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Abrasive erosion of polyurethane

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The surface physical and chemical effects of abrasive erosion of polyurethane in three different fluids (H_2O, polyacrylamide and NaOH) containing quartz particles have been investigated respectively. The surface profiles, elements constitutions, binding energies and functional groups of polyurethane surfaces before and after abrasive eroding have been analyzed with scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectrometer (FT-IR). The surface physical effects of the abrasive erosion process were found to be microcutting, high-cycle fatigue and plastic fracture. The surface chemical effects turned out to be mechanical rupture of macromolecular chains, thermal decomposition of the allophanate groups and the biuret groups, hydrolysis of carbamate groups, and surface oxidative degradation.

1. Introduction

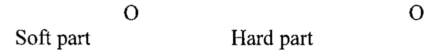
Abrasive erosion is essentially impact erosion with impact angles approaching to zero and is also considered as a type of sliding erosion elsewhere [1, 2]. It usually occurs in a number of hydromachines and oil field equipments such as slurry pumps, drilling mud pumps, cementing pumps, sand pumps and hydrocyclones, etc. Recently, polyurethane has been considered as a suitable erosion-resistant material and put into use. Although the process of sliding erosion has been studied extensively [3–6], the mechanisms of abrasive erosion of polyurethane still remain obscure.

More recently, the physical process and the wear rate of the abrasive erosion of polyurethane have been investigated by Zhang and coworkers [7]. However, in this paper, emphasis is placed on the surface chemical effects of the abrasive erosion of polyurethane in order to achieve a comprehensive understanding of the mechanisms of abrasive erosion for this polymeric material.

2. Experiments

2.1. Experimental material

Polyurethane was chosen as the test samples. The structure of macromolecular chains and cross-linking structure are given as follows:



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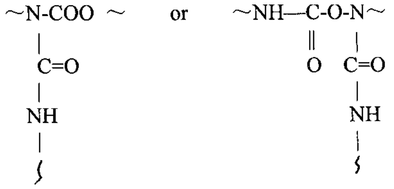

$$\begin{array}{c}\sim\mathrm{N\text{-}COO}\sim\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH}\\ |\\ \wr\end{array}\qquad\text{or}\qquad\begin{array}{ccc}\sim\mathrm{NH}{-\!\!-}&\mathrm{C\text{-}O\text{-}}&\mathrm{N}\sim\\ &\|&|\\ &\mathrm{O}&\mathrm{C{=}O}\\ &&|\\ &&\mathrm{NH}\\ &&|\\ &&\wr\end{array}$$

As shown, the macromolecular chains of polyurethane consist of the soft part of polyether and the hard part of polyisocyanaester. It has cross-linking of isocyanate groups and carbamide groups, and also has hydrogen bonds.

2.2. Experimental method

Using a special abrasive erosion testing machine designed by Zhang *et al.* [7], experiments on polyurethane have been conducted in three different fluids containing quartz particles with grade 7 hardness. These fluid mediums are water (H_2O, pH 7), polyacrylamide solution (PAM, pH 6) and sodium hydroxide solution (NaOH, pH 12). The test parameters are given as follows: (1) velocity of flow: 9.1 m/s; (2) particle concentration: 20wt%; (3) particle size: $300 \sim 450$ μm; (4) fluid medium temperature: 63–67 °C; (5) experimental duration: 120 h.

Before testing, the polyurethane samples were intentionally burnished to remove the pollutants from the surface of samples.

3. Surface analysis

3.1. XPS analysis

XPS analysis of the polyurethane surface was performed to understand the chemical changes during the eroding processes.

The elements and the binding energies for original and worn surfaces of polyurethane are shown as Table I. It can be seen that the atomic concentrations (wt%) of five elements have changed for the worn surfaces.

The C_{1s} spectra on the worn surface of samples are shown as Fig. 1. The prominent peak of the C_{1s} spectrum is symmetric for the original surface and its Full Width at Half Maximum (FWHM) is 1.3 eV. Some

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TABLE I The results of XPS analysis

	Elements composition(wt%)						Binding energy(eV)		
Specimen surface	O	N	Cl	Si	C	Na	O_{1s}	N_{1s}	C_{1s}
Original surface	11.1	2.3	0.4	1.0	85.1	/	533.2	400.5	285.0
Worn surface (in H_2O)	19.3	3.9	0.9	2.4	73.6	/	533.3	400.6	285.0
Worn surface (in PAM)	16.6	1.9	0.4	2.1	79.1	/	532.6	400.3	285.0
Worn surface (in NaOH)	21.0	2.0	0.5	1.4	72.1	3.1	532.3	399.5	285.0

