

MECHANICAL STRENGTH OF INTERFACES IN THERMOPLASTIC POLYMERS

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ABSTRACT

In this introductory 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. Then (fracture mechanics) methods are discussed to determine interfacial "strength". Subsequently the molecular conditions required for stress transfer at the interface of crystal lamellae are investigated as well as the mechanisms leading on the one hand to the *establishment of interfacial strength* during crack healing and welding and on the other hand to the *weakening and final rupture* of a joint under load. These studies, performed with the industrially important semi-crystalline polyethylene, polypropylene and polyamide have permitted to define optimum welding conditions. The influence of a heterogeneous phase, glass fibers, on the quality of a weld-line in polyamide has been assessed using laser extensometry to follow 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.

1. INTRODUCTION

Interfaces in modern materials are frequent; in fact for many years now important results in improving the properties of homogeneous, continuous thermoplastic matrices were obtained through their 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. Interfaces *separate two dissimilar materials*, they are also formed as *phase boundaries* in semi-crystalline polymers or between identical or compatible polymers brought into *contact during welding*. In view of possible traces left from the joining process, a *weld-area* or *region* must also be considered as a - three-dimensional - interface. In all cases it is generally required that the stresses transmitted across such interfaces are comparable to those within the bulk polymer while avoiding undue *local concentration of strain or stress*, which might endamage the polymer microstructure. In order to establish strong interfaces between chemically - but also mechanically - different materials, intimate physical contact and chemical compatibilization are generally required. 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 investigate the stress transmission through interdiffused chain molecules at polymer-polymer interfaces, which is the main source of the build-up of interfacial strength between identical or compatible polymers. Thus we discuss crack healing of amorphous polymers and the compatibilization of incompatible polymers by appropriate use of copolymers (Sect. 3), and the effect on material toughness of the organization and welding conditions of semi-crystalline (Sect. 4) and of short glass-fibre reinforced polymers (Sect. 5). Classical adhesives such as rubber cement or reactive resins will not be considered here. First we have to present, however, the fracture mechanical methods used to quantify the toughness of the here studied materials (Sect. 2).

2. FRACTURE MECHANICAL METHODS TO DETERMINE INTERFACIAL STRENGTH

For an investigation of the *mechanical* effect of molecular and experimental parameters, methods of characterization are indispensable, which try to assess the load bearing capacity of an interface at the different stages of interdiffusion and/or welding. 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 (Fig. 1) have been used for this purpose (Kausch [4], Grellmann et al. [5], Creton et al. [6]). 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.

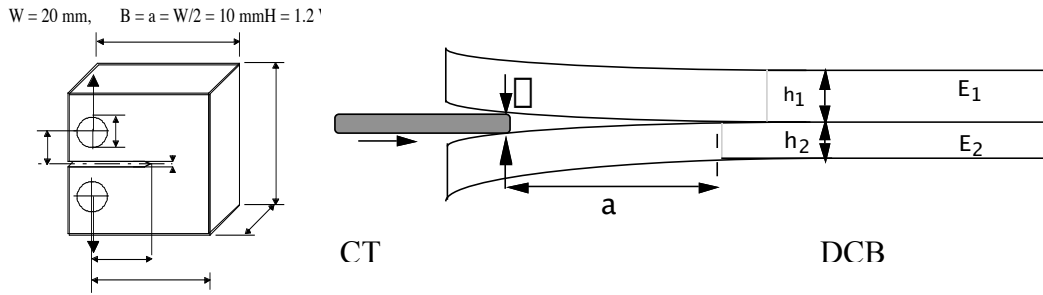


Figure 1: Fracture mechanics specimen commonly used for the characterization of interfacial strength, a) compact tension (CT) and b) (asymmetric) double cantilever beam (DCB)

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

$$K_c = f(a/W) \frac{F_{\max}}{B\sqrt{W}}, \quad (\text{Eq. 1})$$

where $f(a/W)$ is a tabulated correction function (ISO/DIS [7]). K_c corresponds to K_{Ic} if the criteria of Linear Elastic Fracture Mechanics (LEFM) are met. DCB specimens (Fig. 1 b) provide a particularly convenient technique to study the interfacial interaction between dissimilar materials especially if a copolymer is used as a compatibilizer. DCB specimens have two additional advantages; firstly, very small fracture energies (of the order of 1 J/m²) can be determined. Secondly, by employing asymmetric specimens (where the two cantilevers are of different thickness h , occasionally of different elastic modulus E) any tendency of the crack to leave the interface and enter one of the matrices can be corrected for. G_c for asymmetric DCB specimens is determined from the relation of Kanninen as used by Creton [6]:

$$G_c = \frac{3\Omega^2 E_1 E_2 h_1^3 h_2^3}{8a^4 \Omega^2} [C_1^2 E_2 h_2^3 + C_2^2 E_1 h_1^3], \quad (\text{Eq. 2})$$

where $\Omega^2 = C_1^2 E_2 h_2^3 + C_2^2 E_1 h_1^3$ and $C_i = 1 + 0.64(h_i/a)$.

