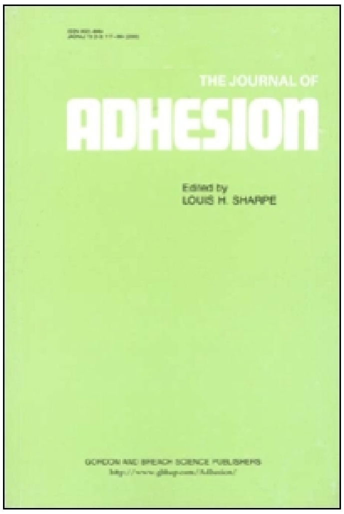

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Interface/Interphase engineering of polymers for adhesion enhancement: Part I. Review of micromechanical aspects of polymer interface reinforcement through surface grafted molecular brushes

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INTERFACE/INTERPHASE ENGINEERING OF POLYMERS FOR ADHESION ENHANCEMENT: PART I. REVIEW OF MICROMECHANICAL ASPECTS OF POLYMER INTERFACE REINFORCEMENT THROUGH SURFACE GRAFTED MOLECULAR BRUSHES

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This article reviews the theoretical principles of macromolecular design of interfaces between glassy polymers as well as those between rigid substrates and elastomers for maximizing adhesion and fracture performance of bonded assemblies. According to contemporary theories, macromolecular "connector molecules" grafted onto solid polymer surfaces effectively improve adhesion and fracture performance of interfaces between polymers by improving the interactions with adjacent materials through one or both of the following mechanisms: (1) interpenetration into adjacent polymeric phase, and (2) chemical reaction/crosslinking with the adjacent material.

It is shown that the effectiveness of the interface reinforcement by surface-grafted connector molecules depends on the following factors: surface density of grafted molecules, length of individual chains of grafted molecules, and optimum surface density in relation to the length of connector molecules. The influence of the above-mentioned physico-chemical parameters of molecular brushes on the interphase-interface reinforcement is discussed and quantified by contemporary theories. Also, the optimum conditions for maximum adhesion enhancement are specified and verified by a range of experimental examples.

Part II of this article demonstrates a novel and relatively simple, industry-feasible technology for surface grafting connector molecules and engineering of

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interface/interphase systems, which is discussed in detail and supported by a range of experimental examples. It is shown, in agreement with contemporary theories, that the use of chemically attached graft chemicals of controlled spatial geometry and chemical functionality enables a significant increase in the strength and fracture energy of the interphase, to the point of cohesive fracture of the substrate, or that of an adjacent medium such as adhesive, elastomer, or other material. This occurs even after prolonged exposure of investigated systems to adverse environments such as hot water.

Keywords: Polymers; Interface modification; Adhesion; Adhesive bonding; Fracture energy; Molecular brushes

INTRODUCTION

The experimental values of fracture energy for high molecular weight entangled polymers is on the order of $G_{Ic} = 100-1000\,\mathrm{J/m^2}$. These values are 2–3 orders of magnitude higher than the theoretical fracture energy (equal to approximately $G_{Ic} = 1\,\mathrm{J/m^2}$) of equivalent systems represented by an array of covalent bonds formed across the adhering surfaces of the bonded assembly. The above disparity indicates that the mechanism and micromechanics of fracture of "real polymers" must, therefore, involve several phenomena not accounted for in classical models and the concepts of adhesion and fracture mechanics in relation to interfaces between two polymers.

This article reviews the theoretical principles of macromolecular design of polymer interfaces by interpenetrating or surface-grafted and chemically bonded molecular brushes for achieving maximum adhesion and fracture performance of the interface between bonded polymers. Two practically significant cases are analysed: (1) adhesion at interfaces between glassy polymers, and (2) adhesion between surface-grafted solids and elastomers.

Technologically feasible solutions of the theoretical concepts reviewed in Part I are consequently proposed, supported by a range of experimental examples and discussed in detail in Part II (in this issue). It is shown how the molecular engineering of the interphase and interfaces provides the possibility of tailoring and maximising the performance of adhesively bonded plastics quantified by the strength of adhesion or interface fracture toughness. It is shown, in agreement with contemporary theories, that the use of chemically attached macromolecular graft chemicals of controlled spatial geometry and chemical functionality enables a significant increase of the strength and fracture energy of the interphase to the point of cohesive fracture of the substrate, or that of an adjacent medium such as adhesives, elastomers, or other materials. Hence, the principles of molecular design of the interphase reviewed in this article are shown to be applicable to any adhesively bonded structure, assuming that effective surface grafting of appropriate molecules to the surface can be achieved.

INTERPENETRATING MACROMOLECULAR CHAINS AT INTERFACE BETWEEN GLASSY POLYMERS AND THEIR CONTRIBUTIONS TO INTERFACIAL FRACTURE ENERGY

The Principal Mechanisms of Fracture of Interfaces Between Glassy Polymers

The interphase-interface system between polymeric substrate surface and adhesive or other polymeric, as illustrated in Figure 1, comprises an array of surface-grafted "macromolecular connector" chains, characterized by molecular weight, M_w, which contact an adhesive or other organic material layer characterized by M_c, which is the molecular weight of the chains between cross-links of the cross-linked polymer, or the critical molecular weight for entanglement for uncross-linked (*e.g.*, thermoplastic) polymers. An array of connector molecules crossing the interface leads to the increase of the load-bearing capability of the interface.

In addition to an adequate number of connector molecules bridging the interface, the following three mechanisms, schematically

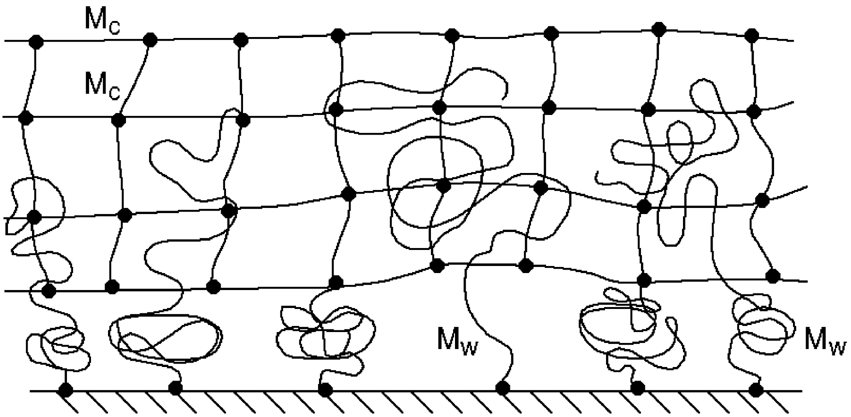

FIGURE 1 Schematic representation of the interphase/interface system involving surface-grafted, interpenetrating and chemically bonded "molecular brushes" in adhesively bonded polymer.

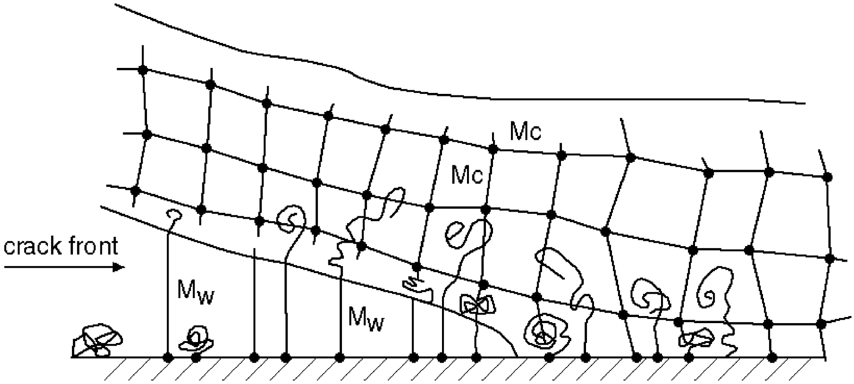

FIGURE 2 Crack propagation along the interface/interphase system involving chemically bonded as well as interpenetrating molecules. M_c, molecular weight of chains between cross-links of a cross-linked adhesive, or matrix; M_w, molecular weight of surface-grafted molecular chains.

illustrated in Figures 2 and 3, may contribute to the interface reinforcement by macromolecular "connector chains":

- chain pull-out,
- chain scission, and
- craze formation and failure.

The mechanism of interfacial interactions and that of the failure mechanism of interfaces between glassy polymers compatibilised by interpenetrating connector molecules, such as di-block or random copolymers, or by surface-grafted molecular chains, has been studied in detail by numerous researchers [1–11].

The following factors were identified in previous research [1–11] as most significant in controlling the fracture performance of interfaces compatibilised by interpenetrating or surface-grafted connector chains.

1. The length of "connector molecules" as determined by the degree of polymerisation, N, of di-block or random copolymers, *i.e.*: $N = M_w/m$, where M_w is the molecular weight of the macromolecular chain, and m is the molecular mass of the monomer.

   The influence of connector molecule length, as characterized by N, is categorised as follows:

   (a) *Small, unentangled, polymer chains* ($N < N_e$): Small chains characterised by $N < N_e$ (where N_e is the threshold of

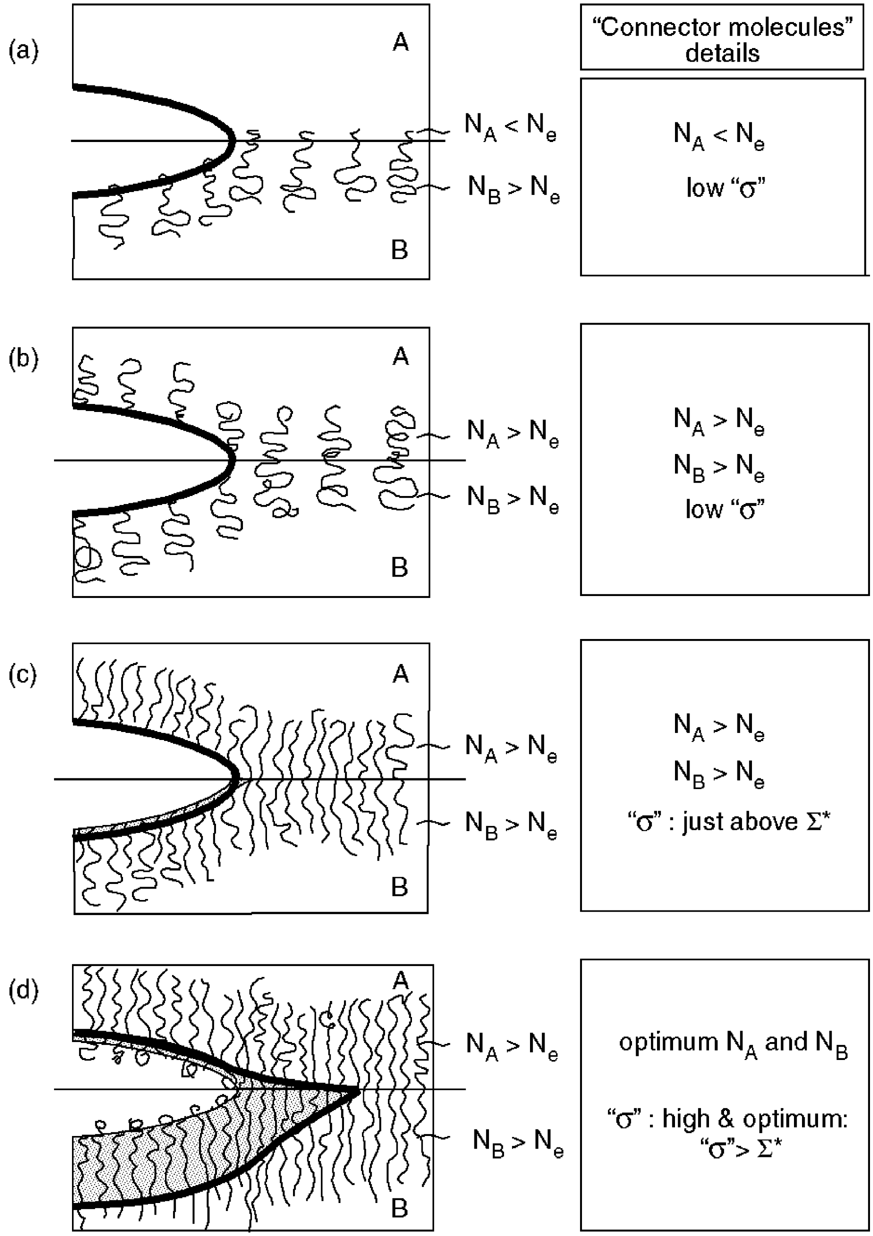

FIGURE 3 Interface/interphase failure modes in relation to relative areal density of "connector molecules" (σ/nm^2) and the length of "connector molecules" (N). *Notes*: (i) $\sigma_{\mathrm{c(A)}} > \sigma_{\mathrm{c(B)}}$; (ii) see text for the description of failure regimes (a) to (d) [σ_c: craze formation stress of polymer (A) and (B)].

molecular entanglement: $N_e \cong 200$) are too short to form entanglements [12] with the adjacent polymer,

   (b) *Entangled polymer chains ($N > N_e$)*: Long macromolecular chains, as characterised by $N \geq 200$, can form physical entanglements with the adjacent, adhering polymer.