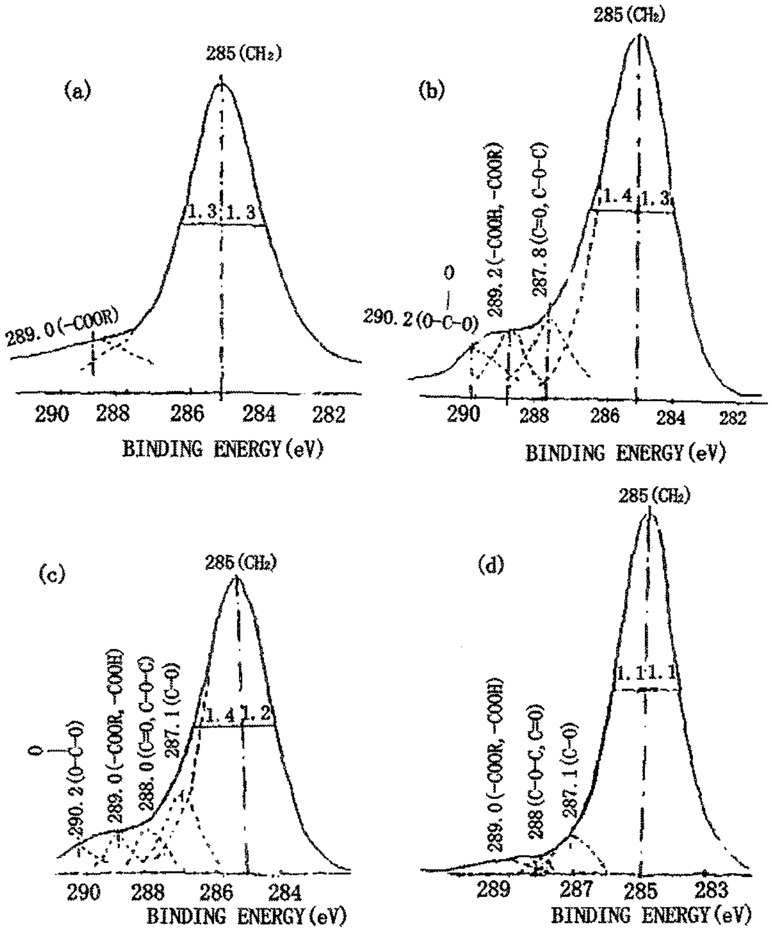
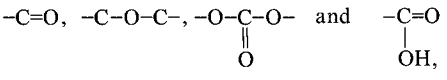


Figure 1 XPS spectra of polyurethane(C_{1s}): (a) Original surface, (b) Worn surface (in H_2O), (c) Worn surface (in PAM), (d) Worn surface (in NaOH).

functional groups like methylene groups (—CH_2) and ester groups (—COOR) can be identified. They are consistent with the structure of macromolecular chains of polyurethane. In addition, the peak of the N_{1s} spectrum on the original surface of the sample is single and the main functional group is C—N.

The peaks of the C_{1s} spectra are unsymmetric for the worn surfaces in three different mediums. The peaks of functional groups containing oxygen, such as,



$$-\mathrm{C{=}O},\quad -\mathrm{C{-}O{-}C{-}},\quad -\mathrm{O{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}}\quad \text{and}\quad -\underset{\underset{\mathrm{OH},}{|}}{\mathrm{C}}\mathrm{{=}O}$$

etc are evident. Moreover, it has been found that the intensity of the higher-binding-energy region of C_{1s} spectra for the worn surfaces is higher than that for the original surface. However, the peak of the N_{1s} spectrum is single.

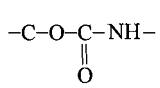
These XPS analyses demonstrate that chemical reaction occurred in the eroding processes.

3.2. FT-IR analysis

The functional groups of macromolecular chains for the original and the worn surfaces of polyurethane have been analyzed respectively with FT-IR.

It was found that the numbers of methylene groups (—CH_2—), carbonyl groups (—C=O) and ether groups (—C—O—C—) decreased and the number of benzene groups increased on the surface eroded in H_2O. Moreover, FT-IR analysis revealed that carboxyl groups were produced on the worn surface (Fig. 2).

