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Polymer 40 (1999) 4451–4458

polymer

Friction induced mechanochemical and mechanophysical changes in high performance semicrystalline polymer

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Received 29 July 1998; received in revised form 11 August 1998; accepted 21 September 1998

Abstract

By using X-ray photoelectron spectroscopy (XPS) and Fourier transform Raman (FT-Raman) spectroscopy, the worn specimens of polyetheretherketone (PEEK) tested under unlubricated sliding friction and wear conditions at a constant sliding speed were investigated in order to reveal mechanochemically and mechanophysically induced structural changes of polymer as well as wear mechanisms on a molecular scale. Chain scission was found on the worn surface layer. The results suggest that oxidation was the major mechanochemical reaction that followed the chain scission on the top surface. Evidence for chain branching or even crosslinking in bulk materials was also presented. Moreover, two-stage loading dependencies were found for both surface and subsurface in the bulk as revealed through wear rate measurement and wear debris analysis. It was proved that a thermo-activation of polymer segments may be responsible for the transition in the dependence of structure on load. The results of the present work also provide a method (based on spectral analyses) that can be used for studying micromechanisms accounting for shear deformation and failure. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyetheretherketone; Wear; Mechanochemistry

1. Introduction

It has been demonstrated that friction and wear are involved mostly in the rather thin layer of a rubbing surface when a bulk polymer serves in tribological environment, leading to consequent mechanophysical and mechanochemical changes in the surface layer [1,2]. As a material's microstructure exerts a critical influence on the wear mechanisms and tribological performance of the polymer, it is necessary to understand structural variation in worn surfaces for both property prediction and material modification.

With respect to technical viability, methods capable of characterizing a thin layer activated by wearing should have (1) a sensitivity adequate to distinguish the surface structure from the bulk, (2) a detection depth equivalent to the surface layer thickness so as to study the structure of interest, and (3) a signal-to-noise ratio high enough to avoid possible interference originating from foreign matter adhering to the frictional surface. By comparing with other methods, X-ray photoelectron spectroscopy (XPS) and Fourier transform Raman (FT-Raman) spectroscopy seem to be feasible, especially because the methods provide detection depths of the order of several nanons [3] and microns, respectively. Therefore, the present work is focused on a direct assessment of structures of the worn surface layer in the scale range of nanons to microns as a function of tribological conditions by using XPS and FT-Raman spectroscopy, with the objective of revealing molecular information about the polymer during wear processes. In particular, polyetheretherkene (PEEK), a typical high performance semicrystalline polymer widely acting as a bearing and slider material, is employed as a model material in this study.

2. Experimental

Powdered PEEK, exhibiting properties similar to those of ICI 150P, was kindly supplied by the Jilin University, China. The polymer was pressed under 7 MPa and 390°C for 15 min into $200 \times 200 \times 4\ \mathrm{mm}^3$ sheets with a plate-frame mold in a hot press and then transferred to a cold press

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PII: S0032-3861(98)00691-0

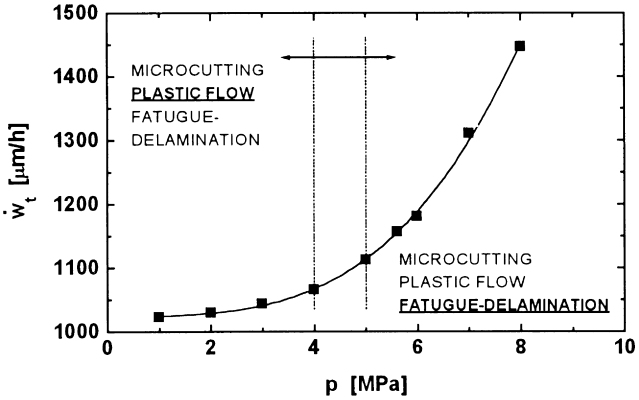


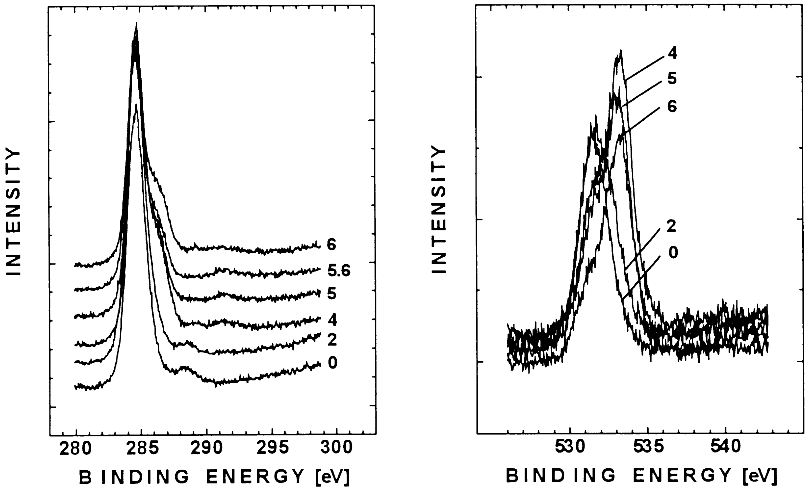
Fig. 1. Time-related wear rates, $\dot{w}_t$, of PEEK as a function of apparent contact pressure, p.

