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Communication

Contact fatigue behaviour of glassy polymers with improved toughness under fretting wear conditions

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Abstract

Semi-quantitative fatigue wear models have been largely derived in order to account for the wear resistance of polymers substrates sliding against rigid counterfaces which are insufficiently rough for the elastic limit of the polymer to be exceeded during micro-asperity deformation. Direct experimental evidence of such contact fatigue processes, however, are scarce: propagating cracks in polymers are difficult to detect on an asperity scale because of the elastic recovery. As a result, the exact nature of the contact damage micro-mechanisms (crack orientation, crack propagation rates, . . .) and the way they relate to the bulk material properties remain largely to be established.

In this investigation, contact fatigue processes within glassy amorphous polymers contacting smooth glass spheres have been studied under small amplitude oscillating micro-motions, i.e. fretting. Under such contact conditions, it was found possible to induce the early development of a crack network at a macroscopic scale without the complications arising from the extensive generation of wear debris at the contact interface. This approach has been applied to homologous polymer series differing by their toughness properties. Two kinds of systems were considered: (i) epoxy networks modified by antiplasticizing additives; (ii) copolymers of methylmethacrylate with either glutarimide or cyclohexylmaleimide moieties. Crack nucleation and propagation micro-mechanisms within these various polymer materials have been investigated from the resources of in situ contact visualisation during the fretting tests. From a detailed mechanical analysis of the local contact conditions, the relationships between the development of cracks and the toughness properties of the polymers have been established.

Keywords: Contact fatigue; Fretting wear; Epoxy; Toughness; Methylmethacrylate random copolymers

1. Introduction

Various semi-quantitative macroscopic fatigue wear models have been derived largely in order to account for the wear resistance of polymers substrates sliding against rigid counterfaces which are insufficiently rough for the elastic limit of the polymer to be exceeded during micro-asperity deformation [1–3]. These theoretical approaches were focused on the prediction of the macroscopic wear behaviour of tribological systems, but little attention was paid to the identification of the fatigue wear damage mechanisms and their relationships with the polymer bulk mechanical properties. Direct experimental evidence of contact fatigue processes, however, is scarce: propagating cracks in polymers are difficult to detect on a micro-asperity scale because of elastic recovery. As a result, the exact nature of the contact damage micro-mechanisms (brittle or fatigue failure) and the manner in which they relate to the fatigue properties of the bulk material remain largely unestablished. In a previous investigation [4], we have demonstrated that macroscopic fretting contacts, between glassy polymers and glass counterfaces, can be used as model single-asperity contacts simulating, on an observable scale, the damage micro-mechanisms which may be induced at the micro-asperity level in real contacts between rough surfaces. Through the use of fretting maps concepts [5,6], specific contact loading conditions can be selected which ensure that superficial fatigue cracking of the polymer substrate is the main induced damage. Using in situ contact visualisation, these failure processes can be monitored under a well-controlled contact stress environment which is an essential prerequisite for any attempt to correlate the contact damage with the bulk materials properties. Although the complex deformation conditions in the contact zone do not reproduce those which are addressed in 'conventional' mechanical testing, the relatively mild strain and strain rates encountered under fretting condition make it possible to establish some relationships between the

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observed cohesive wear damage processes and the bulk failure properties.

The present paper reports on a study of the contact fatigue behaviour of homologous series of glassy polymers which differed essentially by their fracture properties. This work is based upon extensive studies on the structure–property relationship of amorphous polymers which have been carried out in our laboratory over the past years (see for instance [7–9]). From these investigations, two kinds of polymer systems have been selected for the purpose of the current study: (i) methylmethacrylate-based random copolymers whose fracture toughness can be either increased or decreased by the selection of appropriate comonomers; (ii) epoxy resins modified by low molecular weight additives in order to improve the intrinsic low fracture toughness of these materials. The current value of these various polymeric systems is that they allow selective change of the fracture properties without any substantial consequent changes in the elastic and yield properties at room temperature. The main purpose of this work was therefore to determine the sensitivity of the contact cracking behaviour to the fracture toughness of the selected polymers.