On the surfaces eroded in PAM and in NaOH (Fig. 3), the number of methylene groups (—CH_2—) decreased. Moreover, the degree of reduction of methylene groups on the surface eroded in PAM is higher than that in NaOH. The decrease of ether groups (C—O—C) and the increase of amide groups indicate that the covalent bonds of carbon-oxygen (C—O) of



$$-\mathrm{C{-}O{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}NH{-}}$$

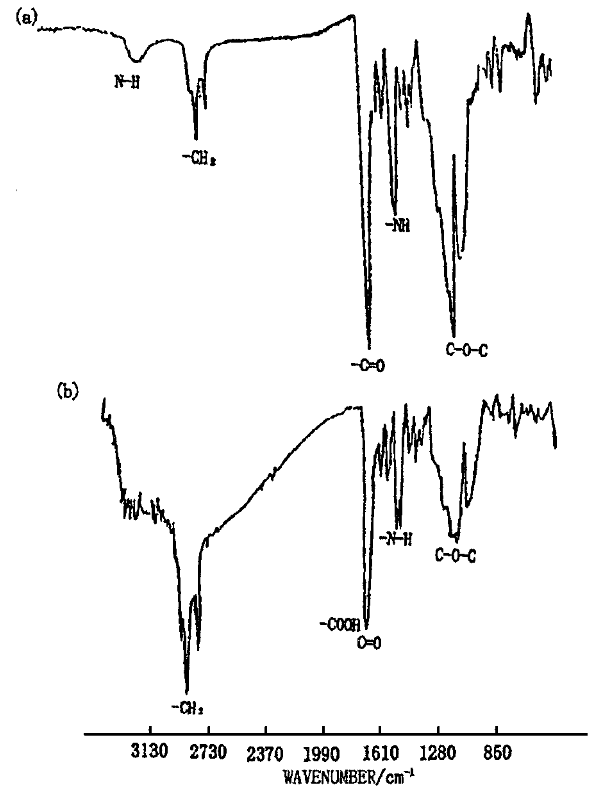


Figure 2 FTIR spectra of polyurethane: (a) Original surface, (b) Worn surface (in H_2O).

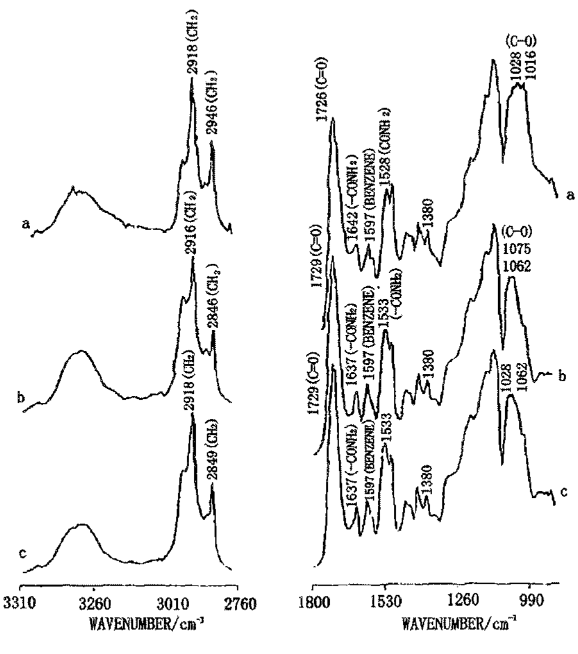


Figure 3 FTIR spectra of polyurethane: (a) Original surface, (b) Worn surface (in PAM), (c) Worn surface (in NaOH).

in the molecular chains were decomposed and the number of carbonyl groups (C=O) was increased. The degree of increase of carbonyl on the surface eroded in NaOH is higher than that in PAM. In addition, the number of benzene groups increased, too.

4. Discussion

4.1. Surface physical effects

SEM observations of the original and the worn surfaces of polyurethane are shown in Fig. 4. A number of parallel ridges that are perpendicular to the sliding direction were observed on the original surface (Fig. 4a). It is a typical abrasion pattern of rubber [8, 9].

On the contrary, the SEM morphology of the worn surface eroded in PAM and in H_2O is rather smooth. However, indentations, scratches, eroding marks, cracks and delaminations of subsurface were found on the worn surfaces (Fig. 4b, Fig. 4c, and d). These features are consistent with a wear mechanism for abrasive erosion of polyurethane that includes fatigue delamination, as well as the microcutting by the abrasives with larger kinetic energy as described previously [7].