to cool down under pressure. The specimens for wear tests were machined from the center of the plates, resulting in an apparent contact area of about 5 × 10 mm^2.

Room temperature sliding wear tests were carried out on a pin-on-ring apparatus under different loads at a constant velocity of 0.4 ms^{-1}. Sliding took place on the molding plane of the specimen pins. The carbon steel ring (0.42–0.45 wt.% C, 0.17–0.37 wt.% Si and 0.5–0.80 wt.% Mn, HRC 50) had a diameter of 40 mm and an initial surface roughness of 0.1 μm. Prior to wear testing, all the samples were preworn so as to average surface conditions and reduce the running-in period. When the apparatus had operated for 2 h in a steady state, the wear test was stopped for every measurement.

Having been tested by the pin-on-ring apparatus, the specimens were washed with acetone and kept in vacuum for 24 h, and then stored for subsequent spectroscopy investigation. The XPS spectra of the PEEK worn surface were recorded by means of a Vacuum Generators Escalb MK II X-ray photoelectron spectrometer with a resolution of 0.8 eV at 240 W (Mg Kα 12 kV). For the purpose of correction of specimen charging, the C1s bands were calibrated by assuming the binding energy of benzene peak as 284.6 eV. In the case of O1s binding energy, only the difference between the two subbands was compared. Multiple Gaussian curve-fitting was used for spectra lineshape determination.

FT-Raman spectra were collected on the worn pin tops with back-scattering geometry using Bruker RS100 FT-Raman spectrometer (laser source: Nd^{3+} : YAG at 1064 nm, power: 50 mW, sampling step: 4 cm^{-1}). 50 scans were performed for obtaining each spectrum. All spectra were recorded from 1000 to 3500 cm^{-1}. In order to get rid of the possible influence of surface roughness on scattering intensity, all the spectra were normalized over the range of 100–3500 cm^{-1}. In addition, Lorenzian function was used to fit the Raman bands so as to avoid errors introduced through Fourier transform and data recording.



a) C1s

b) O1s

Fig. 2. The XPS spectra of the worn specimens, with the numerals standing for the loads employed during wear tests ($p = 0$ means the specimen was only preworn).

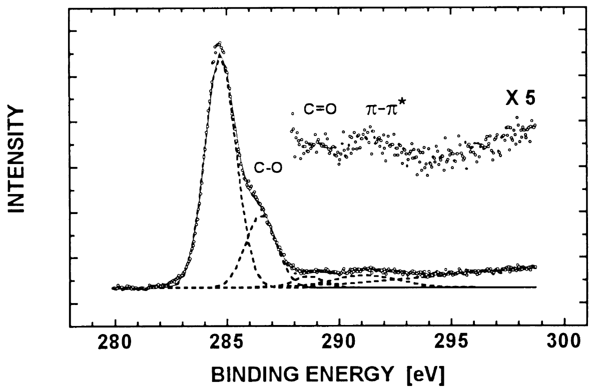


Fig. 3. Typical C1s bands with assignments of the peaks ($p = 4$ MPa). The main peak is the C1s band of phenylene rings.

3. Results and discussion

For the convenience of discussion, the experimental results of sliding wear tests carried out on PEEK [4] are briefly reviewed as follows. There was a transition from a milder wear to a severer wear as illustrated by the time-related wear rate, $\dot{w}_t$, vs. contact pressure, p, in Fig. 1. According to wear mechanism studies [4,5], it is known that a combination of microcutting, plastic flow and fatigue-delamination was responsible for the wear behavior, with a different dominance of the individual effect at different loading conditions. Plastic flow made a higher contribution at lower pressures, and fatigue-delamination played the leading role at higher pressures.