2. Experimental details

2.1. Fretting rig

The contact fatigue behaviour of the materials was analysed under small amplitude oscillating micro-motions, i.e. fretting. Using a specific device mounted on a MTS 810 (Minneapolis, USA) testing system (Fig. 1), triangular shaped tangential displacements in the micrometer range (typically ±50 μm) were applied to the flat polymer specimens contacting smooth glass hemispheres with a 48 mm radius (R_a of the order of a few nanometers). Under the selected normal load, P (from 50 to 200 N), the diameter of the contact area (between 1 and 2 mm) was much larger (by a factor of 10 and more) than the magnitude of the imposed tangential displacement. Due to the reduced slip amplitude within the contact area, such fretting conditions have been shown to be a peculiarly relevant tool to investigate the generation of fatigue cracks at the scale of the macroscopic contact, without the complications arising from particle detachment and wear [4,10]. In addition to the continuous monitoring of the tangential load, Q, and imposed relative displacement, δ, the fretting device facilitated the in situ microscopic observation and recording of the contact area through the glass counterface. Crack initiation and propagation within the epoxy materials were monitored as a function of the number of cycles (up to 5×10^3). The low frequency of the imposed tangential displacement (1 Hz) minimised any thermal fatigue effects induced within the contact.

2.2. Materials

2.2.1. Epoxy polymers

The epoxy formulations were based on a mixture of diglycidylether of Bisphenol A (DGEBA) and diamino-diphenylmethane (DDM) whose chemical formulae are reported in Table 1. The DGEBA and DDM monomers are commercial chemicals purchased from Bakelite (Germany, grade Rutapox 162) and Acros Organics (France), respectively. The

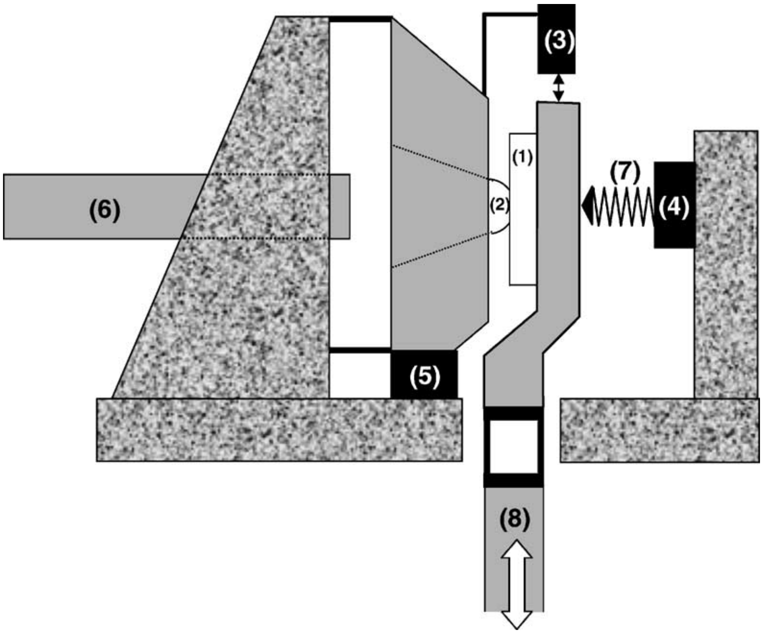
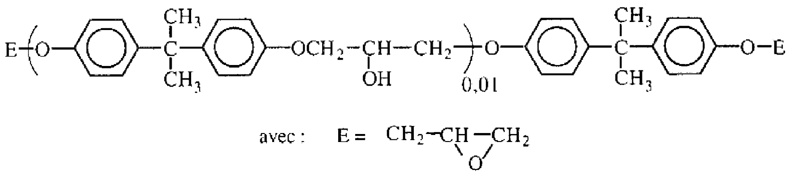
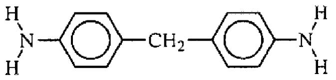
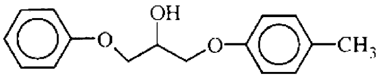
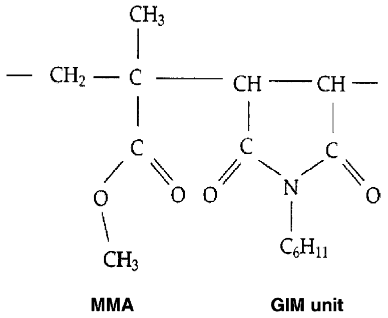
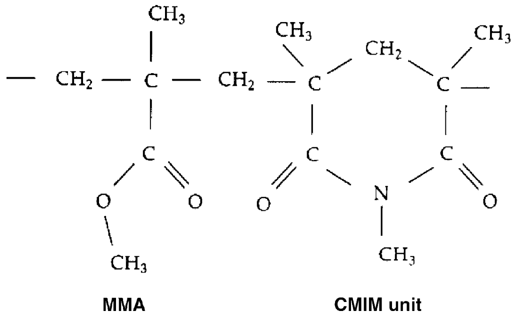


Fig. 1. Schematic of the fretting device. (1) Polymer flat specimen; (2) spherical glass counterface; (3) displacement transducer; (4) normal load transducer; (5) tangential load piezoelectric transducer; (6) microscope and CCD camera; (7) contact loading system.