3. HEALING OF INTERFACES IN AMORPHOUS POLYMERS

Crack healing is defined as restoring interfacial strength to the two faces of a fracture surface - or more generally, to any two flat surfaces - brought into intimate contact at a temperature $T > T_g$. In the case of two identical or compatible glassy polymers interfacial strength 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 (Figs. 1 and 2). Such studies have started more than 20 years ago (Kausch [4], Wool [21]); later techniques permitting the tracing of a molecule on its path across an interface (reviewed by Creton [6]) have led to a very clear picture of the molecular origin of interfacial strength (Fig. 2).

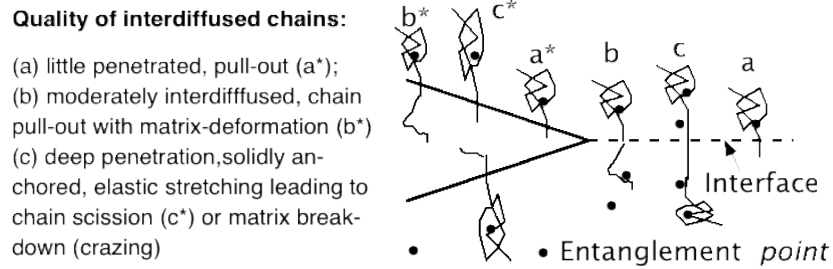


Figure 2: Schematic representation of the behaviour of chains, which have penetrated an interface between compatible amorphous polymers, as a function of the depth of their penetration

Referring to Figure 2 and the cited literature [2,4,6] we can safely state that the forces transmitted across the gradually opening of the former interface are the higher the more numerous the intersecting chain backbones and the deeper their penetration into the opposite matrix. As a function of healing time t_h more and more chains advance from (a) to (c). Studying the healing of poly(methyl methacrylate) at $T > T_g$, Kausch [4] has shown that the strength K_c , of broken CT specimens increased during healing with $(t_h)^{1/4}$. To explain this scaling he has postulated that the *average* curvilinear displacement ($\langle \ell^2 \rangle^{1/2} = (2Dt_h)^{1/2}$) 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:

$$\langle \ell^2 \rangle^{1/2} \sim (2Dt_h)^{1/2} \sim n(t_h) \sim (G_c), \text{ and } K_c \sim (G_c)^{1/2} \sim (t_h)^{1/4}. \quad \text{Eq. (3)}$$

The molecular micromechanics illustrated by Figure 2 has been further elucidated by the group of Kramer [6] in their intriguing experiments using deuterated block copolymers of adequately chosen block lengths. Thus they have determined that chain pull-out occurs always 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 \square of connecting chains, crazing rather than chain pull-out will be the dominating mechanism. In poly(2-vinylpyridine), PVP, this transition occurs at $\square_c = 0.03$ connecting chains/(nm)². If the molecular weight M_w 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 $\square_c = 0.03$ connecting chains/(nm)² (Creton [6]).

4. NON-ISOTHERMAL FUSION-WELDING OF SEMICRYSTALLINE POLYMERS

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 [8,9] with non-isothermal fusion welding, explained in Figure 3 using polyamide 12 (PA12) as an example.

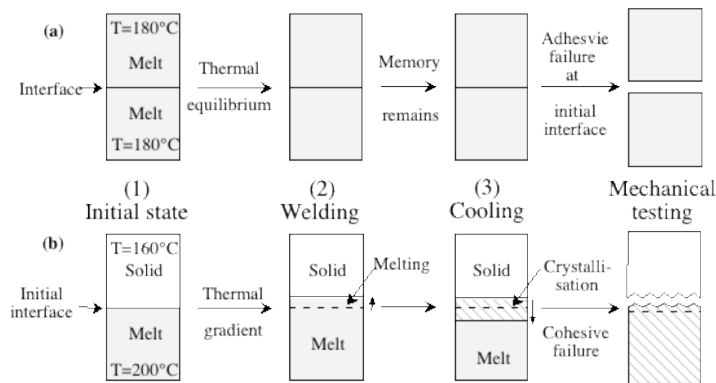


Figure 3: Differences between isothermal and non-isothermal welding (after Manson et al. [8])

In isothermal welding both adherents are brought to the same temperature $T_i=180^{\circ}\text{C}$ above the melting temperature $T_m=178^{\circ}\text{C}$ of the used polymer (Fig. 3a-1). At $T_i > T_m$ the chains are sufficiently mobile to interdiffuse (3a-2). During cooling interfacial strength develops through cocrystallization (3a-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. 3b) the lower plaque (at 200°C) is well above T_m , the upper plaque still solid (3b-1). In their extensive experiments the group of Manson [8,9] has demonstrated that a *temperature gradient across the interface* considerably improves the weld strength, since melting extends into the upper plaque (3b-2). On subsequent cooling (3b-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. 4) 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.[8,9]).