Fig. 2 summarizes the XPS spectra collected on the worn pin tops of PEEK specimens prepared under various loads. It can be seen that the increase in contact pressure predominantly results in a change in the C1s band profile (Fig. 2(a)). While the peak intensities of the C1s bands remain almost unchanged, the main peaks become narrower and the shoulder at 286.5 eV grows stronger with a rise in loading. At the same time, the C1s spectrum gradually loses the weak shoulder at 288.4 eV. According to the results of the binding energies of the C1s photoelectron of aromatic compounds and polymers [6,7], the shoulders at 286.5 and 288.4 eV should be assigned to the single and double carbon–oxygen bonds, C–O and C=O, respectively. To quantify the change with the rise in load, the C1s spectra were de-convoluted. The widths of the C1s components were fixed during spectra de-convolution so as to overcome the difficulty arising from the large discrepancy between the main peak intensity and those of the shoulders. A typical curve fitting result is shown in Fig. 3.

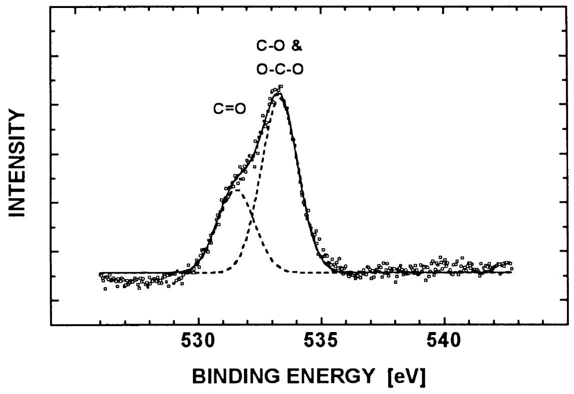


Fig. 4. Typical O1s bands with assignments of the peaks ($p = 4$ MPa).

Similarly, the O1s spectrum exhibits a two-component profile (Fig. 2(b)). When the contact pressure is lower, the band peaks at 531.4 eV. As the load increases, the other Gaussian component, which is centered at 533.2 eV, becomes more and more intense. As phenyl oxide and carbonyl functional groups would be undoubtedly the major forms of oxygen bonding on the PEEK surface, the two components can be regarded as a result of oxygen of C–O σ covalent bonds and of oxygen in carbonyl groups (Fig. 4).

3.1. Chain scission

The most striking result in Fig. 2(a) is the π–π* shake-up peak [7] that appears in the case of moderate loads and has the strongest intensities at 2 and 4 MPa (Fig. 2(a)). As the binding energy of the π–π* shake-up peaks observed here is approximately 291 eV, the existence of single pendent phenyl rings is reflected. The result is factually indicative of scission of PEEK chains that had occurred in the tribological courses. Besides, it is worth noting that the shake-up peak becomes the most intense at moderate loads (i.e. 2 and 4 MPa). Other mechanisms must have accompanied or followed the chain scission. Cross-linking, which was deduced from the thermal degradation analyses of identical specimens [1], might be a result of such complicated reactions. It would be reasonable to think that the mechanochemistry involved was different at different loading regions. At lower pressures, the free radicals formed by scission should terminate quickly before transferring much. At higher loads, however, a higher mobility of the segments might make it easier for the radicals to grow and form branched, or even cross-linked structures.

3.2. Surface oxidization

Figs. 5 and 6 show the differential binding energies, ΔBE, of C1s and O1s through spectra deconvolution. From Fig. 5, it can be seen that the C1s binding energy of the double bonds tend to increase with an increase in load, suggesting that the chemical environment of carboxyl carbon atoms become more and more oxidative. A similar trend can also be perceived though the C1s binding energy of the C–O bonds. In good agreement with the C1s binding energies, the difference in binding energy between the two O1s components also increases with load (Fig. 6). Either the chemical environment of the oxygen corresponding to the 533.2 eV component had grown more reductive or that of the other one (at 531.4 eV) became more oxidative.

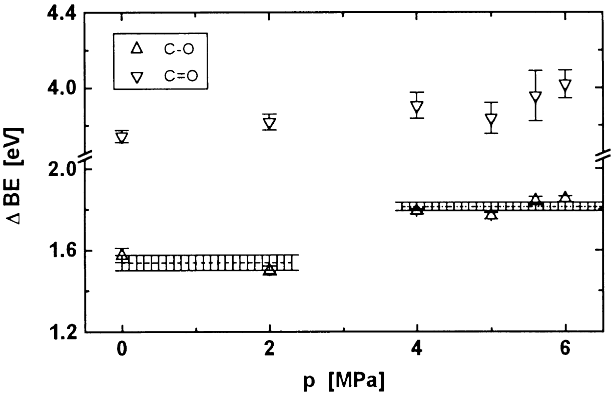


Fig. 5. Differential binding energy, ΔBE, of C–O and C=O peaks of C1s spectra in comparison to benzene as a function of loading.