Table 1
Formulae of the chemicals used in this study

Epoxy polymers	
DGEBA	
DDM	
AM additive	
Poly(methylmethacrylate)-based random copolymers	
Methacrylate-glutarimide copolymers (GIM)	
Methacrylate-maleimide copolymers (CMIM)	

so-called AM low molecular weight additive (Table 1) corresponds to a diarylether of glycerol. It was synthesised in our laboratory according a procedure detailed elsewhere [9]. The additive was incorporated into stoichiometric mixtures of monomers (based on 2 mol of the DGEBA diepoxide for 1 mol of diamine) before cure. The relative molar ratio of the AM additive to diamine was 0.96 mol/mol. Code names for the samples refer to the network acronym, followed when relevant by the additive acronym. Moulded specimens 10 mm thick were cured under nitrogen for 12 h at 80 °C and then post-cured for 24 h at 200 °C in the case of the system without additive and at 160 °C for the modified formulation. It was previously demonstrated from Nuclear Magnetic Resonance (NMR) experiments that the AM additive did not react chemically with the networks [11]. The physical and mechanical properties of the epoxy materials are reported in Table 2. The plasticizing action of the AM additive results in a decrease in the glass transition temperature as compared to the DGEBA/DDM epoxy, but the modified network remains in its glassy state at room temperature while its toughness is increased by a factor of about 2.

Table 2
Mechanical properties and physical properties of the epoxy polymers

	Tg (°C)[a]	E' (MPa)[b]	σ_y (MPa)[c]	K_{IC} (MPa m$^{1/2}$)[d]
DGEBA/DDM	190	2800	100	0.8
DGEBA/DDM/AM	111	3400	110	2.1

Data taken from [9,16].

[a] Measured from the maximum of the loss modulus E'' at 1 Hz using Dynamic Mechanical Analysis.

[b] Conservation modulus measured at 25 °C and 1 Hz.

[c] Compressive yield stress measured at 25 °C and at a strain rate of 2×10^{-3} s^{-1}.

[d] Mode I fracture toughness from notched three point bending specimens.

Table 3
Mechanical and physical properties of the methylmethacrylate-based random copolymers

	Tg (°C)[a]	E' (MPa)[b]	σ_y (MPa)[c]	K_{IC} (MPa.m$^{1/2}$)	Hardness (MPa)[e]
GIM	158	3400	120	2.4[d]	260
CMIM	161	3000	125	0.85[f]	250

Data taken from [7,8,13].

[a] Measured from the maximum of the loss modulus E'' at 1 Hz using Dynamic Mechanical Analysis.

[b] Conservation modulus measured at 25 °C and 1 Hz.

[c] Compressive yield stress measured at a strain rate of $2 \times 10^{-3}\,s^{-1}$.

[d] Mode I fracture toughness from notched three point bending specimens.

[e] Measured using nano-indentation at a constant average strain rate of $0.05\,s^{-1}$.

[f] Estimated from the fretting tests, see text.

2.2.2. *Methylmethacrylate-based random copolymers*

Two kinds of polymer systems were selected from homologous series of methylmethacrylate-based random copolymers which have been synthesised for the purpose of previously reported investigations [7,8,12,13]. The first copolymer was obtained using cyclohexyl-*N*-maleimide (methacrylate-maleimide copolymers (CMIM), Table 1) as a comonomer. The selected maleimide content was 25 mol%. Prior to analysis, the polymer was purified by precipitation with methanol from a chloroform solution. This operation allowed removal of low molecular weight chains (typically $M_w < 5000\,g\,mol^{-1}$). The weight average molecular weight of the CMIM copolymer was $156\,000\,g\,mol^{-1}$.

N-Methylglutarimide in a ratio of 76 mol% was used as a comonomer for the second polymer system (methacrylate-glutarimide copolymers (GIM), Table 1). This material was supplied by Röhm and Hass (Kamax T 260). The weight average molecular mass of the copolymer was $106\,000\,g\,mol^{-1}$.

Before use, the polymer powders were dried under vacuum at 110 °C for 24 h in order to eliminate water. Plane sheets 10 mm thick were subsequently prepared by compression molding under vacuum at a temperature around 220 °C in order to avoid any preferential orientation effects. Some of the physical and mechanical properties of the selected polymer systems are reported in Table 3.