2. The surface density, σ (number of grafted molecular chains per nm^2).
3. The breakage strength, f_b, and fracture energy, G_c, of individual molecular chain: G_c/σ.
4. The formation of and subsequent failure of a craze ahead of the propagating crack.

Interface Failure Modes and Micromechanical Models of Fracture of Interfaces Between Glassy Polymers

Interface Fracture by Chain Pull-out

Xu *et al.* [7] have proposed and analysed in detail the model of reinforcement of the interface between glassy polymers by interpenetrating molecular chains failing by the pull-out mechanism (Figure 3a). The fracture energy, G_o, of the interface according to this model, is expressed by the following relationship:

$$G_o \propto \sigma l_o{}^2 \propto \sigma N^2, \tag{1}$$

where σ is the surface density of grafted chains, l_o is the molecular chain's contour length (as embedded in the adjacent polymer), and N is the degree of polymerisation of the molecular chain of the graft molecule.

Interface Fracture by Chain Scission

In some cases the surface density, σ, of long chains bridging the interface is below the minimum required for exerting the stress sufficient for plastic deformation (yielding) of one of the adhering polymers (see Figure 3b). If both ends of the interpenetrating connector molecules, *e.g.*, di-block copolymer, are sufficiently long and hence well "anchored" in each adherend through the entanglement ($N > N_e$), whilst the stress exerted across the interface translates to the forces sufficient to break individual chemical single C–C bonds along the backbone of individual connector chains, the interface will fail through chain scission. The stress, σ_i , that the interface can sustain under these conditions is

$$\sigma_i \sim f_b \sigma, \tag{2}$$

where f_b is the force required to break individual molecular chains.

Interface Fracture by Crazing

When surface density, σ, of sufficiently long connector molecules ($N > N_e$) increases, the load-bearing capability of the interface will increase accordingly. Once the critical surface density, $\sum^*$ ($\sum^*$: surface density at transition from chain scission to interface crazing) is reached, the interface undergoes significant plastic deformation and the craze is formed (see Figures 3, 4, and 5) ahead of the crack tip. Creton *et al.* [5] and Brown [6, 15] have proposed and verified a model involving the formation and failure of a craze at interfaces between polymers. This involves, as illustrated in Figures 4 and 5, the formation of separate strands or fibrils which are connected by cross-ties to the neighbouring strands. Upon further interphase deformation these are stretched, increasing the stress at the crack tip and increasing the craze width. Once the craze is large enough due to deformation, it fails by both chain pull-out as described by Xu *et al.* [7] and the chain scission. Brown has determined that with the craze formation and subsequent failure the interface fracture energy, G_o, depends only on the surface density, σ, of grafted macromolecular chains and not on the molecular chain length. According to this model,

$$G_o \cong (f_b \sigma)^2, \tag{3}$$

where f_b is the force required to break individual molecular chains.

Creton *et al.* [5] and Norton *et al.* [16] fully verified Brown's model and provided a detailed discussion of interface failure involving chain scission, pull-out, and crazing. A range of di-block copolymers characterised by varying length N_1 and N_2 of blocks, and different matrix polymers characterised by varying degree of polymerisation, N_c, were used in these works. Some important details of these works are discussed in the following section.

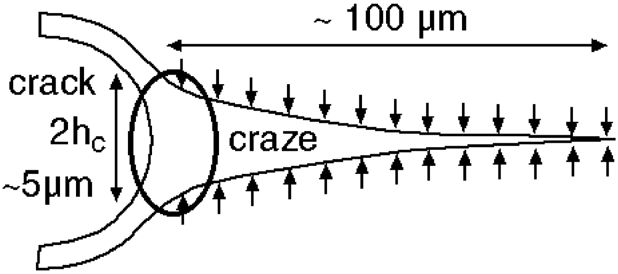

FIGURE 4 Schematic representation of a craze at the crack tip in glassy polymers (Reprinted with permission from *Plastics, Rubber and Composites Processing and Applications*, [8]).

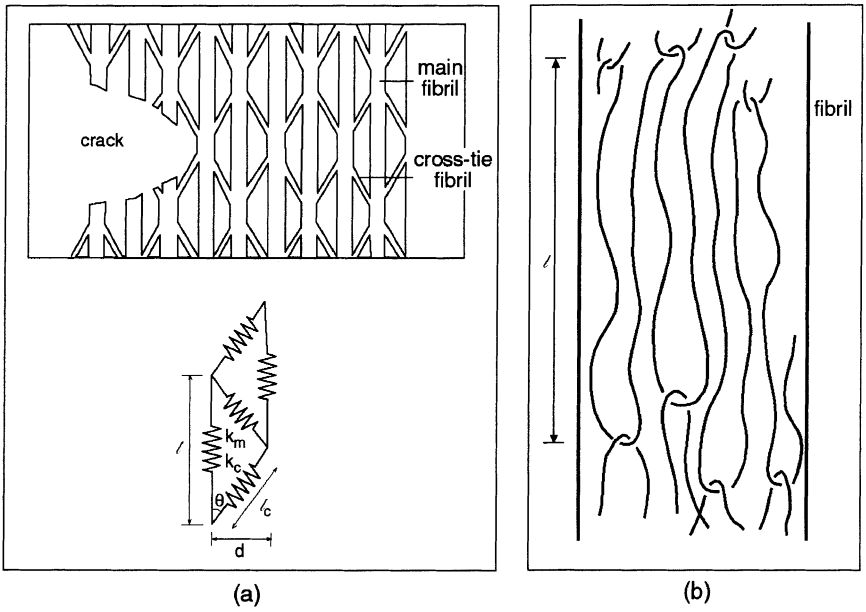

FIGURE 5 Schematic representation of (a) the microstructure of the craze and the corresponding "discrete spring network" model [9] [8]. (Reprinted with permission from *Macromolecules* [9], Copyright 1995, American Chemical Society), and (*b*) the structure of the fibril with entangled polymer chains immediately ahead of the crack tip (Reprinted with permission from *Plastics, Rubber and Composites Processing and Applications* [8]).

The Mechanism of Compatibilisation and Reinforcement of Interfaces Between Glassy Polymers

The use of di-block copolymers for compatibilisation of phase-separated blends of immiscible polymers [1–4] gave rise to a series of studies targeting the detailed explanation of micromechanical aspects of processes due to which the presence of "an array of connector molecules" leads to the reinforcement of the interface between two slabs of glassy polymers.

It was shown by Creton *et al.* [4] in their work on compatibilisation of blends of polystyrene (PS) and polyvinyl pyridine (PVP) that only those block copolymers are effective in preventing interface failure (by total delamination) in which each block has a polymerisation index $N \geq 200$. This critical length, N_e, corresponds to the average chain length between entanglements of the homopolymers. Creton's study has demonstrated the feasibility of the entanglement mechanism in effectively reinforcing the interface between originally immiscible or incompatible blend ingredients.

In the subsequent seminal work of Creton *et al.* [5], the following parameters pertinent to controlling the fracture performance of the interphase of the PS-PVP system were investigated in detail:

1. the surface density: σ (chains/nm^2) of "connector molecules", and
2. the length of PS and PVP blocks (determined by degree of polymerisation: N_{PS} and N_{PVD}) in the di-block copolymer.

All fracture surfaces were analysed by forward recoil spectrometry (FRES) for determining the locus of failure and surface density of "connector chains." The latter was determined by the use of deuterium-labelled PS blocks.

The following significant observations were made in Creton *et al.* [5]

1. Very little increase in the interface fracture energy was observed when the length, N, of the di-block element was below the threshold molecular entanglement length, N_e ($N < N_e$). As shown in Figure 6, a linear increase of G_{Ic} was observed with increasing surface density, σ, from approx. 1.2 J/m^2 for the bare PS-PVP interface up to a certain saturation level. The latter is reached at $\sigma = 0.1$ chains/nm^2, at which the maximum $G_{Ic} \cong 4$ to 6 J/m^2 is reached. This value is well below the 500 J/m^2 of pure PS matrix.
2. When the length of di-block elements of "connector molecules" is increased to N_e and above, effective entanglements are formed between the homopolymer matrix and block copolymer chains. Consequently, significant increase in fracture energy of the interphase, G_{Ic}, is observed. The relationship between G_{Ic} (per individual chain) and N_{PVP} is illustrated in Figure 7.
3. For di-block elements characterised by $N > N_e$, two regions are observed regarding the influence of surface density, σ, of "connector molecules" on fracture energy of the interphase (see Figure 8, which illustrates the data originally presented in Figures 19 and 21a in Creton *et al.* [5]):
   (a) region of σ between 0 to approx. 0.012 chains/nm^2 characterised by no or a very insignificant increase in G_{Ic}, and
   (b) a region for $\sigma > 0.012$ chains/nm^2 in which a significant (near-linear) increase in G_{Ic} is observed with increasing σ.

   It must be noted [5] that the slope of the linear plot G_c *vs.* σ in Figure 8 gives $G_c \propto \sigma^2$, which is consistent with Brown's model (See Equation (3)) of the craze failure.