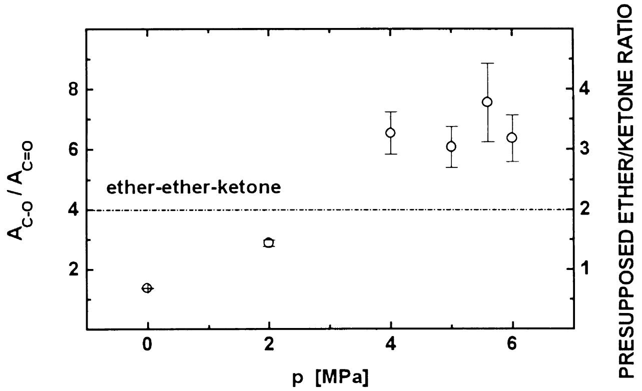


Fig. 7. Integrated intensity ratio of C–O to C=O, $A_{C-O}/A_{C=O}$, of the C1s spectra as a function of loading (normalized to total carbon intensity each). The dashed line indicates the presupposed ether/ketone ratio.

Compared to the chain scission obtained from changes in the π–π^* transition (Figs. 2(a) and 3), the increasing trends of the binding energies suggest that oxidization should be a general step in the mechanochemical reactions of the tribological process.

Moreover, Fig. 5 indicates that the C1s binding energy of the C–O single bond falls into two levels depending on the range of loads that the specimen had been subjected to. The ΔBE value of the specimens tested under higher loads is about 0.24 eV higher. Considering that C–O single bonds in the specimens can only belong to phenolic and carboxylate structures had they not been of phenyl ether, the radicals produced by chain scission during wear tests must have ended as phenolic structures at lower loads and as carboxylates when the contact pressure was higher.

Figs. 7 and 8 show the ratios of the integrated intensity of C–O single bonds over that of the carbonyl groups, $A_{C-O}/A_{C=O}$, calculated from the C1s and O1s spectra, respectively. Each of the figures illustrates an increasing trend in the ratio with increasing loads, indicating a rise in both carbon and oxygen in σ bonds. The increase in the C–O single bond amount with loading further proves that oxidation was an important step during the wear tests.

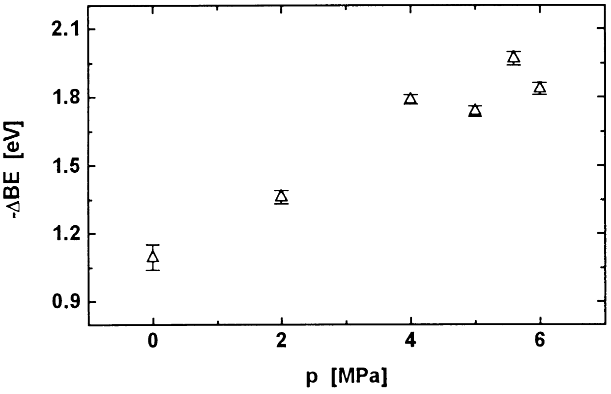


Fig. 6. Difference in binding energy, ΔBE, between C–O and C=O peaks of O1s spectra as a function of loading.

3.3. Two sorts of oxidation mechanisms

In order to analyze further the chemical changes during wear, the measured intensity ratio, $A_{C-O}/A_{C=O}$, is compared to the calculated atomic content ratio in PEEK. From Figs. 7 and 8, it can be seen that the experimentally obtained value tends to increase with an increase in contact pressure. The measured loading dependencies of the ratio $A_{C-O}/A_{C=O}$ in both figures intersect the theoretical line only at mediocre loads. This means that the worn surface would have the same composition as that of the bulk PEEK only at moderate contact pressures of 2 and 4 MPa.

Notice that the maximum of the π–π^* shake-up peak intensity under the corresponding loads in Fig. 2(a) may be attributed to the highest residual contents of the pendent phenyl rings. These results indicate that the oxidation subsequent to radical formation was associated with different mechanisms under different loads. When the contact pressure was low, the radicals were localized. The ring radicals of the broken chains tended to terminate by redox reactions with heterogeneous materials such as ferrous compounds, leading to surplus phenolic groups on the worn surface. As loading was increased, the mobility of the PEEK segments became higher and made the radical chain reaction involve more polymer chains. The relatively higher stability of the aromatic ketone radicals only made it easier for carbonyl-containing groups to be oxidized and separated from the chains, leaving more caboxylate residuals while resulting in a higher $A_{C-O}/A_{C=O}$ ratio.