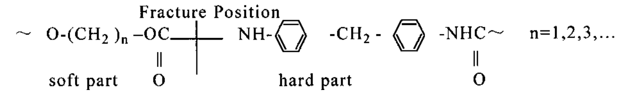
As for the worn surface eroded in NaOH, ploughings, scratches and accumulations of plastic deformations were found (Fig. 4e). Based on these observations, its wear mechanisms would be microcutting by abrasive particles with a certain kinetic energy, plastic fracture resulted from local plastic deformation and corrosive attack of NaOH. No delamination of the subsurface was found, which must be due to the corrosive action of NaOH. Moreover, the wear rate of polyurethane eroded in NaOH is the largest by comparison with that in the other two mediums.

4.2. Surface chemical effects

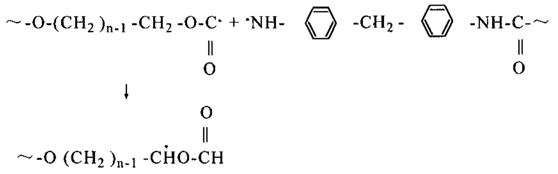
4.2.1. Fracture of macromolecular chains

FT-IR analysis revealed that the methylene groups ($-CH_2-$) and ether groups ($-C-O-C-$) decreased dramatically and the benzene increased (Figs. 2 and 3). It shows that the fracture of macromolecular chains occurred and the fractured site is the covalent bonds of $-CH_2-CH_2-$ at the soft part of the macromolecular chains as well as $-C-N-$ at the connection of the hard part and the soft part for the molecule chain.

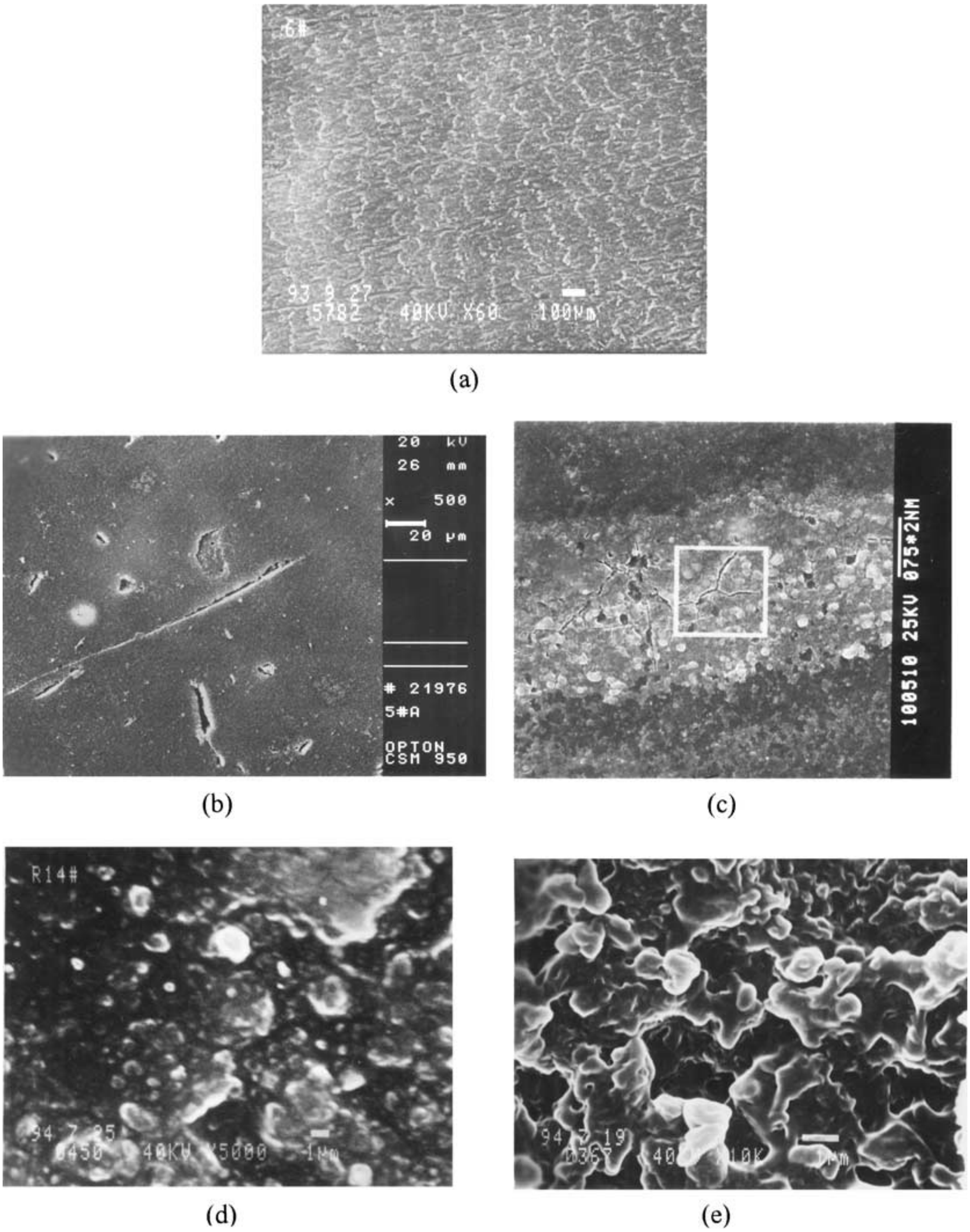
The position of fracture is given as follows:



The free radicals are:



The above conclusions could be proved from the changes of atomic concentration (wt%) of elements by XPS analysis, i.e., the relative weight concentration of carbon decreased on the worn surfaces eroded in the three mediums respectively and that of nitrogen increased on the worn surface eroded in H_2O (See Table I). While the macromolecular chains rupture, free radicals are produced. Then the ruptured free radical in the subsurface transfers to the adjacent macromolecular chains and results in the degree of cross-linking being increased, thus, the polyurethane sample might become brittle and produce micro-cracks. This is one



(a) (b) (c) (d) (e)

Figure 4 SEM micrographs of the surfaces of polyurethane: (a) Original surface, (b) Worn surface (in H_2O), (c) Worn surface (in H_2O), (d) Worn surface (in PAM), (e) Worn surface (in NaOH).

of the reasons inducing fatigue delamination of the subsurface of polyurethane eroded in PAM or in H_2O.

Referring to the micro-rupture models for polymers, i.e., the weakening of the hydrogen bonds and intermolecular Van der Waals forces, as well as the fracture of chemical bonds [10], the fracture process of macromolecular chains could be described further. By the action of microcutting or microtearing of flowing abrasive particles, both the hydrogen bonds and intermolecular Van der Waals forces of the irregularly oriented macromolecular chains were weakened, which caused the weakening of partial intermolecular attraction and the slipping of intermolecular chains. As a result, the degree of physical cross-linking decreased and some chemical bonds in the higher stress-intensity zone were ruptured. It is likely that the fractured site of the chains is at the soft part adjoining the connection of the hard part and the soft part of the macromolecular chains as the most easily cleaved chemical bonds are Carbon-Nitrogen (C—N) bonds. These covalent bonds have lowest chemical energy and large bond length [11]. The above conclusions could be proved from the decrease of $-CH_2$, C—O—C and the increase of benzene as well as the decrease of weight concentration (wt%) of carbon on the worn surface eroded in the three different mediums respectively.

4.2.2. *Thermal degradation*

Thermal degradation is the thermal decomposition of group, which is resulted from the decomposition of both the allophanate groups and the biuret groups.

Under the action of impacting, scratching, rolling and rubbing of particles on the surface of polyurethane, the hysteresis set of polyurethane occurs and the maximum shear stress generates at a certain depth beneath the surface [12] when a tangential force (friction force) acts on the surface of polyurethane. The above phenomena induce the hysteresis loss (heat) and raise the temperature of the subsurface which is higher than that of the surface as the heat transfer condition of the surface is much better [13].

As the accumulated heat is generated at a certain depth beneath the surface of polyurethane being in rubbery state, the kinetic energy of the macromolecule could be enhanced. Thus, the cross-linked covalent bonds and the molecular chain covalent bonds such as C—N and C—C might be fractured when the kinetic energy of the macromolecular chains becomes larger than the bonding energy of the crosslinked covalent bonds. Therefore, the degree of cross-linking decreased. For example, as the decomposition temperatures of allophanate and biuret are 146°C and 144°C respectively [14], these two kinds of groups are decomposed.