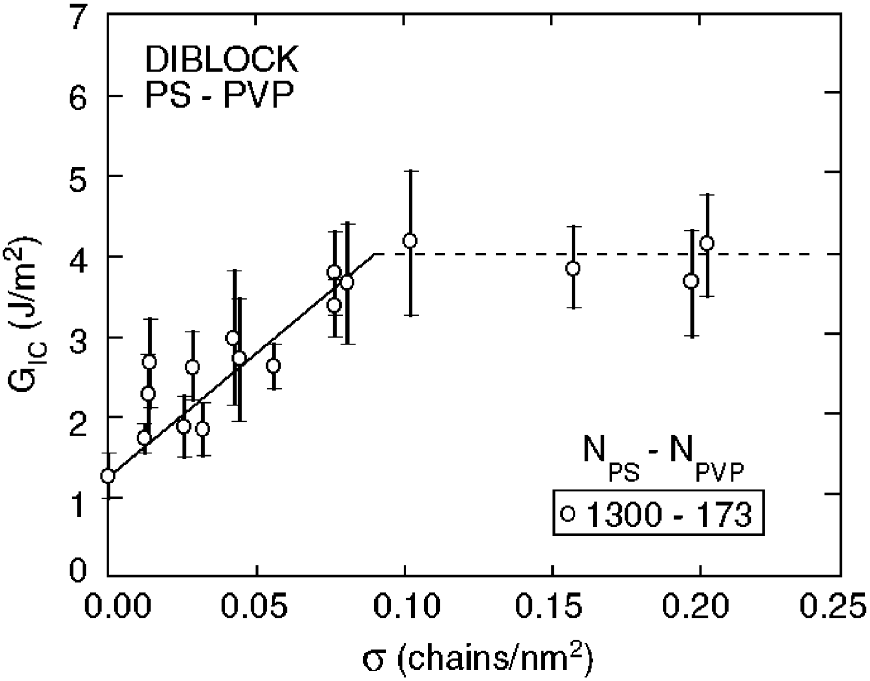

FIGURE 6 Fracture toughness, G_{Ic}, of PS-PVP interface reinforced with diblock PS-PVP copolymers with a short PVP block ($N = 173$). (Reprinted with permission from *Macromolecules* [5], Copyright 1992, American Chemical Society).

4. Once adequate N and σ are reached the interphase fails through the craze formation, which, in turn, leads to a significant increase in the value of fracture toughness of the interface. The propagating crack, according to the model of Brown [6], is preceded by a craze schematically illustrated in Figures 4 and 5 [8, 9]. According to Brown's model, illustrated in Figure 5a, in the craze zone each molecule is entangled a number of times and the "entanglement zone" comprising several entanglements is stretched into a single fibril (see Figure 5b). The adjacent fibrils are joined together by additional "cross-ties." Due to this, and due to crack propagation, the cross-tie fibrils allow the stress to be transferred to its neighbours ahead of the crack tip.

Consequently, the craze behind the crack tip is not completely unloaded after fracture and transfers an additional amount of stress to the unbroken fibril, causing it to fail, typically by disen-

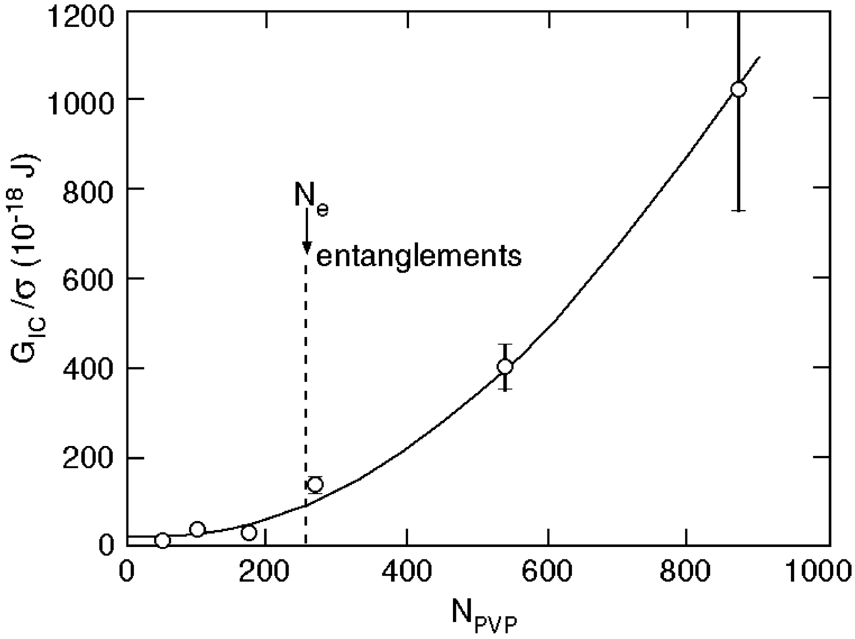

FIGURE 7 Fracture toughness (G_{Ic}/per chain) of PS-PVP interface as a function of the degree of polymerisation (N) of PVP block. (Reprinted with permission from *Macromolecules* [5], Copyright 1992, American Chemical Society).

tanglement and pull-out of individual chains from the fibril structure. As a result of this, the critical energy release rate, G_{Ic}, is related to the square of effective density of load-bearing "connector molecules" in accordance with Equation (3).

Sha *et al.* [9] analytically investigated Brown's model of the "fibril/cross-tie fibril network" model represented by a discrete spring network (see Figure 5a). The length of the main fibril (l) and the cross-tie "spacing" (d) with the spring constants k_m and k_c, respectively, represent elastic properties of entangled molecular chains. The continuum model consequently developed by Sha *et al.* [9] fully verified Brown's prediction and was successfully used for predicting molecular weight dependence of fracture toughness of polymers, fracture toughness of entanglement networks, and the kinetics of polymer welding.

The work of Creton *et al.* [5], additionally supported by Brown's craze failure model [6] as discussed above, showed that: (1) the

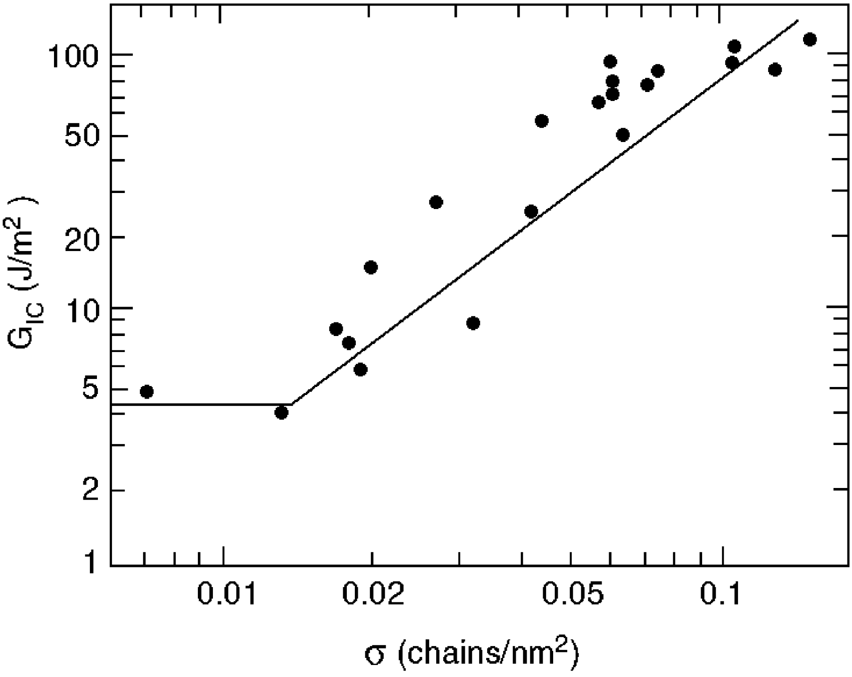

FIGURE 8 Fracture toughness, G_{Ic}, of PS-PVP interface as a function of surface density (σ/nm^2) of block copolymer chains for 800–870 PS-PVP block copolymer. (Reprinted with permission from *Macromolecules* [5], Copyright 1992, American Chemical Society).

interfaces between glassy polymers are effectively reinforced by interpenetrating "connector molecules" in the form of di-block copolymers or surface-grafted chains [10], and (2) the effectiveness of the reinforcement strongly depends on the area density and the molecular weight of the blocks which, in turn, decide on the nature of the failure mechanism.

The seminal value of Creton *et al.* [5] and Brown [6] resides in the full explanation of micromechanical phenomena regarding interphase reinforcement and that of various modes of failure mechanism which, in turn, can be effectively used for designing the interphase system in adhesively bonded structures, composite materials, or other practical applications of adhesion science. The above are briefly summarised by the diagrams shown in Figure 3, which illustrate the performance of the interface between materials A and B, exhibiting noticeable difference in craze formation stress, σ_c ($\sigma_{c(A)} > \sigma_{c(B)}$). The following modes are observed regarding interphase failure mechanisms *versus* interphase parameters such as the surface density, σ, of "connector molecules" and their length, N:

mode (a): $\boldsymbol{N < N_e}$. The chain blocks which are shorter than N_e are easily pulled out without significant plastic deformation of the interphase/interface region. Very low G_c increase observed.

mode (b): $\boldsymbol{N > N_e}$ ***and low surface density***, $\boldsymbol{\sigma}$. The "connector chain" blocks are longer than entanglement length, N_e, but grafting density, σ, is low. The following is observed:

- maximum stress at the interface is lower than the yield stress;
- no significant plastic deformation;
- block copolymer chains fail by scission close to their mid-point;
- values of G_c are low.

mode (c): $\boldsymbol{N > N_e}$ ***and surface density***, $\boldsymbol{\sigma}$, ***just above*** $\boldsymbol{\Sigma^*}$. The following is observed:

- stress at the interface very close (just above) to the yield stress;
- stress at the interface is high enough to initiate a narrow craze locally in the material, exhibiting lower craze formation stress, σ_{craze};
- most of the interface breaks by scission of fibrils of block copolymer chains close to their midpoint; and
- increase in G_c is observed due to high σ and narrow craze formation in polymer (A).

mode (d): $\boldsymbol{(N \cong N_{\mathrm{OPT}}) > N_e}$, ***and*** $\boldsymbol{\sigma > \Sigma^*}$ ***and*** $\boldsymbol{\sigma \cong \sigma_{\mathrm{OPT}}}$. The length and surface density of "connector molecules" is high and near optimum. The following is observed:

- the stress at the interface is high enough to create craze ($\sigma_i > \sigma_{\text{craze}}$);
- the craze in the form of fibrils and cross-ties (see Figure 5) is stretched, and strands at the crack tip are broken;
- individual chains in the fibrils are extracted by pull-out; and
- cross-ties between fibrils transfer part of the stress to the neighbouring fibril. Very high G_c is observed due

to significant plastic deformation and stress dissipation within the craze zone.

The Maximum Interface Reinforcement in Relation to Graft Surface Density and the Length of Graft Molecules

The maximum surface density of graft molecules that can be effectively attached to the substrate surface is inversely proportional to the length of grafted chains measured by their degree of polymerisation, N. Norton *et al.* [16] and Sha *et al.* [10] verified the above in their work on the mechanism of reinforcement of the interface between an epoxy substrate, and surface-grafted carboxylic acid-terminated, deuterated polystyrene chains (dPS-COOH) of varying length ($N = 159$ to 1788). The COOH-terminated PS was reacted with the epoxy substrate containing excess (50% molar excess) of amine hardener (triethylenetetramine: TETA).

Any unattached dPS-COOH chains were removed by washing the cured substrate in an ultrasonic bath for 20 min followed by drying. FRES and neutron reflectometry were used for determining surface density of grafted chains and the structure of the interface.

The ensuing results from Norton *et al.* [16] are illustrated in Figure 9. Figure 9a illustrates the profile of surface density of connector molecules *versus* polymerisation index, N, of dPS-COOH in Norton *et al.* experiments [16]. It is shown that, as anticipated, the maximum surface density, σ, is inversely proportional to the length, N, of connector molecules.

With regards to the interface reinforcement *versus* the length of dPS-COOH chains it has been observed by both, Norton *et al.* [16] and Sha *et al.* [10] that a well-defined maximum is achieved when the length of grafted chains is in the vicinity of $N = 838-1000$.

The presence of the maximum at $N = 1000$ arises from the combination of the following factors:

1. the decrease in the maximum deliverable σ with the increase in N, and
2. the variation of the interface failure mechanism with increasing N.