In fact, a transition in reaction mechanism at around 4 MPa can also be perceived through the loading dependencies of C1s binding energy (Fig. 5). Obviously, effects of thermo-activation should also be observed in the subsurface of the worn specimens, i.e. the portion in the bulk material several microns beneath the worn surface.

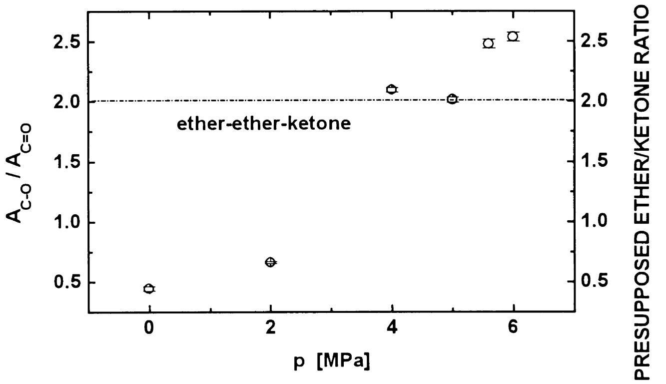


Fig. 8. Integrated intensity ratio of C–O to C=O, $A_{C-O}/A_{C=O}$, of the O1s spectra as a function of loading (normalized to total carbon intensity each). The dashed line indicates the presupposed ether/ketone ratio.

3.4. Structure of a thicker surface layer of the worn specimens and the chemical reactions involved

The FT-Raman spectra of the worn surface of the PEEK specimens tested under different loads are shown in Fig. 9. In contrast to the results of the XPS spectra (Figs. 7 and 8), the Raman spectra of all the specimens are still characterized by typical PEEK bands [8] at 806, 1145, 1201, 1600, 1645 and 3060 cm^{-1} (see Table 1), respectively. The chemical structure of the worn specimens within the near infrared Raman sampling depth (i.e. a thickness of several microns) does not differ much with a typical molded PEEK plate. A comparison of the Raman bands may yield information about the structure in these thicker surface layers that had been subjected to wear stress.

In Figs. 10 and 11, the integrated intensities of the ketone band and ether anti-symmetric mode are compared with those of the phenyl ring and skeleton, respectively. The corresponding intensity ratios are illustrated in Fig. 12. A survey of Figs. 10 and 11 reveals that intensities of these four bands tend to vary with loading conditions. More importantly, all the loading dependencies change significantly at around 4 MPa. This phenomenon is demonstrated more clearly in Fig. 12, indicating the effect of contact pressure on the intensity ratio of the carbonyl stretch mode to the ring band is much more profound than that of the ether mode to the skeleton band. When the load is lower than 4 MPa, both the intensity ratios are independent of the contact pressure. At higher loads, the relative content of diphenyl ketone is higher and tends to decrease with a further rise in loading. Therefore, changes in structure of PEEK during wear was more pertinent to ketone groups than to ether groups, and different mechanisms controlled the tribochemical reactions at the two ranges of loads.

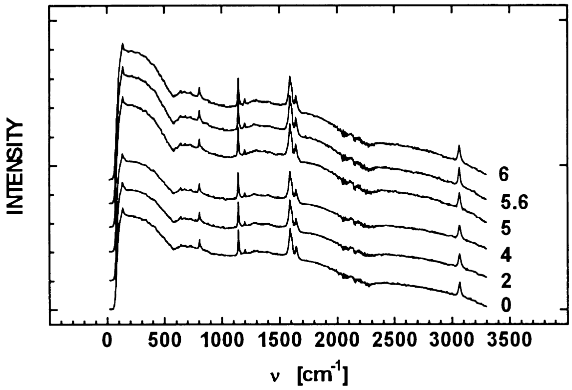


Fig. 9. Raman spectra of the worn specimens, with the numerals standing for the loads employed during wear tests.

If oxidation of PEEK chains can be neglected in the thicker layer of the worn surface, the free radicals originating from chain scission could have propagated to form branched or even cross-linked structures so long as the ether ether ketone segments had enough mobility. The reaction had to end through recombination and/or disproportionation (transfer of substituents). In contrast, the fluorone structure might have been mechanochemically induced as was reported by Cole et al. [9] during pyrolysis analysis of PEEK in its carbon fiber prepregs. As the carbonyl stretching band of fluorone, which should appear at a wavenumber not lower than 1700cm^{-1}, is not observed in the Raman spectra in the present work, this could not be the mechanism for the specimens subjected to loads within the loading range concerned. In other words, the reactions involving the PEEK ketone group should be its removal from PEEK chains and/or shifting from the *para*-substitution site to other sites, rather than any transition from diphenyl ketone to more aromatic structures. The level-off between 0 and 4 MPa, therefore, confirms that carbonyl and phenylene ring tends to leave the PEEK chain together. That is, the radicals formed through chain scission did not propagate much prior to their termination. Either ether and ketone links of PEEK are identical to the mechanochemical chain scission or the difference in their reactivity was compensated through disproportionation. The result is consistent with what was found in the XPS sampling depth in which macromelecular free radicals did not transfer much before they terminated under such low contact pressures. In contrast, the higher ketone-to-ring intensity ratio