Therefore, the thermal decomposition of functional groups in the hard part of the macromolecular chains and in the cross-linking part of polyurethane occurs. Thermal decomposition might be the main cause for the occurrence of a number of cracks and delaminations on the surface eroded in H_2O or in PAM (Fig. 4c and d). However, as the phenomena of thermal decomposition are very complicated, further work is still needed.

4.2.3. *Hydrolysis*

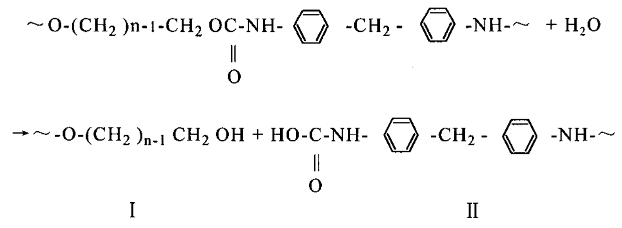
Increase in the relative weight concentrations for oxygen on the worn surface (Table I) means that oxygenolysis or hydrolysis might have occurred.

From analyzing of the polyurethane surface eroded in H_2O by FT-IR, it has been found that the number of carbonyl groups on the worn surface is decreased and the single peak is changed into double peaks. Moreover, the carboxyl groups can be found at the position of these peaks (Fig. 2). The above proves the occurrence of hydrolysis during the wear process of polyurethane eroded in H_2O as hydrolysis is one of the causes for the appearance of carboxyl groups.

As for the worn surfaces of polyurethane eroded in PAM and in NaOH, it has been found by FT-IR analysis (Fig. 3) that the amide groups and carbonyl groups are increased, which means the emergence of hydrolysis. Moreover, the degree of hydrolysis of the surface eroded in NaOH is the highest by comparison with that in the other two fluids.

The strongly polarized carbamate groups (—NHCOO—) in macromolecular chains could result in hydrolytic degradation once the temperature is high enough [15, 16]. The experimental temperature of mediums is about 63°C–67°C in a slurry tank, which is lower than that in an annular pipe. Moreover, the mechanical stimulation of the flowing particles on the surface eroded in mediums might strengthen the interaction between the macromolecular chains on the surface and the mediums, and then results in the hydrolysis of carbamate groups.

The reaction process is given as follows:



The reaction product (I) is easy to be flushed away as it is located in the soft part of the chains. However, the reaction product (II) is situated at the hard part of the chains.

Due to the fluid medium of PAM being acidic (pH 6), the number of carbonyl groups and amide groups on the worn surface eroded in PAM is increased (Fig. 3). Therefore, the degree of hydrolysis in PAM is higher than that in H_2O. As the hydronium ion (H^+) in acidic solution is combined at the polar carbonyl oxygen and made positively charged ($C{=}^{+}OH$), the electronic cloud is transferred to the oxygen of the carbonyl group and made the carbonyl carbon atom strongly positively charged. Thus, it is easy to produce nucleophilic addition reaction. Moreover, the action of cohering particles of solution (PAM) could make the interaction between surface and flowing particles much stronger. Therefore, a lot of reaction products (I) are flushed away. However, the reaction products (II) still exist on the surface as they are located in the hard part of the macromolecular chains of polyurethane, which induce the number of carbonyl groups and amide groups to be increased (Fig. 3). Because the molecular weight of the reaction products is decreased, the mechanical properties of polyurethane becomes so poor that the wear resistance is decreased.

Among the three different fluids, due to the medium of NaOH being basic (pH 12) and containing sodium, the hydrolysis for the surface eroded in NaOH is most complete. Moreover, the groups of —OR' in RCOOR' are easily replaced by the high-nucleophilic and basic groups of —OH [11], which induces carboxyl groups (COOH) to be produced. As soon as the occurrence of carboxyl groups, the reaction between carboxyl groups and basic group of —OH occurs and then produces salt. All of these reaction processes could be proved from the existence of sodium on the worn surface eroded in NaOH (Table I). For the above reasons, the increase in the number of carbonyl groups and the wear rate are the most, moreover, no crack and indentation occurs on the worn surface eroded under this condition.