The interfaces grafted with short graft molecules ($N < N_e$) fail through the chain pullout, as illustrated in Figures 3a and 7. As the length, N, increased up to approximately $N \cong 400$, a narrow craze can be formed. Due to the short chains length the craze is narrow in this domain and fails partially by chain disentanglement from the

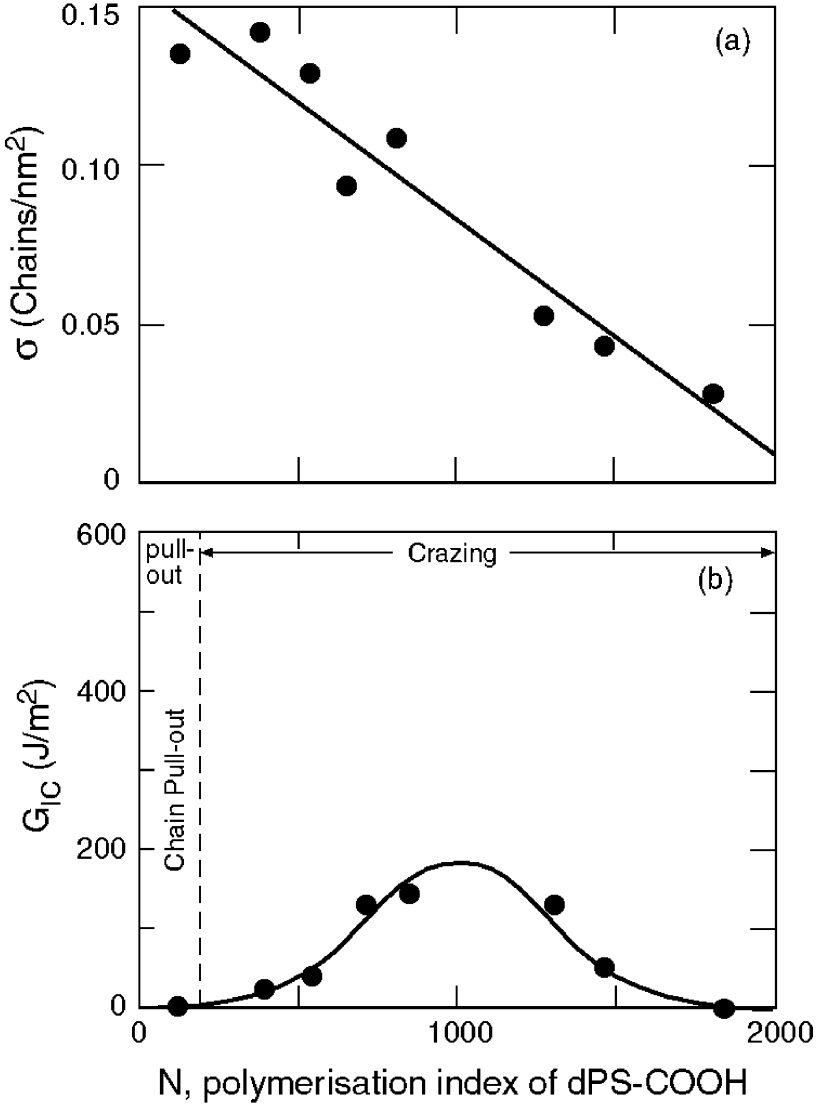

FIGURE 9 The influence of connector molecule length (measured by the degree of polymerisation, N) on the maximum surface density of grafted connector chains and interface reinforcement measured by fracture energy, G_{Ic}. (Reprinted with permission from *Macromolecules* [10], Copyright 1996, American Chemical Society): (a) surface density of connector chains *versus* the length ($L \propto N$) of PS-COOH) connector molecules, and (b) fracture toughness of PS/PS-COOH epoxy interface *versus* the length ($L \propto N$) of PS-COOH connector molecules.

craze (almost all dPS-COOH chains are found on the surface of the epoxy substrate).

For longer chains, at the connector length close to the optimum ($N = 830-1000$), a relatively high graft density can still be achieved (in the range of $\sigma = 0.05$ to 0.1 chains/nm^2). This, combined with good chain interpenetration into the PS substrate, leads to excellent interface reinforcement, leading to the formation of a wide craze ahead of the crack tip in the PS (see Figure 3d), and the fracture energy, G_{Ic}, reaching that of the bulk PS. At higher lengths of connector chains (e.g., $N \cong 1480$ and 1790), very low effective graft density is achievable, and the relatively few but well-anchored chains fail by narrow craze formation and chain scission ($N \cong 1480$), and for the longest chains ($N \cong 1790$) by scission prior to crazing.

FRACTURE OF INTERFACES INVOLVING GLASSY AND SEMICRYSTALLINE POLYMERS IN RELATION TO CRACK TIP PLASTICITY AND INTERFACIAL ZONE WIDTH

As discussed in models developed by Creton *et al.* [5] and Brown [6, 15], the fracture energy of systems involving glassy and semicrystalline polymers is typically controlled by the plastic deformation of the growing craze ahead of the propagating crack tip. The stress through most of the craze has a constant value, σ_{craze}, and is essentially a material constant for a given polymer.

According to the Dugdale model of fracture [14], where the crack propagates through a thin deformation zone such as craze, the fracture energy, G_c, is expressed as follows:

$$G_c = \delta_c \, \sigma_{\text{craze}}, \tag{4}$$

where δ_c is the critical crack opening displacement and σ_{craze} is the stress in the craze zone.

The critical crack opening displacement, δ_c, is related to the craze width, h (see Figure 4) through the following expression:

$$\delta_c = h(1 - v_f), \tag{5}$$

where v_f is the volume fraction of the fibrils.

Considering Equations (4) and (5), the following relationship is obtained:

$$G_c \sim \sigma_{\text{craze}} \, h(1 - v_f). \tag{6}$$

In a simplified form, Equation (6) can be presented as follows:

$$G_c \sim \sigma_{\text{craze}}\, h. \tag{7}$$

Equations (6) and (7) explain, that the fracture energy of the interface/interphase system is dependent on the craze stress and the width of the craze. Equation (7) is identical to that shown by Creton in [26].

When applied to bonding of two polymers, Equation (7) can be translated into fracture energy of the system, in which two bonded materials are separated by an interphase/interface system of width, h.

Schnell *et al.* [27] have investigated the influence of the interphase width on adhesion and fracture performance of interfaces in glassy polymers. Their experiments involved interfaces between immiscible polymers: polystyrene (PS) and poly (p-methylstyrene) (P_p MS), as well as between two miscible polymers (PS-PS system). In order to avoid the influence of the molecular weight of the polymer substrate on the interface performance, sufficiently high molecular weight ($M_n > 8M_c$) was used in all experiments. In this regime the fracture toughness of the bulk PS is no longer molecular-weight dependent.

Schnell *et al.* [27] commented that: (1) for interfaces between weakly immiscible polymers, the surface density of interpenetrating chains of the two homopolymers σ, and the entanglement length cannot be controlled independently, and (2) both of these parameters are contained in a single and controllable quantity, *i.e.*, interfacial width, h.

The width of the interface in Schnell *et al.* [27] experiments was controlled by varying the temperature (125 to 180°C), and time (5 to 95 h) of annealing. Neutron reflectivity allowed the nondestructive determination of interfacial width, h, within the range of 2 to 30 nm with an accuracy of ± 0.5 nm.

The outcome of experiments carried out for a broad range of MW combinations of PS and P_p MS, as illustrated in Figure 10, demonstrated that in adhesion of high molecular weight polymers ($N \gg N_e$) the width of the interface/interphase zone, h_I, appeared to be the main parameter controlling the fracture toughness of the interface between a given pair of polymers. The adhesion energy, G_c, as seen in this figure is well correlated with the width of the interface/interphase zone regardless of the molecular weight of PS and P_p MS used in experiments.

Another important observation from the Schnell *et al.* data [27] is that for the polymers used in their experiments adhesion becomes independent of the interface width for $h > 11$ nm. This value

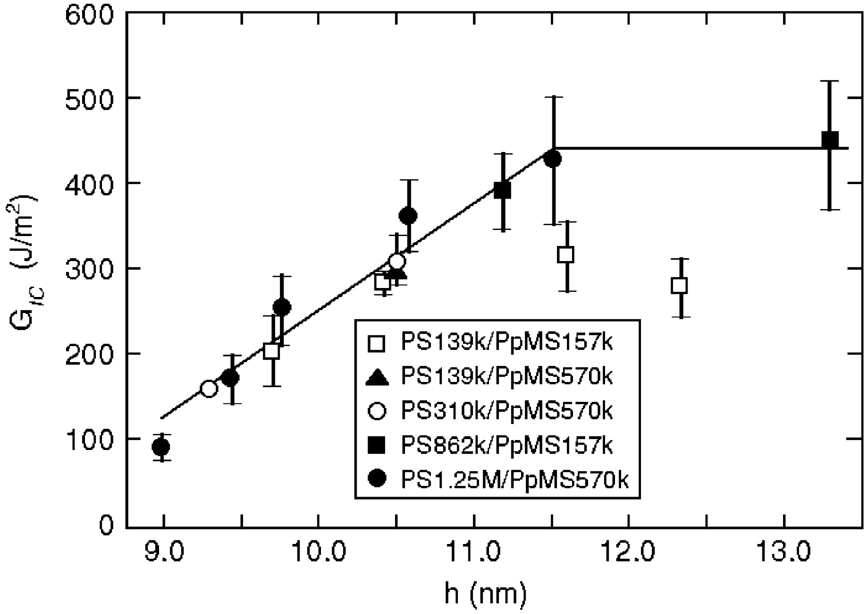

FIGURE 10 Fracture energy, G_{Ic}, of interface between PS/P$_P$MS substrates (various molecular weights of PS and P$_p$MS) as a function of the interface/interphase width (*h*). (Reprinted with permission from *Macromolecules* [27], Copyright 1996, American Chemical Society).

approximately corresponds to the average effective entanglement length in PS (9.3 nm).

The same authors conducted further experiments [28] in which poly(bromostyrene-styrene)–polystyrene (PBr-S-PS) was used for achieving interface widths lower than 9 nm. In Schnell *et al.* [28], data obtained by other researchers [29, 30] were used to further verify the hypothesis concerning the adhesion energy dependence on the interface width. The resultant data are illustrated in Figure 11, which supports the earlier observations and conclusions.

The dependence of interface fracture performance on the interface width falls, in accordance with Schnell *et al.* [28], into 3 distinct regimes (see solid circles in Figure 11).

Regime I:	low interface/interphase width ($h < 6$ nm), in which no increase of fracture energy is observed with the increasing interfacial width.
Regime II:	$6 < h < 11$ nm characterised by a steep increase in fracture toughness.