Table 1
Assignments of the Raman bands [8]

Raman shift, cm^{-1}	Intensity characteristics[a]	Assignment
3066.7	m	C–H in-plane stretch of phenyl rings
1645.4	m	Carbonyl stretching in ketone
1595.3	s	Phenylene ring stretching
1201.9	w	Phenylene ether anti-symmetric stretch
1145.9	s, n	Ether–ether–ketone skeleton vibration
808.5	m	C–H out-of-plane deformation of phenylene rings

[a] w = weak, m = medium, s = strong, n = narrow.

observed in the specimens tested at elevated loads suggests another reaction mechanism, through which more phenylene rings accompanied ketone to change. Chain branching, or even cross-linking, may be responsible for the phenomenon, because the reactions involved one carbonyl group with more than one diphenyl ketone group. In contrast, the decrease in the ketone-to-ring intensity ratio with load at a high loading region represents a drop in chain scission owing to a rise in chain mobility.

In a word, the above-observed two-stage behavior rooted in the difference in PEEK mobility during the stress history. Under lower loads, the PEEK segments were frozen as glass and stress-induced radicals could result in only scission of chains. As the load became higher, frictional surface temperature tended to increase, giving the affected segments more mobility and making it easier for the radicals to propagate. At even higher loads, however, stress scission of the chains became difficult because chain disentanglement was easier. It is thus reasonable to believe that the origination of the observed mechanochemical transition is the activation of segments through glass transition driven by a certain level of contact pressure.

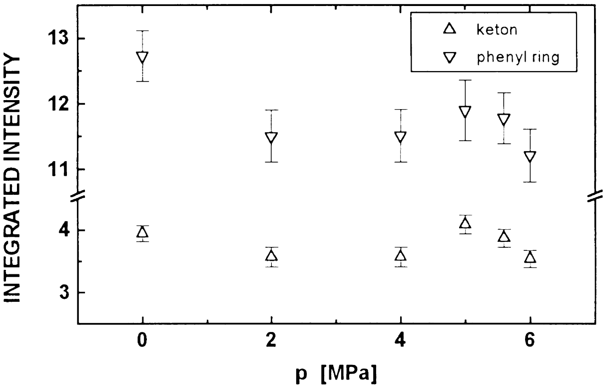


Fig. 10. Integrated intensities of phenylene ring and carbonyl stretching bands as a function of loading.

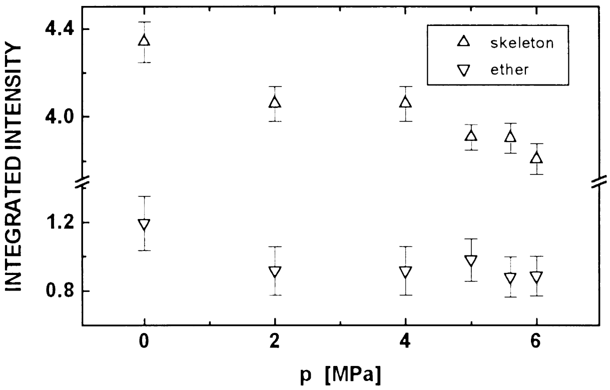


Fig. 11. Integrated intensities of skeletal vibration and ether anti-symmetric stretching bands as a function of loading.

3.5. Conformation of segments

Although the detailed chain scission mechanism needs further examination with other methods, it is informative to analyze the Raman shifts, which are able to reflect changes in conformation of the corresponding vibrating species, provided there is no chemical changes involved, as in crystalline fibers [10]. As a result of the diversified nature of the ordinary linear polymer, Lorentzian centers were adopted to analyze all the bands.