3. Results and discussion

3.1. *Epoxy polymers*

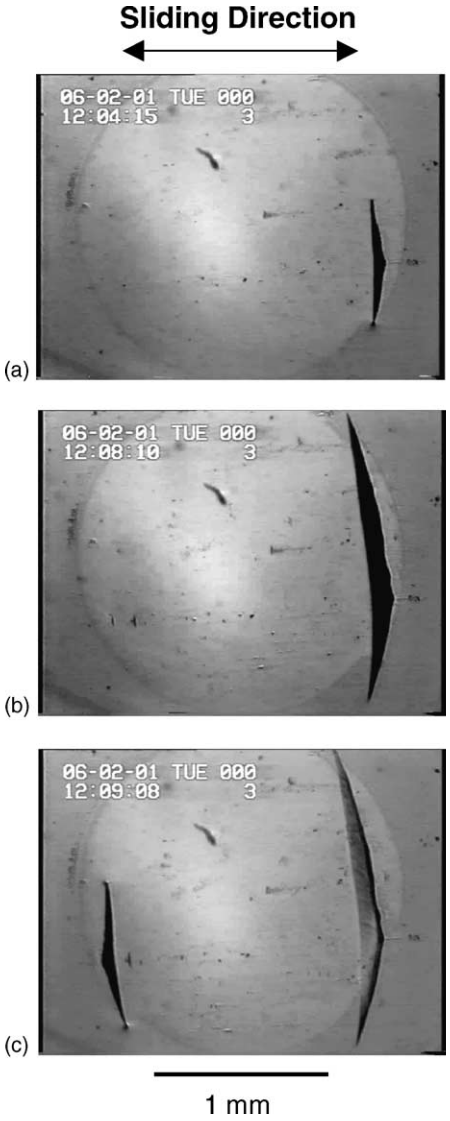


Fig. 2. In situ pictures of the contact area during a fretting test using the DGEBA/DDM epoxy system: (a) 570 fretting cycles; (b) 750 fretting cycles; (c) 800 fretting cycles.

A typical example of the development of the crack network, within the DGEBA/DDM resin, is shown in Fig. 2 for a normal load of 100 N. The calculation of the maximum von Mises stress using Hamilton's theory [14] for the contact stresses demonstrated that the epoxy was loaded elastically. The observed material degradation is dominated by the nucleation and the propagation of two major cracks located close to the edge of the contact and at two approximately symmetrical locations orthogonal to the sliding direction. As was unambiguously reported in previous papers [4,15], these cracks are induced under Mode I opening due to the predominantly tensile/compressive nature of the local loading at the edge of the contact area. Under similar contact loading conditions, no cracks were detected within the DGEBA/DDM/AM network up to 5×10^3 fretting cycles. Although some slight wear degradation could be observed within the contact area (Fig. 3), the epoxy network with the included additive can be considered as essentially undamaged at the end of the fretting test. A relevant comparison of the two materials requires, however, the quantification of the magnitude of the contact stresses at the edge of the contact. The latter are a function of the contact geometry and the contact loading parameters, but also of the material

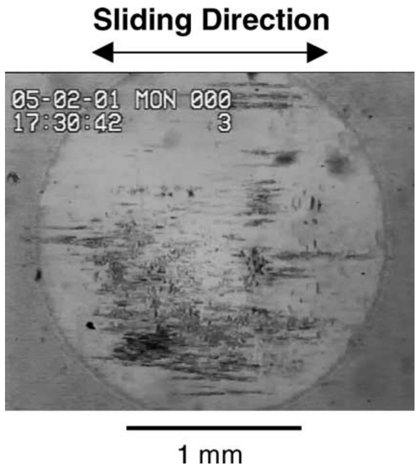


Fig. 3. In situ picture of the contact area during a fretting test using the DGEBA/DDM/AM epoxy system after 5×10^3 fretting cycles.

mechanical properties and naturally the coefficient of friction. As a result, a comparison of the variations in the contact fatigue behaviour under similar contact loading conditions does not necessarily reflect a change in the intrinsic crack propagation resistance of the material.

As a first approach, the stress state at the crack location can be estimated from the maximum value of the tensile stress, $\sigma_{xx}^{\max}$, at the edge of the contact. For a sliding sphere on an elastic semi-infinite medium, $\sigma_{xx}^{\max}$ is given by Hamilton's theory [14]:

$$\sigma_{xx}^{\max} = \frac{3P}{2\pi a^2}\left[\frac{1-2\nu}{3} + \frac{4+\nu}{8}\pi\mu\right] \qquad (1)$$

where P is the normal load, μ the coefficient of friction, ν the Poisson's ratio and a the radius of the contact area which incorporates the effect of the materials Young's modulus.

In the context of this study, the assumption of an elastic contact response is justified by the very low viscoelasticity of the materials at ambient temperature and loading frequency (the loss tangent, $\tan\delta$, is about 0.03 at 1 Hz for both the DGEBA/DDM and the DGEBA/DDM/AM networks).