4.2.4. *Surface oxygenated degradation*

As seen from the peaks of C_{1s} levels (Fig. 1), the sorts of carbon-oxygen functional groups, including

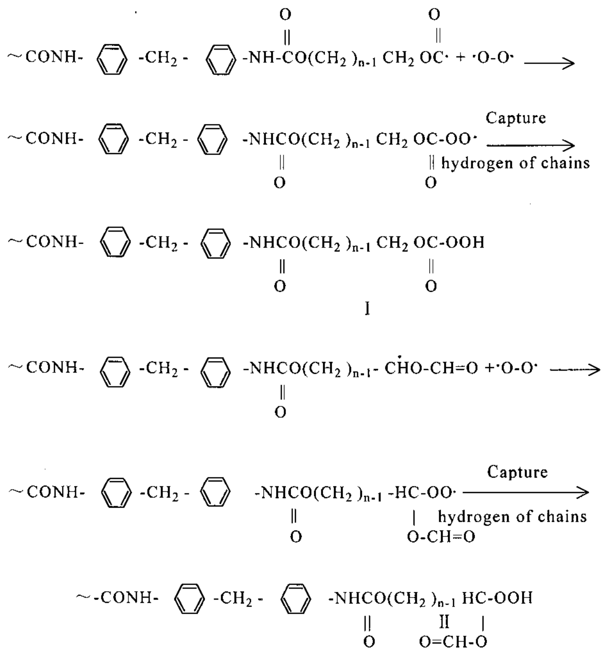
$$-\mathrm{O}-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-,\ \mathrm{R}-\underset{\underset{\displaystyle \mathrm{OH},}{|}}{\mathrm{C}}=\mathrm{O},\ \mathrm{C}-\mathrm{O},\ \mathrm{C}=\mathrm{O}$$

on the worn surfaces eroded in the three different fluids are more than that on the corresponding original surfaces. Moreover, the peak area in the region of high-binding energy of C_{1s} levels on worn surfaces eroded in PAM and in H_2O is much larger than that on the original surfaces (Fig. 1). It shows the surface being degraded by oxidation.

In addition, from the infrared peaks, it can be found that the methylene groups decrease and the 'V' shape occurs at higher-wave-numbers than for the surface eroded in water (Fig. 2). It shows that some of methylene groups at the soft part of the macromolecular chains are oxygenated and the oxidative products are carboxyl groups being bonded to each other by hydrogen bonds [16].

Due to the rupture of the covalent bonds of $-CH_2-CH_2-$ at the soft part as well as $-C-N-$ at the connection of the hard part and the soft part of macromolecule chains, active free radicals emerge. The ruptured active free radicals are apt to react with oxygen in water. The main oxidative product is peroxide. However, by means of a series of reactions and transmutations, the peroxide might turn into an oxidative product containing carbonyl groups ($-C{=}O$). Because the molecular weight of oxidative products is decreased, the mechanical properties of polyurethane become so poor that its wear resistance is decreased, some of the oxidative products containing carbonyl groups are flushed away.

The free radicals reaction process of oxygenation is given as follows,



The reaction products I and II are easily flushed away as they locate at the soft part of the macromolecular chains. Therefore, the carbonyl groups of ester groups on the worn surface eroded in H_2O are decreased in large numbers (Fig. 2). On the contrary, the carbonyl groups on worn surfaces eroded in PAM and in NaOH are increased (Fig. 3). Therefore, referring to the above free radicals reaction processes, it could be inferred that the degree of oxygenation for the surface eroded in H_2O is the most by comparison with that in the other two fluids according to the change of carbonyl groups. The above results could prove that the degree of hydrolysis of polyurethane eroded in PAM or in NaOH is higher than that eroded in H_2O, which causes a lot of methylene groups at the soft part of macromolecular chains to be flushed away. Therefore, the oxygenation of active free radicals for surfaces eroded in PAM or in NaOH is constrained. So, it would be concluded that the oxygenated degradation is not the main chemical effect of polyurethane samples eroded in PAM and in NaOH.

5. Conclusions

Under the present testing conditions, the surface physical effects of polyurethane eroded in three different mediums are microcutting, plastic fracture, and corrosion. Apart from the above, fatigue delamination is observed in the subsurface of polyurethane eroded in H_2O or in PAM.

The surface chemical effects of polyurethane eroded in three different mediums are:

a) Mechanical rupture of macromolecular chains. The position of fracture is the covalent bonds of $-CH_2-CH_2-$ at the soft part as well as the $-C-N-$ at the connection of the hard part and the soft part of the macromolecular chains.

b) Thermal degradation of allophanate groups and biuret groups.

c) Hydrolysis of carbamate groups. It is the main chemical effect of polyurethane eroded in PAM and in NaOH respectively.

d) Surface oxygenated degradation of methylene groups and ether groups. It is the main chemical effect of polyurethane eroded in H_2O.

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