Figs. 13 and 14 show the Raman shifts of the 1145 cm^{-1} band and the 806 cm^{-1} band as a function of loading, respectively. Similar to the findings of the previous sections, two-stage loading dependencies can also be observed in the both figures. With increasing loading, the wavenumbers tend to decrease in the case of lower loads but increase under higher loads. In consideration of the fact that the 1145 cm^{-1} skeleton band is assigned to the in-plane rocking of the ethylene species C=C in *para*-substituted rings, a higher wavenumber should be indicative of a rigidity resulting from larger spatial hindrance, which might be attributed to: (1) an increase in ketone-to-ether ratio, (2) additional substitution formed through oxidation, and/or (3) conformation changes arising from the thermomechanical history. As

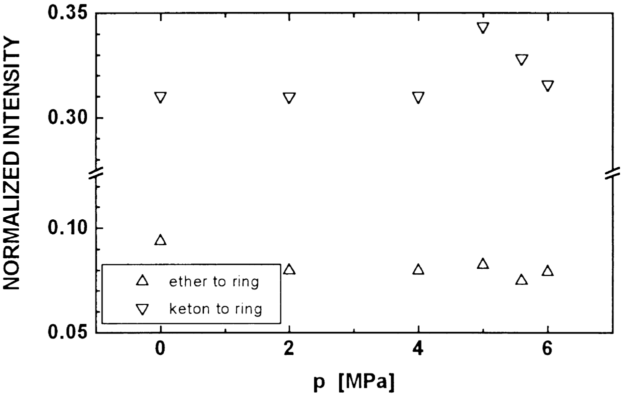


Fig. 12. Integrated intensity ratio of ether and ketone stretching bands to phenylene ring stretching.

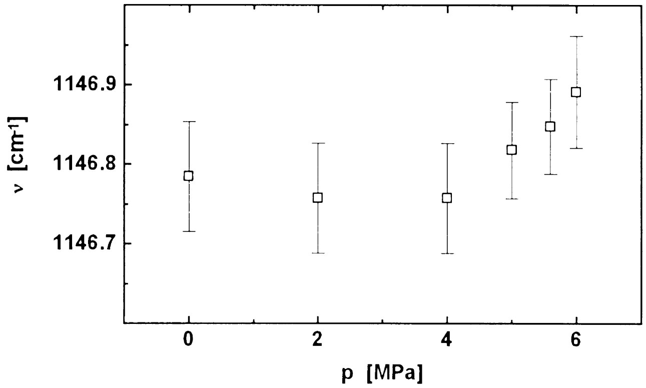


Fig. 13. Raman shift, ν, of 1145 cm^{-1} band as a function of loading.

the preceding section shows no trace of any profound oxidation in the Raman sampling depth, the oxidation related substitution is out of the question. Therefore, the result in Fig. 13 must have originated mainly from a chain scission related reaction and conformation variation. If the effects of the chemical reaction can be ignored, the obvious increase in frequency with load beyond 4 MPa suggests an activation of PEEK segments in the surface layer. When the segments had been activated, the residual strain became much larger as compared with the case at lower loads, and tended to increase with loading. Moreover, as this in-plane mode shows that the chains were in compression, an opposite trend should be observed for the out-of-plane band of the ring C–H mode if there was no macroscopic residual strain in the polymer. Fig. 14 reveals that the assumption is not true. The Raman shifts of 806 cm^{-1} band have the lowest values below 2 and 4 MPa, and also tend to become higher with a further increase in loading. That is, the chains were indeed in compression macroscopically, as could be expected from a common sense of mechanics of elastoplastic materials.

It is worth noting that the Raman shifts do not monotonously increase with the load. Neither Raman intensity analyses in the previous section showed an evidence of oxidation, nor did the carbonyl easily leave the chain. Therefore, the decrease in the two wavenumbers with contact pressure at lower loads confirms that the chains were in tension or were less incompressive within the sampling depth. These complicated changes need further consideration on a microscopic scale.

Usually, the neighboring rings of PEEK should be on planes with angles near the value in crystal phase [11], that is, about 20°. As the resonance between the rings and the bridging groups, O and C=O, can compensate the increase in energy caused by the spatial hindrance effect, certain coplanar conformations can be probably formed in quenched specimens. It is reasonable to believe the thermomechanical history of the current wear tests would facilitate such a change in conformation, for it allows an efficient quenching and chain orientation. Had this mechanism been true, the residual strain energy would have been stored in the segments in two forms, one being elastic and the other plastic as in the coplanar conformation. Similar to the intensity ratio shown in Fig. 12, Raman shifts of the ring modes should also reach a maximum when a specimen had been subjected to a load of 5 or 5.6 MPa. From the deconvolution results of the ring band (Fig. 15), it can be seen that it is the case for the Lorentzian component at 1595 cm^{-1} corresponding to PEEK in the ordered region [12]. In contrast, the other component at around 1610 cm^{-1}, which pertains to PEEK in the disordered region [12], follows almost exactly