The validity of Hamilton's equation under a fretting loading is also restricted to gross slip conditions. From an examination of the fretting loops giving the tangential load as a function of the imposed displacement (Fig. 4), it was easily verified that the experiments were carried out within the gross slip regime. The strong increase in the plateau values of the tangential load corresponding to the gross slip stage indicates that the coefficient of friction evolves over times which are of the same order of magnitude as the crack initiation times. These non-constant contact fatigue conditions complicate the quantitative analysis of the cracking behaviour and especially any attempt to correlate the fretting data with conventional bulk fatigue properties. As a first approach, the value of the coefficient of friction at the onset of crack initiation ($\mu = 1.3 \pm 0.1$) was selected for the calculation of $\sigma_{xx}^{\max}$ within the unmodified DGEBA/DDM network. As no crack was detected for the DGEBA/DDM/AM network, the maximum value of μ was used for the computation of the maximum tensile stress, i.e. $\mu = 1.2 \pm 0.1$. In the application of Eq. (1), these slight differences in the coefficient of friction were in fact balanced by the differences

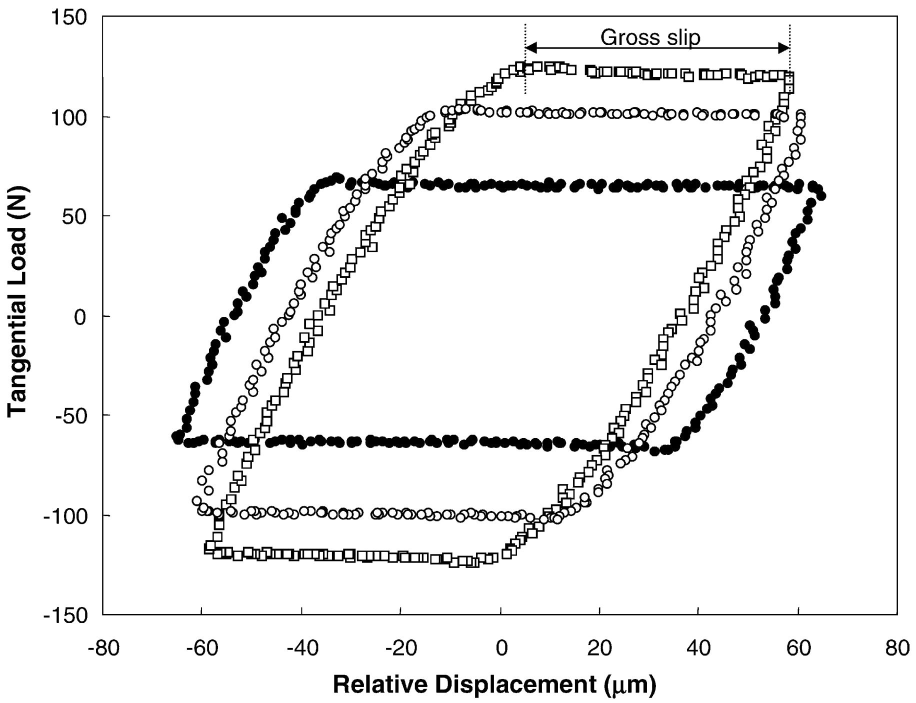


Fig. 4. Fretting loops giving the tangential load as a function of the imposed relative displacement (DGEBA/DDM): (●) 10 cycles; (○) 300 cycles; (☐) 550 cycles.

in the contact area which resulted from variations of the Young's modulus of the epoxy networks. At room temperature, the antiplasticizing action of the AM additive induces an increase of the Young's modulus of the modified epoxy network which can be attributed to the depression of the sub-Tg β relaxation [16]. Accordingly, the measured contact radius was lower for the DGEBA/DDM/AM epoxy ($a = 1.0$ mm) than for the DGEBA/DDM network ($a = 1.1$ mm). From an Hertzian contact analysis, the corresponding quasi-static moduli can be estimated to be 2600 and 3300 MPa for the DGEBA/DDM and DGEBA/DDM/AM materials, respectively, which is consistent with the dynamic bulk modulus data reported in Table 2.

Using the above parameters, Eq. (1) provides about the same value of the maximum tensile stress at the edge of the contact, $\sigma_{xx}^{\max} = 100 \pm 10$ MPa, for both epoxy systems. The improved contact fatigue resistance of the modified epoxy network can therefore unambiguously attributed to the enhanced crack initiation and propagation resistance of this material in Mode I, which might be correlated to the two-fold increase in the fracture toughness (Table 2). In a previous investigation by Sauvant and Halary [16], this strong toughening effect was assigned to the very special morphology of the material. During the network construction, the initially miscible AM additive gives rise to nanoscale phase separation [9,11]. Tentatively, a realistic mechanism might involve a stress concentration localised in the nanophase domains able to favour plastic flow and dissipation at the crack tip, in agreement with the accepted toughening mechanism involved in rubber toughened epoxy systems.