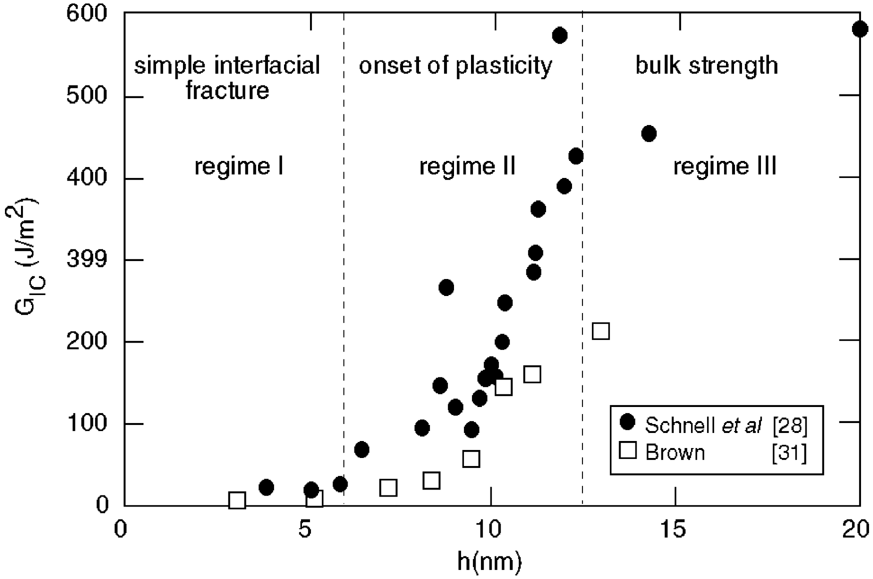

FIGURE 11 Fracture energy, G_{Ic}, of interfaces between various polymers (PS/P$_p$MS; PS/PBrS and PS/PMMA) as a function of the interface/interphase width (h). (Reprinted with permission from *Macromolecules* [28, 32], Copyright 1996, American Chemical Society).

In this regime the polymer chains on either side of the interface/interphase zone begin to form mechanically effective entanglements, and a plastic deformation zone (craze) is formed ahead of the crack tip. The chain scission inside the plastic zone becomes the dominant failure mode with increasing interface width, resulting in a steep increase in G_c.

Regime III: $h \geq 12\,\text{nm}$, characterised by fracture toughness approaching that of the bulk polymer. At this level of interfacial zone width, the interdiffusing polymer chains form entanglements as effective as the adjacent bulk phase polymer.

It has been noted by Schnell *et al.* [28] that:

(1) the interface/interphase zone width in this regime roughly equals the entanglement length of PS (9.3 nm), and
(2) it is not anticipated that the above will hold for lower molecular weight systems, where G_c will be a

> function of a combination of interfacial zone width and molecular weight.

A discrepancy is, however, revealed between the above suggestion of universality of relationship between G_{Ic} and interface width, and the results of further analysis of earlier [10, 16] and the most recent works [30–35] on interface reinforcement and its relation to the interface width. The ensuing discussion below appears to suggest that the mechanism of phenomena involving interaction of macromolecular chains in the narrow interfacial zone may be significantly more complex than that suggested by Schnell *et al.* [27, 28] above.

Brown [32] has presented an interesting insight into this issue. He has analysed the relationship between the width of the interface between polymers and its toughness by comparing experimental results with those calculated using the following model expressing interface fracture toughness, G_{Ic}, as a function of interacting materials properties and the relative interface width, h_r:

$$G_c = \frac{A}{\ln\left(\left\{1 - \left[\frac{1.2\sigma_d}{\Sigma(h_r)f_b}\right]^2\right\}^{-1}\right)}. \tag{8}$$

In Equation (8), A is a constant, σ_d is the craze stress, f_b is the force to break a chain, and $h_r = h_I/L_e$, where L_e is the mean distance between entanglements along a chain (tube diameter).

The model proposed by Brown [32] is based on a well-verified model of toughness of the interface between two materials, A and B, *versus* known interface profile represented by the following function:

$$\phi_A(z) = \frac{1}{2}(1 + \tanh(2z/a_I)), \tag{9}$$
$$\phi_B = 1 - \Phi_A,$$

where $\phi_A(z)$ is the volume fraction of polymer A at a position, z, relative to the center of the interface and the interface, width, a_{I}, is given by

$$a_I = \frac{2b}{\sqrt{6_{\chi AB}}}. \tag{10}$$

In Equation (10), b is the statistical segment length and χ is the Flory-Huggins segment-segment interaction parameter.

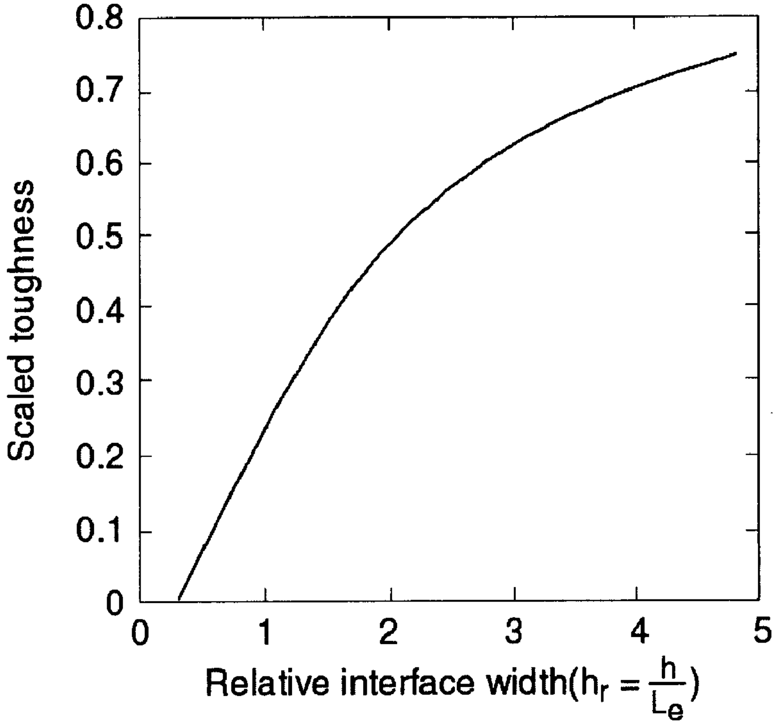

FIGURE 12 Fracture toughness of interface in relation to relative interface width, h_r, calculated using Eq. (8). (Reprinted with permission from *Macromolecules* [32], Copyright 1996, American Chemical Society).

The graphical solution of Equation (8) is presented in Figure 12, which presents the relative fracture toughness *versus* relative interface width. Brown's experimental results for the PS/PMMA interface are illustrated in Figure 14 by open squares.

It is shown by Brown through the comparison of the above experimental results with those calculated by Equation (8) that the model significantly over-predicts fracture toughness for interfaces of width less than approximately twice the distance between chain entanglements, but is correct for $h_r \geq 2$.

Brown has offered the following significant conclusions based on his theoretical and experimental work on PS/PMMA interface toughness.

1. At the interface width equal to or below the entanglement length, the measured toughness is significantly less than predicted.

2. The interface toughness remains low until the interface width is longer than the mean entanglement spacing, and then reaches maximum at the width of probably about 3 times the entanglement length.
3. The assumptions that chain entanglement density remains constant through the thickness of interface and that the probability of a chain passing through the interface can be described just by volume fraction appear to be incorrect.

Conclusions (1) and (2) above are additionally supported by a set of reinterpreted data of Sha *et al.* [10] and Norton *et al.* [16] concerning the reinforcement of interface between PS and epoxy substrate surface-grafted with dPS-COOH molecules of varying length; $N = 160$ to 1790. Their original results can be reinterpreted by relating the length of connector molecules, N, to the entanglement length of polystyrene

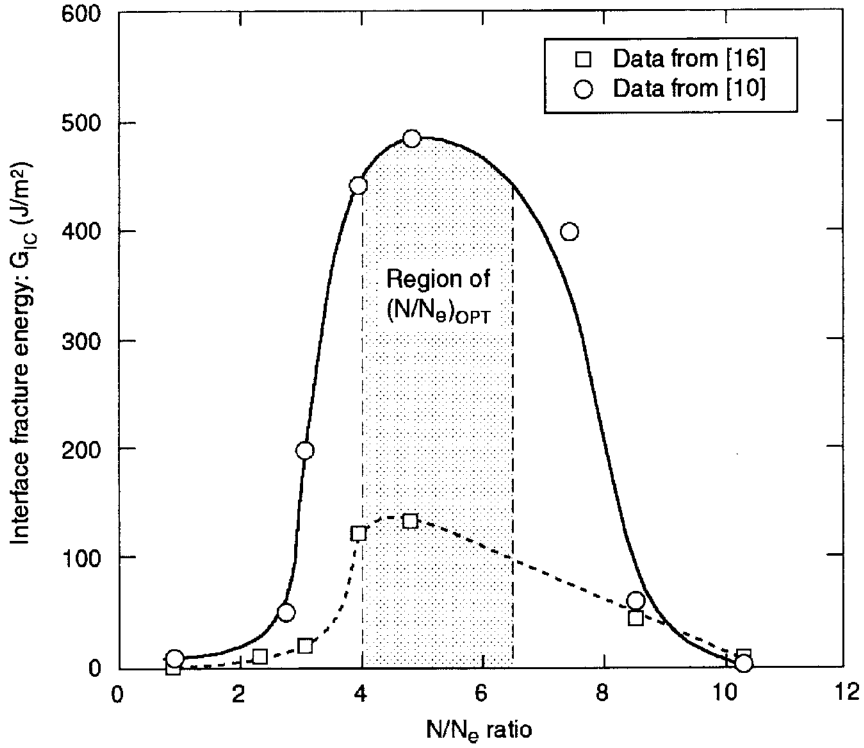

FIGURE 13 Interface fracture toughness, G_{Ic}, as a function of relative length of connector chains: N/N_e (reinterpreted data from [10] and [16]).

($N_e = 173$ [10]) and further relating this parameter (N/N_e) to the fracture toughness of the interface.

Figure 13 graphically illustrates this relationship. It is seen from this figure that the appreciable interface reinforcement by surface-grafted connector chains is observed in the systems analysed in Sha *et al.* [10] and Norton *et al.* [16] only when the length of connector chains, N/N_e, is at least 2.5 to 3 times as great as the entanglement length of PS ($= 173$), whilst the maximum clearly appears to be in the range of $N/N_e \cong 4$ to 6.5.

Benkoski *et al.* [31] have provided significant new insight (albeit differing from the earlier arguments presented in the proceeding discussion of this section) into the influence of the interface structure and width on interface reinforcement.

Their work addressed the mechanism of the PS-PVP interface reinforcement through the use of random copolymers: poly(d-styrene-r-2-vinylpyridine) [dPS_f-r-PVP_{f-1}] with varying fraction ($f = 0.21$ to 0.8) of styrene. These were synthesised to approximately 10% completion to avoid composition drift. It was observed that the maximum interface toughness achieved, $G_{Ic} = 55\,J/m^2$, was 3 times less than that observed by Dai *et al.* [34, 35] for similar systems involving composition-drifted PS-r-PVP copolymer.

In order to investigate and explain the reasons for this difference, an artificial composition drift was introduced by Benkoski *et al.* [3] by blending two or more of the compositionally-uniform copolymers. In the interface zone, these copolymers form distinct layers exhibiting composition drift between adjacent interfaces. The blends used in experiments allowed varying of this artificial composition drift in the range of $\Delta f = 0.2$ to 0.6.

The ensuing reduction in the enthalpy of mixing of two blend components exhibiting different mer fraction, f_i, of a given component in the copolymer, is represented as an effective χ parameter,

$$\chi_{\text{eff}} = \chi(f_1 - f_2)^2. \tag{11}$$

Combining Equations (10) and (11) leads to the expression

$$h_I = \frac{2b}{\Delta f_i \sqrt{6\chi}}, \tag{12a}$$

which explains that the interface compatibilised with the copolymer blend exhibiting the largest composition gap ($\Delta f_{\max}$) will be narrowest.

