromechanics as illustrated by Figure 1 has been further elucidated by the group of Kramer [7] in their intriguing experiments using deuterated block copolymers of adequately chosen block lengths. Thus they have determined that chain pull-out occurs preferentially if the mass of the penetrated part of a molecule, $M_p$, is smaller than the molecular weight between entanglements, $M_e$ (a-chains). Pull-out will also occur if $M_p$ is somewhat larger than $M_e$, and if the forces transmitted by the penetrated chains are insufficient to initiate matrix crazing (b-chains). However, with increasing areal chain density $\Sigma$ of connecting chains, crazing rather than chain pull-out will be the dominating mechanism. In poly(2-vinylpyridine), PVP, this transition occurs at $\Sigma_c = 0.03$ connecting chains/(nm)$^2$. If the molecular weight $M_n$ of the diffusing chains is much larger than $M_e$, and if they are solidly anchored in both adherents (c-chains), they must either be broken during crack opening (c*) or give rise to matrix crazing. In polystyrene (PS) this transition of the main fracture mechanism occurs at $\Sigma_c = 0.03$ connecting chains/(nm)$^2$ (Creton [7]). Since the cross-section of a PS-chain amounts to 0.73 nm$^2$ one obtains the surprising result that only a fraction of 0.03/0.73 = 0.022 of all chains (packed in parallel so as to intersect a given plane) need to be loaded in order to give full short-time strength to an interface.
Fusion-welding of semi-crystalline thermoplastics

The main mechanism to establish interfacial strength in semi-crystalline thermoplastics is co-crystallization of chains from either side of the joint after mixing through interdiffusion at $T_i > T_m$. Among the many techniques to heat a joint and melt the polymer in the interfacial region we only discuss the quite recent progress obtained by the group of Manson [12, 13] with non-isothermal fusion welding, explained in Figure 2 using polyamide 12 (PA12) as an example.

In isothermal welding both adherents are brought to the same temperature $T_i=180^\circ$C above the melting temperature $T_m=178^\circ$C of the used polymer (Fig. 2a-1). At $T_i > T_m$ the chains are sufficiently mobile to interdiffuse (2a-2). During cooling interfacial strength develops through cocrystallization (2a-3). However, during isothermal welding wetting is much slower and essential features of the lamellar organization in the interfacial region may be retained (memory effect), which favour subsequent adhesive fracture at the interface, thus accounting for lower values of $G_c$. In non-isothermal welding (Fig. 2b) the lower plaque (at 200°C) is well above $T_m$, the upper plaque still solid (2b-1). In their extensive experiments the group of Manson [12, 13] has demonstrated that a temperature gradient across the interface considerably improves the weld strength, since melting extends into the upper plaque (2b-2). On subsequent cooling (2b-3), the morphology of the lower, initially molten plaque is altered (continuous lamellar structures grow across the interface). The superior strength of such interfaces (Fig. 3) can be ascribed, therefore, to good interfacial wetting on the one hand, and to the efficient stress transfer by crystal lamellae, which change the nature of the interfacial fracture from adhesive to cohesive (Manson et al.[12, 13]).

In non-isothermal welding, $G_{ic}$ can be calculated as:

$$G_{ic} = 8.6 \text{ kJ/m}^2$$

Figure 3: Comparison of isothermal and non-isothermal weld-strength of PA 12 (after [13]).
Quality of weld-lines in glass fiber reinforced thermoplastics

In Sections 2 and 3 we have shown the strong dependence of strength development on molecular mobility and crystallization behaviour. In welding of glass fibre reinforced thermoplastics particular attention has to be paid to the behaviour of the fibres in the weld zone. The presence of glass fibres is likely to (i) influence the interdiffusion of molecules, (ii) speed up crystallization by nucleation, and (iii) weaken the weld-line by adverse orientation of the fibres. A conventional stress-strain curve gives some global information on possible changes of yield stress and fracture strength of a welded sample using the weld-strength factor; however, more pertinent information is obtained from a study of the local strains in the weld-zone as for instance through laser extensometry (see Bierögel et al. [14, 15] for details of the method). Essential results for un-welded and welded injection moulded plates of polyamide 6 containing respectively 10 and 30 wt.-% of short glass fibres are shown in Figure 4. The distribution of local strains $\varepsilon_l$ is plotted as a function of time $t$ of tensile drawing (which is equivalent to global strain $\varepsilon_i$).

![Figure 4: Local strains $\varepsilon_l$ in polyamide 6 materials: a) un-welded with 10 wt.-% of fibres designated as 10, b) polyamide with 10 wt.-% welded to the same material (10/10) and c) polyamide 10 wt.-% welded against 30 wt.-% (10/30) (after Grellmann et al. [14, 15]).](image)

The un-welded 10 wt.-% sample shows a rather homogeneous distribution of $\varepsilon_l$ up to the maximum applied deformation at $t = 320$ s and a global strain $\varepsilon_i$ of about 14% (Fig. 4a). As to be expected, weld-lines give rise to a gradually increasing local strain concentration (Figs. 4b and c). It should be noted that the region with higher local strains is much wider (about 10 mm) than the visible weld-line (about 1 mm) and that the strain concentration is more important for the weld-line 10/30 between the dissimilar materials than that of 10/10 (Figs. 4c and b).

In order to characterize the strain heterogeneity quantitatively it is useful to define a heterogeneity parameter $H$ as follows:

$$H = \frac{\varepsilon_{i_{\text{max}}} - \varepsilon_{i_{\text{min}}}}{\varepsilon_i}$$  \hspace{1cm} \text{Eq.(3)}

In Figure 5 the heterogeneity parameter $H(t)$ is plotted as a function of the progressing tensile experiment. After some fluctuation of $H$ at very small strains it reaches a minimum, the value of which depends on sample composition; it is smallest for the un-welded material (10) and largest for the dissimilar weld-line (10/30). The differences between the studied materials increase with increasing overall strain. Figure 5 nicely demonstrates that the heterogeneity parameter $H$ permits a much more detailed characterization of weld-line behaviour than the ratio of tensile strengths of welded and un-welded samples, which in the above case all turn around 59 to 66 MPa, which is close to the tensile strength of the unmodified PA6 matrix, namely 60 MPa (Grellmann et al.[15]).
Conclusions

The molecular requirements to establish stable joints between thermoplastic polymers have been discussed. Weld-line strength of unfilled amorphous polymers (PMMA, PS) derives from the formation of entanglements in an interfacial region some 20 nm deep. In semi-crystalline polymers (PE, PP) optimum conditions are obtained in non-isothermal welding, which leads to good interfacial wetting and efficient stress transfer by co-crystallization of chains within a transverse region of typically 10 to 50 μm. The weld-line effects in short glass fibre filled polyamide extend over a region of some mm as determined by a sensitive method (laser extensometry), which also permits to judge weld-line quality from the observed strain heterogeneity $H$.

References

6. Ramsteiner, F. this Meeting

Figure 5: Heterogeneity of polyamide 6 materials as a function of global strain (expressed by the measuring time $t$ (after Grellmann et al. [14, 15]))