3.2. *Methylmethacrylate-based copolymers*

A systematic investigation of the contact fatigue behaviour of the GIM and the CMIM copolymers has been carried out at various imposed normal loads within the elastic range of the polymers. Whatever the contact load, a strong difference was observed in the development of the cracks network for the two materials (Fig. 5). For the CMIM system, the nucleation of cracks at the edge of the contact area was immediately followed by a brittle propagation stage. In contrast, crack propagation within the GIM copolymer occurred in a much more progressive manner and multiple cracks initiation was often observed.

Crack propagation within CMIM was also associated with a slight but perceptible decrease in the contact tangential stiffness (Fig. 6), which was not the case for the GIM copolymer. As was reported in a previous study [4], the contact stiffness is strongly sensitive to the extent of crack propagation through the thickness of the polymer body. As cracks propagate, a substantial part of the imposed relative displacement can be accommodated through the alternate opening and the closing of the cracks during the fretting cycles, instead by a purely elastic deformation of the bulk polymer. The fact that a drop in contact stiffness is not perceptible for the GIM polymer could therefore be sensibly interpreted as evidence of a limited propagation of the observed surface cracks through the thickness of the specimens.

As for the epoxy polymers, a quantitative comparison of the contact fatigue behaviour was attempted on the basis of an estimate of the maximum tensile stress at the edge of the contact. Once again, the coefficient of friction of the

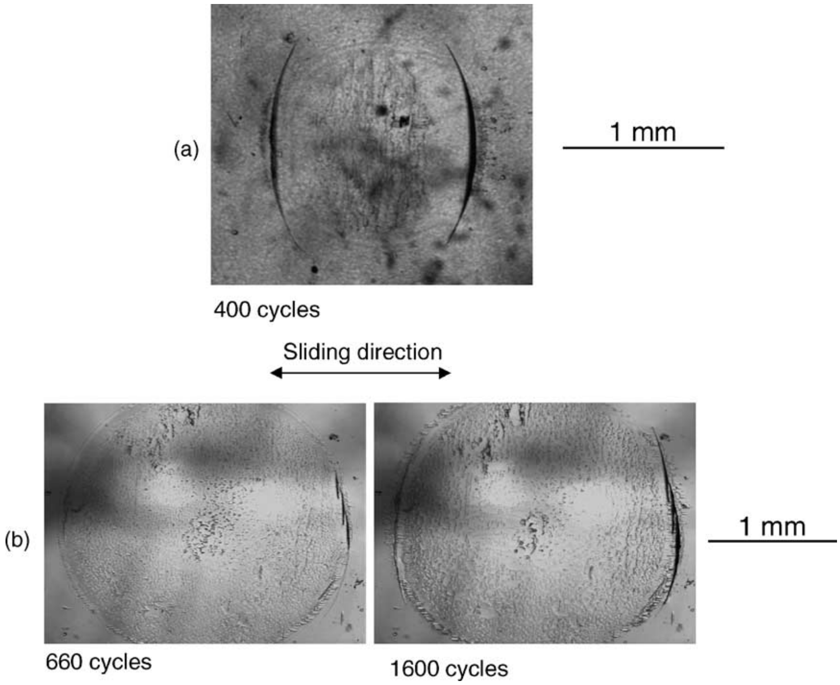


Fig. 5. In situ contact pictures showing the crack network development of the (a) CMIM ($P = 20$ N) and (b) GIM ($P = 165$ N) copolymers.

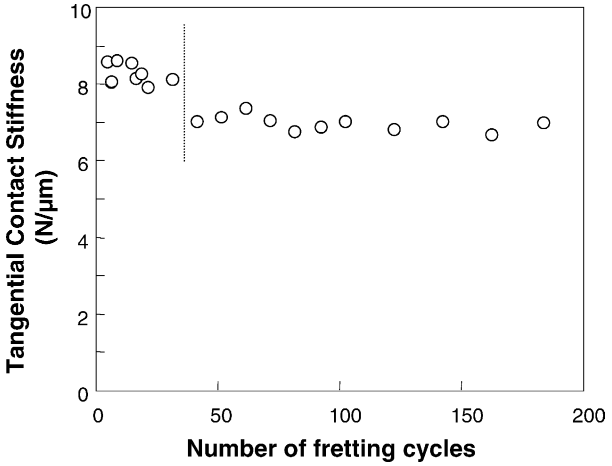


Fig. 6. Changes in the tangential contact stiffness as a function of the number of cycles for the CMIM copolymer ($P = 200$ N).