Experimental data of Benkoski *et al.* (see Figure 8 in [31]) demonstrated that the interface toughness, G_{Ic}, increases exponentially

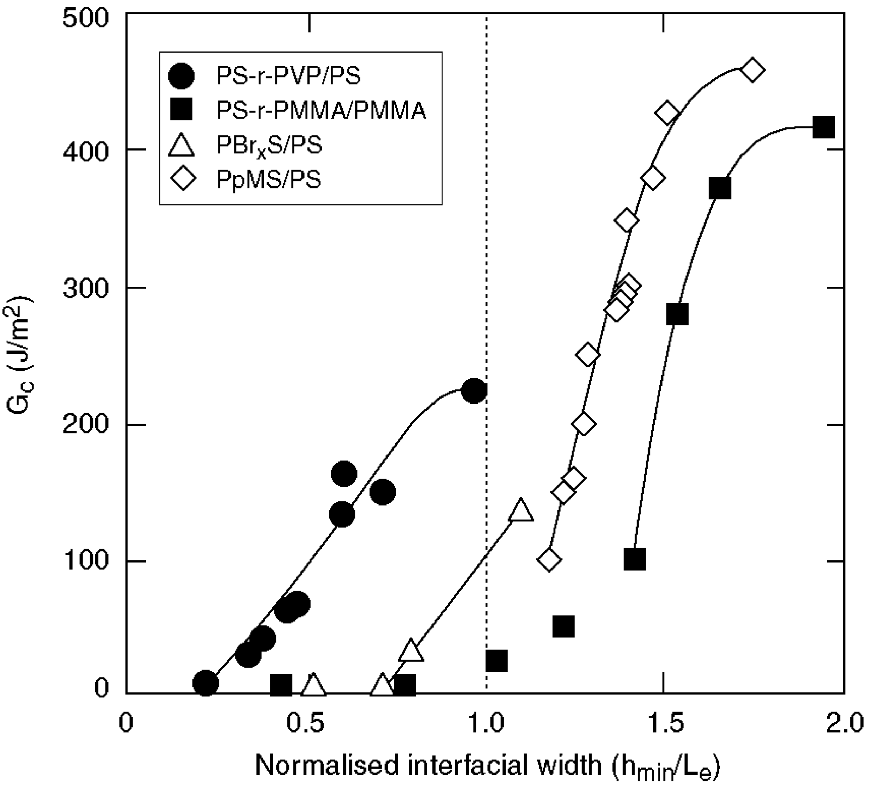

FIGURE 14 Interfacial fracture toughness *versus* normalised interface width (h/L_e). Note that none of the data sets discussed in the section below and represented in this figure seem to correlate well after normalization. Circles represent the PS-r-PVP/PS interfaces from Benkoski *et al.* [31] and Dai *et al.* [35], open squares represent PS-r-PMMA/PMMA data from Brown [32], full squares represent P$_p$MS/PS data from Schnell *et al.* [27], and triangles represent PBr$_x$S/PS data from Schnell *et al.* [28]. (Benkoski, J. J., Fredrickson, G. H., and Kramer, E. J. "Effects of composition drift on the effectiveness of random copolymer reinforcement at polymer-polymer interfaces," *Journal of Polymer Science: Part B: Polymer Physics*, Copyright 2001, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

(with the power of 2) with decreasing $(\Delta f_{\max})$. It was also observed [in line with Equation (12a)] that the fracture toughness increases with increasing interface width.

A significant peculiarity was also noted: it was observed that the onset of crazing at the dPS$_f$-r-PVP$_{f\text{-}1}$ interface occurred at $G_{Ic} =$

10 J/m^2 at the interface width, $h = 2.1$ nm. This value is well below the distance between entanglements $L_e = 7.65$ nm for PS.

According to the current belief (see the above discussion based on previous research [10, 16, 27, 28, 32]), an effective reinforcement through bridging entanglements in the interface may be anticipated only when the interface width, $h_{\min}$, is greater than the distance between entanglements, *i.e.*, for:

$$h_{\min}/L_e \geq 1. \tag{12b}$$

Benkoski *et al.* [31] analysed a number of sets of experimental data on interfaces reinforced with di-block or random copolymers [27, 28, 31, 32, 35]. The ensuing results relating interface fracture energy, G_{Ic}, to $(h_{\min}/L_e)$ are illustrated in Figure 14.

In this figure, it is clearly seen that:

- the lack of correlation between G_{Ic} *versus* $(h_{\min}/L_e)$ for different systems suggests that the formation of entanglements in the interface zone is not the sole reason for the development of fracture toughness in the systems involving copolymers as interface compatibilisers.
- polymer interfaces compatibilised by dPS$_f$-r-PVP$_{f\text{-}1}$ random copolymers with the composition drift exhibit significant increase in fracture toughness. For the systems investigated in Benkoski *et al.* [31] this occurs at interface width approximately equal to 1/3 of the entanglement length of the adjacent polymer, *i.e.*, PS.

The above observations and the fact that an interface as narrow as 2.1 nm is shown to be able to sustain a craze led Benkoski *et al.* to the following suggestions.

1. The chemistry and structure of random copolymers may be responsible for their effectiveness in interface reinforcement.
2. The conformation of a random copolymer loop may lead to significantly increased friction over that of a di-block copolymer during entangled chain loop pullout. This is due to the fact that both ends of a random copolymer loop must be simultaneously dragged through its surroundings.
3. The relationship “G_{Ic} *versus* interface width” does not have the previously suggested universality.

FRACTURE OF INTERFACES BETWEEN SOLIDS GRAFTED WITH CONNECTOR CHAINS INTERPENETRATING INTO CROSSLINKED ELASTOMERS

The mechanism of enhancement of adhesion between elastomers and surface-grafted solids or that between two cross-linked elastomers through interpenetrating connector molecules is similar to that relevant to glassy polymers. It needs to be noted, however, that the cohesive strength of elastomers is typically an order of magnitude (or more) less than that of glassy polymers. Thus, a significantly lower level of interfacial stress is required for initiating and propagating the fracture along the interface involving elastomers. Consequently, molecular connections that would provide a relatively low stress transfer capability to the interface, and thus insufficient for crazing glassy polymers interface would be, on the other hand, adequate for initiating an interfacial crack along the elastomer interface. The latter is usually accompanied by significant viscoelastic deformation in a broad region around the crack tip. This results in high viscoelastic deformation losses and, hence, dissipation of substantial amounts of energy translated into additional increase in fracture energy of interfaces between crosslinked elastomers or rigid substrates and elastomers.

In addition to the above, viscoelastic losses in elastomers are temperature- and rate-dependent factors that contribute to the overall crack tip energy losses.

Hence, the discussion in this section is restricted to very low crack propagation rates and other factors that minimise contributions of far field viscoelastic losses to the fracture energy of elastomers.

It was de Gennes [18] who first analysed the concept of flexible connector molecules anchored irreversibly at the substrate surface and entangled with the elastomeric adhesive layer. Subject to sufficient length ($N > N_e$) and other contact conditions, grafted connector molecules interpenetrate the adjacent elastomeric adhesive and, subsequently, assist with the enhanced mechanical coupling of the elastomer to the substrate. The advancing fracture crack front stretches the molecular chains, which leads to their cohesive fracture, or allows for the extraction of the chains (see Figure 2). The energy required to stretch and extract molecular chains to the total displacement is irreversibly lost. This energy is significantly greater than the thermodynamic energy required to fracture brittle materials according to the classical Griffith's equation.

In the simplest case of van der Waals interactions (we use here an example of connector chains and adhesive polymer being identical) in the macromolecular chain/elastomer system, the fracture energy associated with deformation and extraction of connector chains is

$$G = 2\gamma\ (1 + \sigma N), \tag{13}$$

where γ is the surface energy of the polymer and that of connector chains and σ is the surface density of connector chains.

In the case of dissimilar chemistry of the connector molecules and adhesive polymer, the fracture energy related to the deformation and extraction of connector molecular chains is

$$G = W(1 + \sigma N), \tag{14}$$

where W is the thermodynamic energy of adhesion.

It has been shown by experiments carried out by various researchers [19, 20] that surface-grafted and interpenetrating molecular chains significantly enhance adhesion between solid substrates and elastomers.

The experiments discussed in Léger *et al.* [19] and Brochard–Wyart *et al.* [20] involved grafting a controlled surface density of "molecular brushes" and determining the increase of the normalized fracture energy (G) through peel or JKR (Johnson-Kendall-Roberts) tests, or normalized tensile bond strength.

Figure 15a illustrates the experimental results obtained on the influence of surface density of two types of polydimethylsiloxane (PDMS) connector molecules on the enhancement of adhesion of a PDMS elastomer to a silicon wafer [19].

All the interactions present in the case illustrated in Figure 15a are of the van der Waals type only, with the fracture energy increase resulting from the disentanglement and extraction of molecular chains of connector molecules from the cross-linked matrix of the PDMS elastomer. On this basis, considering the surface energy, γ, of the interacting materials (*i.e.*, PDMS elastomer and that of surface-grafted PDMS connector molecules being equal), surface density, σ of connector molecules and N, the number of monomers in the macromolecular chains of connector molecules, the following expression for fracture energy is obtained [21]:

$$G - W \cong \gamma N\sigma. \tag{15}$$

De Gennes [23] determined that above a certain critical surface density of grafted molecules, σ_{OPT}, the full penetration of surface-grafted macromolecular chains into the network of an adjacent polymer could

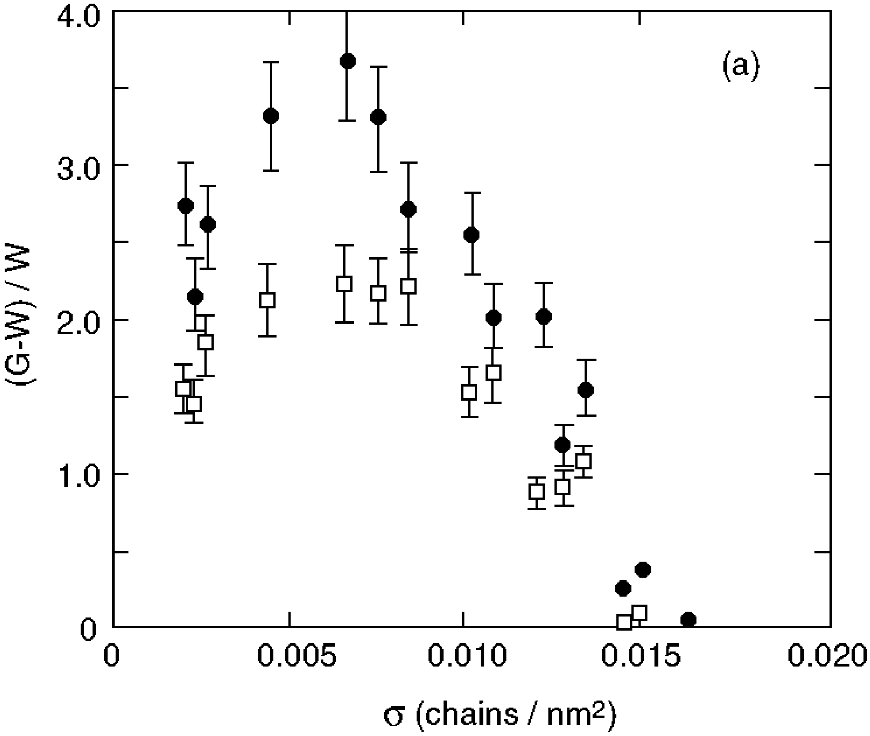

FIGURE 15 (a) Normalized fracture energy: $(G-W)/W$ for the molecular brush/elastomeric adhesive interphase interacting through van der Waals interactions only, as a function of the surface density, σ, for two PDMS elastomers in contact with silicon wafers grafted with irreversibly adsorbed chains. W is the thermodynamic work of adhesion, $W = 2\gamma$, with γ the surface energy of PDMS $\gamma = 21.6\,\mathrm{mJ/m^2}$ at 25°C. The *filled symbols* correspond to a molecular weight between cross-links in the elastomer of $M_c = 24.2\,\mathrm{kg\,mol^{-1}}$, while $M_c = 10.2\,\mathrm{kg\,mol^{-1}}$ for the *open symbols*. The fracture energy, G, has been measured by peel tests performed at the rate of 0.17 mm/s. The molecular weight of the surface-grafted chains is $M_w = 2.42\,\mathrm{kg\,mol^{-1}}$. (From L. Léger, E. Raphael, and H. Hervet, "Surface anchored polymer chains: Their role in adhesion and friction." *Polymers in Confined Environments, Advances in Polymer Science*, **138**, 185, Figure 11, 1999. Copyright © 1999 Springer).