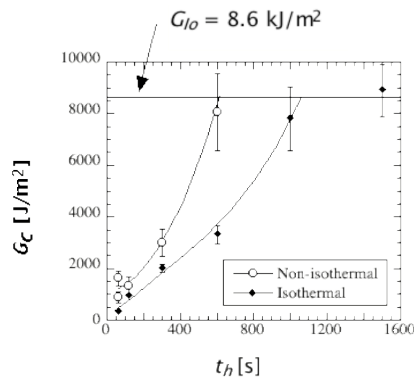


Figure 4: Comparison of isothermal and non-isothermal weld-strength of PA 12 (after [9])

5. QUALITY OF WELDLINES IN GLASS FIBER REINFORCED THERMOPLASTICS

In Sections 3 and 4 we have shown the strong dependence of strength development on molecular mobility and crystallization behaviour. In welding of glass fiber 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 by laser extensometry (see Bierögel et al. [10,11] 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 5. The distribution of local strains ϵ is plotted as a function of time t of tensile drawing (which is equivalent to global strain $\bar{\epsilon}$).

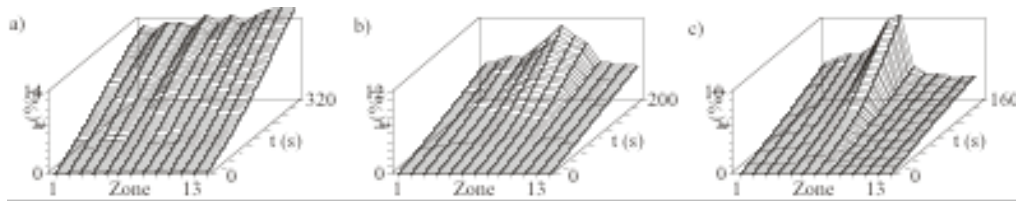


Figure 5: Local strains ϵ in polyamide 6 materials: a) un-welded with 10 wt.-% of fibres designated as 10, b) polyamide with 10 wt.-% welded to the same material (10/10) and c) polyamide 10 wt.-% welded against 30 wt.-% (10/30) (after Grellmann et al. [10, 11])

The un-welded 10 wt.-% sample shows a rather homogeneous distribution of ϵ up to the maximum applied deformation at $t = 320$ s and a global strain $\bar{\epsilon}$ of about 14% (Fig. 5a). As to be expected, weld-lines give rise to a gradually increasing local strain concentration (Figs. 5b 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. 5c and b).

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

$$H = \frac{\epsilon_{\max} - \epsilon_{\min}}{\bar{\epsilon}} \quad \text{Eq.(4)}$$

In Figure 6 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 6 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.[11]).

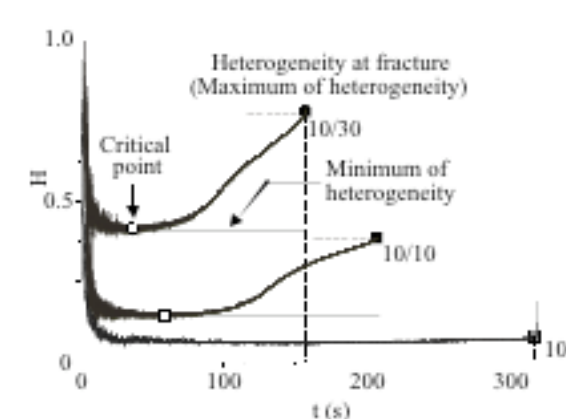


Figure 6: Heterogeneity of polyamide 6 materials as a function of global strain (expressed by the measuring time t (after Grellmann et al. [10, 11])

6. CONCLUSIONS

The molecular requirements to establish stable joints between thermoplastic polymers have been discussed. For unfilled amorphous polymers (PMMA, PS) strength criteria can be derived from an entanglement model. 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 newly formed crystal lamellae. A sensitive method (laser extensometry) has been applied to short glass fibre filled polyamide to measure the distribution of local strains around a weld-line and to judge its quality from the determined heterogeneity.

7. REFERENCES

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