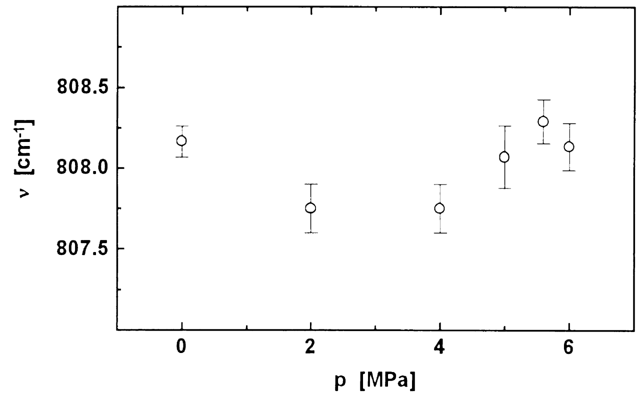


Fig. 14. Raman shift, ν, of 806 cm^{-1} band as a function of loading.

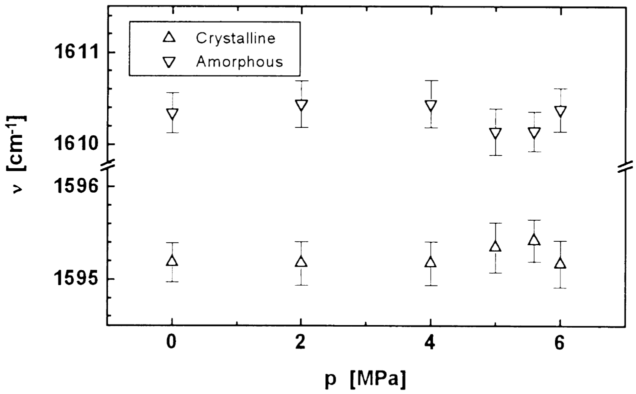


Fig. 15. Raman shifts, ν, of prime and shoulder peaks of phenylene ring stretching bands as a function of loading.

an opposite trend. Supposing the activated PEEK had been subjected mainly to shear stress during wear tests, ordering might have helped to stabilize the high energy coplanar conformation and would have made the chains in compression along the backbone. When a pre-existing order lacked, such unstable conformations cannot be achieved and chains had to be in tension as a result. Although the deduction requires collaborative experiments such as polarized Raman scattering to prove, the results of Raman shifts in Figs. 13–15 further evidence that certain activation of the segments plays an important role in determining material resistance to the mechanical load.

4. Conclusions

It was demonstrated that chain scission is the general feature of the mechanochemially induced changes in the polymer structure during sliding wear tests. By taking advantage of different sampling depths of XPS and Raman spectroscopy, it was proved that the tribomechanical chemistry on worn surfaces is different from that in the bulk. Oxidation of the polymer is evident on the worn surface but not at the subsurface several microns below.

In addition, it was demonstrated that the mechanism of the tribomechanical chemistry is also different when the polymer is subjected to different levels of loads, in analogy with the transition of wear mechanisms with a rise in loading revealed by wear rate measurement and fractal analysis of wear particles [4,5]. On the top surface, chain scission tended to be followed mainly by ring oxidation at lower contact pressures, but by oxidation of carbonyl groups when the load exceeded a certain critical loading. It was deduced that the transition in reaction mechanisms had originated from the activation of the segments by frictional heat. In the layer of microns thickness next to the surface, evidence of a parallel transition in reaction mechanism was also observed. At lower contact pressures, chain scission between the neighboring rings dominated. Beyond the critical load, higher segment mobility caused radicals to propagate, resulting in branching or even cross-linking of the chains. Variation in segment conformation with load, as revealed by analyzing the Raman shifts, indicated that certain coplanar ether ether ketone conformers might exist during wearing.

In consideration of the fact that the present sliding wear condition approached pure shearing, it can be estimated that similar molecular mechanism would be tenable in the case of not only tribological tests [5,13] but also other deformation and failure processes owing to shear. Future work should be focused on verification of this estimation. Moreover, localized stress will be correlated with activation energy of segmental motion and bond energies of main chains.

Acknowledgements

The authors express their gratitude to Prof. Gi Xue and Drs. Yun Lu, Shi Jin, Fengting Li, Zhongren Yue and Rong Zeng for the help received. The support of the National Natural Science Foundation of China (Grant No.59725307), Guangdong Provincial Natural Science Foundation of China (Grant No.940144), the Trans-Century Training Programme Foundation for the Talents of the State Education Commission of China are gratefully acknowledged. Dr. T.Q. Li is grateful to the support of the Laboratory of Polymeric Composite and Functional Materials, The State Educational Commission of China (Grant No.19703).

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