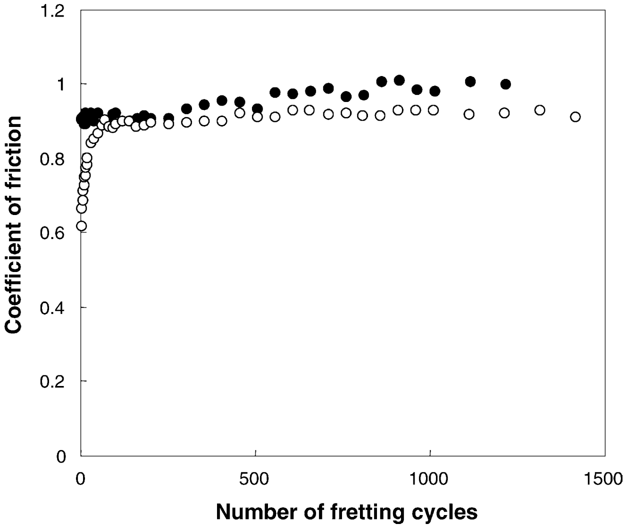


Fig. 7. Coefficient of friction of the CMIM/glass contact as a function of the number of fretting cycles: (●) $P = 100$ N; (○) $P = 200$ N.

copolymers increased as the tests proceeded, with a variation which was dependent upon the level of the normal loading (Fig. 7). As a first approach, the value of μ at crack initiation was taken into account in the calculation of $\sigma_{xx}^{\max}$. The results are reported in of a 'S–N' fatigue diagram giving the maximum applied tensile stress as a function of the number of cycles to crack initiation, N_a (Fig. 8). These data show a marked increase in the contact fatigue resistance of the GIM copolymers compared with the CMIM material.

As was mentioned above, the contact stresses at the crack location are essentially of a tensile nature (Hamilton's theory establishes that σ_{xx} and σ_{yy} are principal stresses at the contact edge in the contact midplane). The observed contact cracking mechanisms may thus interestingly be compared to previously reported investigation of the micro-deformation mechanisms of thin copolymers films strained in tension and observed by transmission electron microscopy [12,13]. Depending upon the temperature and the composition of the methylmethacrylate copolymers, competitive deformation processes in the form of crazes or homogeneous shear deformation zones were identified. For the CMIM copolymer under investigation, extensive craze formation was observed at room temperature as a result of the embrittlement of the copolymers by the maleimide comonomers. Due to the intrinsic brittleness of the CMIM system, macroscopic fracture test using classical notched bulk specimens were not practicable. An estimate of K_{IC} can, however, be provided by the measurement of the critical crack length, a_c, in the contact plane at the onset of brittle propagation. According to a classical fracture mechanics approach, the fracture toughness may be estimated from $\sigma_{xx}^{\max}\sqrt{\pi a_c}$, which yield a fracture toughness of about 0.85 MPa m$^{1/2}$, i.e. less than that of a PMMA homopolymer (1.20 MPa m$^{1/2}$).

In contrast, straining of the GIM copolymer thin films at 20 °C resulted in the extensive formation of shear bands in addition to crazes (as a comparison PMMA shows

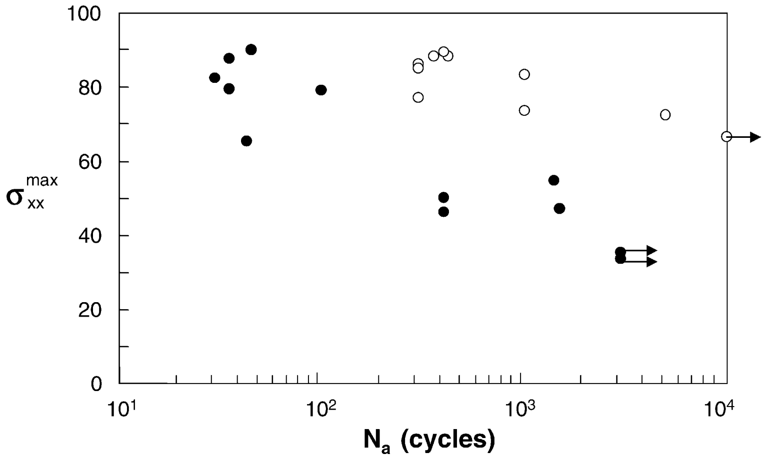


Fig. 8. Endurance diagram giving the maximum tensile stress at the edge of the contact, $\sigma_{xx}^{\max}$, as a function of the number of fretting cycles to crack initiation, N_a: (●) CMIM; (○) GIM. The arrows correspond to run-outs.

predominantly crazes under comparable conditions). This behaviour reflects the increased plastic yielding ability, or ductility, of the GIM copolymer and has a strong beneficial effect on the macroscopic fracture toughness which is about twice the K_{IC} of PMMA (Table 3).