not be achieved. Figure 15 (adopted from Léger *et al.* [19]) illustrates the behaviour of graft chemicals, when adsorbed from solution of the carrier liquid at varying concentrations. The most favourable conditions for the provision of maximised adhesion exist when single macromolecular chains, appropriately separated, are adsorbed and

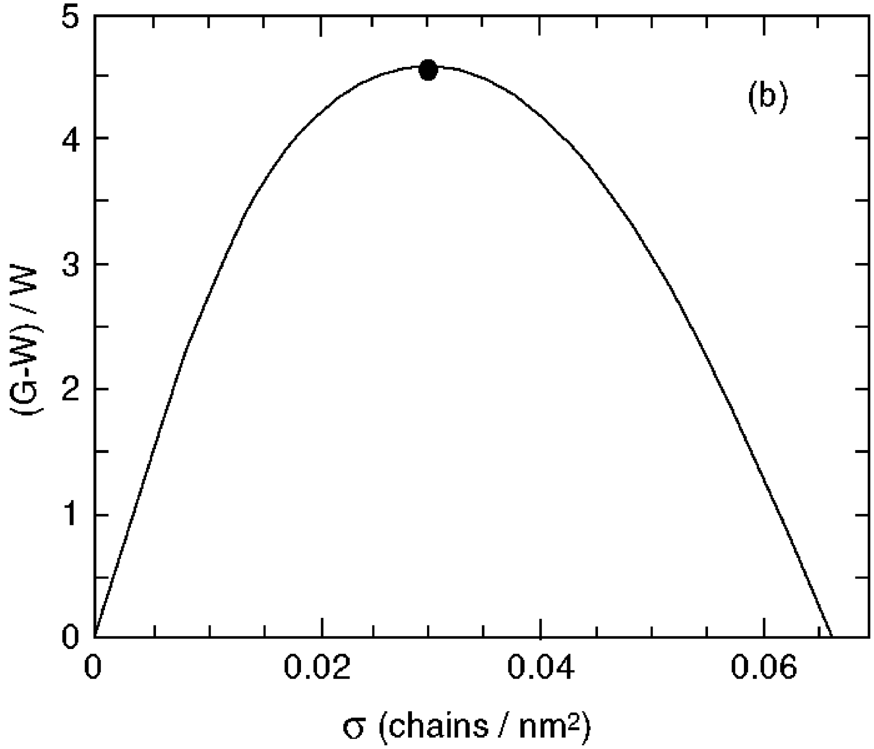

FIGURE 15 (b) Numerical solution of Eq.(17) regarding the enhancement of adhesion measured by the increase in normalized fracture energy: $(G-W)/W$ for connector molecules characterized by $N = 743$ interacting with cross-linked PDMS elastomer with $N_c = 230$. (From L. Léger, E. Raphael, and H. Hervet, "Surface anchored polymer chains: Their role in adhesion and friction." *Polymers in Confined Environments, Advances in Polymer Science*, **138**, 185, Figure 14, 1999. Copyright © 1999 Springer).

grafted at the polymer surface. The increase of concentration leads to clustering of entangled multiple chains up to the point when excessive amount leads to the creation of a new surface which lacks the ability to interpenetrate into an adjacent adhesive.

Therefore, Equation (15) holds for the local volume of grafted chains, $\Phi \ll 1$, or $\Phi \ll N_c/N^{3/2}$($\Phi = 1.0$ for polymer melts or 100% solids, or, alternatively, $0 < \Phi < 1.0$ for dilute solutions). For $\Phi > N_c/N^{3/2}$, the connector molecules are less efficient in interacting with the cross-linked network of the host polymer due to the reduction in the extent of entanglement. For this condition ($\Phi > N_c/N^{3/2}$) then [23], Equation (15) is replaced by Equation (16):

$$G - W \cong \gamma N \sigma (1 - \Phi). \tag{16}$$

For the boundary condition $\Phi = \sigma^{2/3} N_c^{\ 1/3}$, Equation (16) becomes:

$$G - W \cong \gamma N \sigma (1 - \sigma^{2/3} N_c^{\ 1/3}). \tag{17}$$

The following is seen from Equation (17):

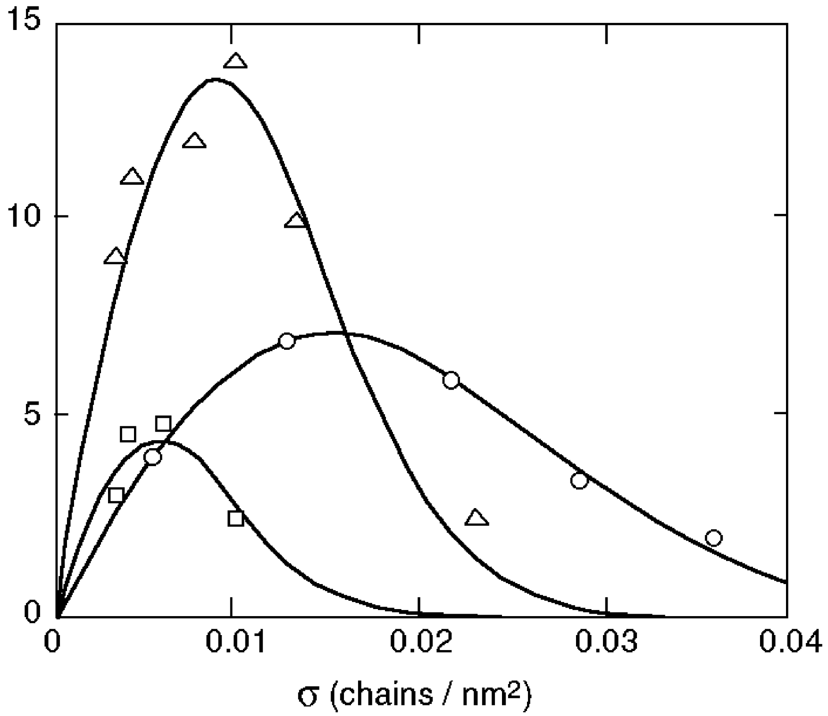

FIGURE 16 Normalized fracture energy: $(G-W)/W$ as a function of the surface density of grafted connector chains, σ, measured by the JKR test at a fracture propagation rate of 0.1 mm/s, for: □ a grafted connector chain with $M_w = 55\,\mathrm{kg\,mol^{-1}}$ and $M_c = 17\,\mathrm{kg\,mol^{-1}}$; ○ an irreversibly adsorbed PDMS layer with $M_w = 57\,\mathrm{kg\,mol^{-1}}$ and $M_c = 13\,\mathrm{kg\,mol^{-1}}$; and △ an irreversibly adsorbed PDMS layer with $M_w = 140\,\mathrm{kg\,mol^{-1}}$ and $M_c = 13\,\mathrm{kg\,mol^{-1}}$. The full lines are only guides for locating the optimum. (From L. Léger, E. Raphael, and H. Hervert, Surface anchored polymer chains: Their role in adhesion and friction. *Polymers in Confined Environments, Advances in Polymer Science*, **138**, 185, Figure 17, 1999. Copyright © 1999 Springer).

1. For $\sigma > N_c{}^{-1/2}$, the connector molecules completely separate from the network and G reduces to W.
2. The optimum adhesion occurs for:

$$\sigma_{\mathrm{OPT}} \cong 0.465\, N_c^{-1/2}. \tag{18}$$

3. The corresponding value of the optimum fracture energy, G_{OPT}, is:

$$G_{\mathrm{OPT}} - W = 0.186\gamma \frac{N}{N_c^{1/2}}. \tag{19}$$

Figure 15b illustrates the results of Equation (17) solved numerically for $N = 743$ and $N_c = 230$, and $\gamma = 21.6\,\mathrm{mJ/m^2}$ at 25°C [19].

Another set of experiments (as carried out by Léger *et al.* [19]) yielding similar quantitative results are illustrated in Figure 16. In this case, connector molecules exhibiting $N = 743$ are interacting with PDMS polymer characterized by $N_c = 230$, and $N = 770$ with $N_c = 176$.

It is clearly seen from the graphs presented in Figures 15 and 16 that there is a distinct optimum (σ_{OPT}) in the surface density (σ) of

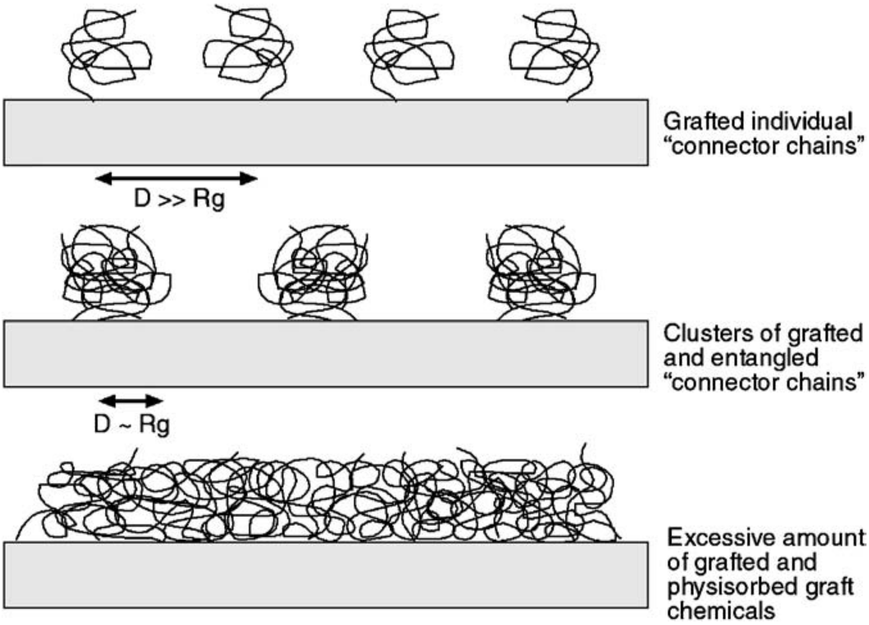

FIGURE 17 Schematic representation of behaviour of graft molecules adsorbed onto the substrate surface from various concentration in the carrier liquid (Adapted from Tang, I. and Szleifer, H., *Europhys. Lett.* **28**(1), 1994).

interpenetrating connector molecules which has to be achieved in order to maximize the adhesion between a surface-modified substrate and the adhering polymeric material, such as an adhesive, or matrix in the case of composite materials.

As theoretically determined by de Gennes [18, 23], Léger *et al.* [19], and Brochard–Wyart [13], and as seen from Figures 15–17, a gradual increase in the bond strength occurs with the increasing surface density of grafted molecules for $\sigma < \sigma_{\mathrm{OPT}}$, as a result of entanglement of surface-grafted macromolecular chains with the adjacent polymer, in good agreement with Equation (17).