4. Conclusion

The contact cracking processes induced within homologous glassy amorphous polymers differing essentially by their fracture toughness have been investigated using small amplitude oscillating micro-motions, i.e. fretting conditions. Under such a loading, the main initial damage was related to the nucleation and growth of cracks at the edge of the contact by a fatigue process. With respect to these degradation processes, the contact under investigation may thus be considered as a model macroscopic ‘single-asperity’ contact which simulates the initial microscopic particle detachments processes occurring in a real multi-asperities contact under fatigue wear conditions.

Under similar contact stress environments, a relationship has been clearly established between the contact fatigue endurance of the polymers and their Mode I toughness properties. The existence of such a relationship is supported by the essentially tensile nature of the observed cracks. It can also be noted that the correlation between a “unit rupture” parameter such as toughness and contact fatigue cracking processes has often been reported especially in the context of elastomers wear (see [17] for example).

In addition, this study also demonstrated that the sensitivity of amorphous polymers to contact damage processes can be tailored by some alterations of the chemical composition resulting, for example, from the addition of specific comonomers or additives during the polymerisation steps.

References

[1] V.K. Jain, S. Bahadur, Development of a wear equation for polymer–metal sliding in terms of the fatigue and topography of the sliding surfaces, Wear 60 (1980) 237–248.

[2] V.K. Jain, S. Bahadur, Experimental verification of a fatigue wear equation, Wear 79 (1982) 241–253.

[3] J.K. Lancaster, Materials-specific wear mechanisms: relevance to wear modelling, Wear 141 (1990) 159–183.

[4] A. Chateauminois, M. Kharrat, A. Krichen, Analysis of fretting damage in polymers by means of fretting maps, in: V. Chandrasekaran, C.B. Elliott (Eds.), Fretting Fatigue: Current Technology and Practices, ASTM STP 1367, American Society for Testing and Materials, West Conshohocken, 2000, pp. 325–366.

[5] L. Vincent, Materials and Fretting. Fretting Fatigue ESIS 18, Mechanical Engineering Publications, London, 1994. pp. 323–337.

[6] S. Fouvry, P. Kapsa, L. Vincent, Quantification of fretting damage, Wear 200 (1–2) (1996) 186–205.

[7] P. Tordjeman, L. Teze, J.L. Halary, L. Monnerie, On the plastic and viscoelastic behavior of methylmethacrylate-based random copolymers, Polym. Eng. Sci. 37 (10) (1997) 1621–1632.

[8] L. Teze, J.L. Halary, L. Monnerie, L. Canova, On the viscoelastic and plastic behaviour of methylmethacrylate-co-*N*-methylglutarimide copolymers, Polymer 40 (4) (1998) 971–981.

[9] V. Sauvant, J.L. Halary, Novel formulations of high-performance epoxy-amine networks based on the use of nanoscale phase-separated antiplasticizers, J. Appl. Polym. Sci. 29 (3) (2001) 759–774.

[10] M. Kharrat, A. Chateauminois, A. Krichen, Analysis of the fretting behaviour of a glass/epoxy interface, in: D. Dowson (Ed.), Tribology for Energy Conservation, Elsevier, Amsterdam, 1998, pp. 379–387.

[11] V. Sauvant, F. Laupretre, NMR investigation of the miscibility of new antiplasticizers in densely cross-linked epoxy-amine resins, Polymer 43 (4) (2002) 1259–1265.

[12] C.J.G. Plummer, H.-H. Kausch, L. Teze, J.L. Halary, L. Monnerie, Microdeformation mechanisms in methylmethacrylate-glutarimide random copolymers, Polymer 37 (19) (1996) 4299–4305.

[13] P. Tordjeman, J.L. Halary, L. Monnerie, A.M. Donald, On the role of entanglements in the embrittlement of poly(methylmethacrylate)-based random copolymers, Polymer 36 (8) (1995) 1627–1633.

[14] G.M. Hamilton, Explicit equations for the stresses beneath a sliding spherical contact, Proc. Inst. Mech. Eng. 197C (1983) 53–59.

[15] M.C. Dubourg, A. Chateauminois, B. Villechaise, In situ analysis and modeling of crack initiation and propagation within model fretting contacts using polymer materials, Tribol. Int. 36 (2003) 109–119.

[16] V. Sauvant, J.L. Halary, Improvement of the performance of epoxy-amine thermosets by antiplasticizer-induced nano-scale phase separation during cure, Comp. Sci. Technol. 62 (4) (2002) 481–486.

[17] M. Barquins, A.D. Roberts, Rubber friction variation with rate and temperature: some new observations, J. Phys. D 19 (1986) 547–563.