For the surface density of grafted macromolecular chains exceeding σ_{OPT}, only partial penetration into the adjacent adhesive or matrix occurs. It may be considered that the following may be simultaneously occurring: (1) only a fraction of grafted chains fully penetrate into adjacent polymer, (2) fractional length penetration of some chains occurs, and (3) some chain ends are rejected by the network of the adjacent polymer.

This leads to the gradual decrease of bond strength or fracture energy to the level equal to that of an unmodified substrate when $\sigma > N_c^{-1/2}$.

FRACTURE OF INTERPHASES INVOLVING CONNECTOR MOLECULES GRAFTED TO THE SUBSTRATE SURFACE AND CHEMICALLY BONDED TO THE ADJACENT POLYMER

Fracture of Individual Macromolecular Chains

The microscopic aspects of the fracture of individual macromolecular chains, as applicable to connector molecules or, alternatively, to a cross-linked polymer, were first analyzed by Lake and Thomas [17]. Considering the mean radius of the macromolecular tube, $R_o = aN_c^{1/2}$, where a is the statistical size of the monomer segment, and N_c is the number of monomers constituting a macromolecular chain of the cross-linked polymer, the chain density, ν, per unit surface of ideal fracture area is:

$$\nu = \frac{1}{N_c^{1/2} a^2}. \tag{20}$$

Each molecular chain exposed to the fracture propagation plane behaves similarly to a small spring, which is totally deformed at fracture. The theory of Lake and Thomas [17] assumes that: (1) all bonds in the molecular chain must be stressed to the limit of their strength prior to a break of chemical bonds; and (2) *all* bonds in the chain are subsequently breaking. Therefore, the total energy, G_c, required for the macromolecular chain fracture is:

$$G_c = N_c U_c, \tag{21}$$

where U_c is the energy required to break an individual covalent bond in the chain.

Thus, the fracture energy involving v chains in the fracture plane is:

$$G = v\, NU = \frac{U}{N^{1/2} a^2}. \tag{22}$$

Fracture of Two Polymeric Surfaces Connected by an Array of Chemically Bonded Connector Molecules

According to Lake and Thomas [17], the fracture energy, G, of two-plane polymeric surfaces connected by v macromolecular chains is expressed by Equation (22).

Raphaël and de Gennes [24] have determined that the adhesion enhancement provided by surface-grafted and chemically bonded macromolecular chains is expressed as

$$G_b = W_a + W_b N\sigma, \tag{23}$$

where N is the polymerization degree of connector molecules, W_a is a reversible energy of adhesion between the bare (ungrafted substrate) and the adjacent polymer (due to van der Waals forces only), and W_b describes the energy required to disrupt a dense array of chemical bonds crossing the plane between adhering surfaces:

$$W_b = \frac{U_b}{a^2}, \tag{24}$$

where U_b is the energy of a bond occupying an area of a^2.

The adhesion enhancement by interpenetrating molecular chains (G_i) has been described by Equation (14). A comparison of Equations (23) and (14) thus provides a qualitative estimate of gains (ΔG_b) offered by chemically bonded (G_b) *versus* interpenetrated (G_i) molecular chains [25], *i.e.*,

$$\Delta G_b \sim \frac{W_b}{W_a} \Delta G_i. \tag{25}$$

Brochard–Wyart and de Gennes [25] have also proposed a criterion for a transition from the interfacial failure mode to cohesive failure, as

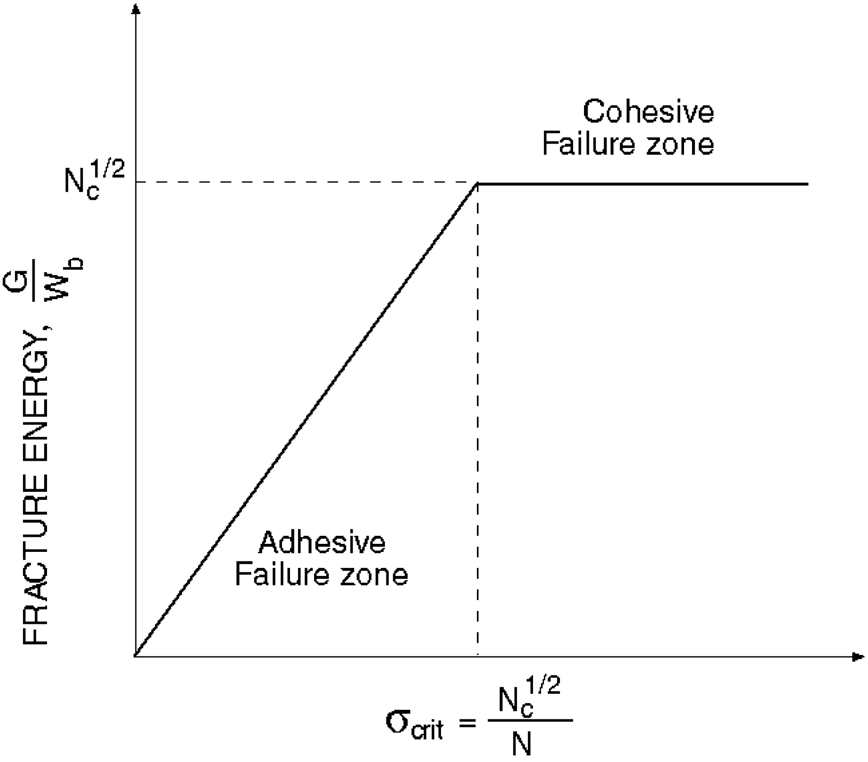

FIGURE 18 Fracture energy *versus* surface graft density, σ, in the case of grafted and chemically bonded macromolecular connector chains [25]. (Copyright (1996) from Brochard–Wyart, F. and de Gennes, P. G., *The Journal of Adhesion* 57, 21–30 (1996). Reproduced by permission of Taylor & Francis, Inc., http://www.routledge-ny.com).

illustrated in Figure 18, for interfaces involving grafted macromolecular connector chains characterized by N, which are chemically bonded to an adhesive characterized by N_c.

The "cut-off" point in terms of critical surface density, σ_{CRIT}, of connector molecules at which the fracture energy, G_c, of the adjacent polymer (adhesive) becomes smaller than that of the array of grafted connector chains, G_b, is proposed to be:

$$\sigma_{\mathrm{CRIT}} = \frac{N_c^{1/2}}{N}. \tag{26}$$

It has been concluded by Brochard–Wyart and de Gennes, based on the findings illustrated in Figure 18, that graft densities above $\sigma > \sigma_{\mathrm{CRIT}}$

would not offer any benefits in terms of further improvement of bond performance. As admitted by Brochard–Wyart and de Gennes [25], the validity of criterion in Equation (26), as based on the "transition fracture energy," has been questioned by a referee in whose opinion the criterion would be more representative of the "transition stress." The same authors suggested, however, that for their systems the structure of the relation between applied stress and G is the same for both modes: thus, at their scaling level, they were inclined to think that the failure mode switching was reasonably described by Equation (26).

Whatever the outcome of the discussion on the definition and quantitative measure of the transition energy or transition stress, as expressed by Equation (26), the following conclusions are clear from the discussion encompassed in this and the preceding section.

1. At the interfaces reinforced by surface-grafted macromolecular connector chains which are chemically bonded to an adjacent elastomer, the following applies:
   - an increase in graft density from zero to a certain cut-off value (σ_{CRIT}) (as expressed by Equation (26)) results in a linear increase of interface fracture energy in agreement with Equation (22), and
   - for graft densities ($\sigma \geq \sigma_{\mathrm{CRIT}}$) no further increase of joint fracture energy can be anticipated.
2. At the interfaces reinforced by surface-grafted connector chains which are interpenetrating into an adjacent elastomer, a distinct maximum/optimum (σ_{OPT}) is recorded for joint fracture energy *versus* graft density, as expressed by Equation (18). An increase of σ above σ_{OPT} results in the decrease of fracture energy enhancement due to decreasing efficiency of interdigitated macromolecular chains. The latter has been discussed in detail by de Gennes [23] and Léger *et al.* [19], who have shown that for $\sigma > N_c^{-1/2}$, the molecular brush segregates completely from the network of the adjacent polymer, and the adhesion energy, G_o, reduces to W (see our earlier discussion regarding Equation (17)).

CONCLUSIONS

1. Adhesion and fracture performance of interfaces between polymers can be effectively improved and controlled by suitable macro-molecular "connector molecules."
2. "Connector molecules" grafted onto solid polymer surfaces can interact with adjacent materials (such as adhesives, coatings,

matrix materials, and others) through either one or other combination of the following mechanisms:

   (a) interpenetration into the adjacent polymeric phase, and
   (b) chemical reaction/cross-linking with the adjacent material.

3. The effectiveness of the interface reinforcement by surface-grafted connector molecules depends on the following factors:

   (a) surface density of grafted molecules,
   (b) length of individual chains of grafted molecules, and
   (c) optimum surface density in relation to the length of connector molecules.

4. At the interfaces reinforced by surface-grafted connector chains which are inter-penetrating into an adjacent elastomer, a distinct maximum/optimum (σ_{OPT}) is recorded for joint fracture energy *versus* graft density, as expressed by Equation (18). An increase of σ above σ_{OPT} results in the decrease of fracture energy enhancement due to decreasing efficiency of interdigitated macromolecular chains. The latter has been discussed in detail by de Gennes [23] and Léger *et al.* [19], who have shown that, for $\sigma > \mathrm{N_c}^{-1/2}$, the molecular brush segregates completely from the network of the adjacent polymer, and the adhesion energy, G_o, reduces to W (see our earlier discussion regarding Equation (17)).
5. At the interfaces reinforced by surface-grafted macromolecular connector chains that are chemically bonded with the adjacent elastomer, the following applies:

   (a) an increase in graft density from zero to a certain cut-off value (σ_{CRIT}) (as expressed by Equation (26)) results in a linear increase of interface fracture energy in agreement with Equation (25), and
   (b) for graft densities ($\sigma \geq \sigma_{\mathrm{CRIT}}$) no further increase of joint fracture energy can be anticipated.

6. Sufficiently long ($N > N_e$) connector molecules, of appropriate surface density, provide the effect similar to that of cross-linking with the adjacent material due to the effective "knotting" of entangled molecules of graft chemicals with the chains of the adhering material.
7. The fracture energy of systems involving glassy and semi-crystalline polymers is typically controlled by the plastic deformation and subsequent failure of the growing craze around

the propagating crack tip. Consequently, the most effective "interphase/interface system" for maximising fracture performance and adhesion between such polymers and adjacent materials should comprise graft molecules capable of presenting/creating conditions for the craze formation in the "interphase/interface" zone.

8. The relationship "G_{Ic} *versus* interface width, h" is not universal.
9. The formation of entanglements in the interface zone is not the sole reason for the development of fracture toughness. This conclusion is supported by the following outcome of Benkoski *et al.* [31]:

   (a) the lack of correlation between G_{Ic} *versus* ($h_{\min}/L_e$) for different compatibilising systems (*e.g.*, di-block or random copolymers), and
   (b) the observation that in the dPS_f-r-$PVP_{f\text{-}1}$) system the craze is sustained at the interface width approximately equal to 1/3 of the entanglement length of PS.

10. The chemistry and structure of random copolymers may be responsible for their effectiveness in interface reinforcement over that of di-block copolymers. The above is supported by the following observations:

    (a) the composition drift in random copolymers leads to significant increase in fracture toughness in comparison with those without composition drift, and
    (b) the conformation of a random copolymer loop may lead to significantly increased friction over that of a di-block copolymer during entangled chain loop pullout. This is due to the fact that both ends of random copolymer loop must be simultaneously dragged through its surroundings.

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