Studies on deterioration of EPDM by hypochlorous acid. Part 1. Effect of dissociation of hypochlorous acid on surface morphology of black filled EPDM systems

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INTRODUCTION

In addition to its use in disinfection of the water supply, sodium hypochlorite (NaOCl) is routinely used for sterilising, bleaching and deodorising operations in the food industry, at medical and nursing care facilities, at waste-water treatment plants and in households [1,2]. The chief components of aqueous NaOCl solution are hypochlorous acid (HOCl) and sodium hydroxide (NaOH), the former maintaining an equilibrium with hypochlorite ion (OCl⁻) and dissolved chlorine (Cl₂) in aqueous solution. The HOCl, OCl⁻ and Cl₂ components of the HOCl dissociation equilibrium are known collectively as “free available chlorine” (FAC) and have great oxidising power. The dissociation constant [3] (pKₐ) of the weak acid HOCl is approximately 7.5 at 298 K, and the relative abundance of the OCl⁻ dissociated form thus increases at pH values more alkaline than 7.5, conversely, the relative abundance of HOCl increases at acidic pH, reaching 100%-97% at pH 4-6. At more acidic pH, chlorine is evolved. Since chlorine that cannot be retained in solution presents a hazard through dispersal as a gas, in practice the useful FAC components are HOCl and OCl⁻. Both HOCl and OCl⁻ have a chlorine atom of oxidation number +1 (Cl⁻) in the molecule, and act as powerful oxidising agents because of the strongly electrophilic character of Cl⁻. However, they have different mechanisms of action, and the sterilising and cleaning capabilities of aqueous NaOCl solution depend not on the concentration of FAC (C_FAC) but on the relative abundance of the FAC components.

Besides the ability to degrade organic matter because of the great oxidising power of FAC, an important factor in the sterilising capability of aqueous NaOCl solution is whether it can permeate the plasma membrane that protects bacterial cells. Since the plasma membrane is hydrophobic, the ionic dissociated form OCl⁻ cannot permeate whereas the electrically neutral undissociated HOCl can. The sterilising capability is hence dependent on the electrically neutral undissociated HOCl concentration [4-7], and a popular way of using aqueous NaOCl solution in recent years has been to render the solution weakly acidic with acid to augment the sterilising effect [1, 7]. The cleaning capability of aqueous NaOCl solution, on the other hand, is its ability to remove organic soil from the surface and this is dependent on the concentration of the dissociated form OCl⁻, which has an effective adsorption-substitution action on organic soil additional to its oxidative degradation action [6, 8, 9]. Now that the relation between the dissociation behaviour and sterilisation/cleaning mechanism of NaOCl is understood, control of the pH of the aqueous NaOCl solution according to the purpose of use has become widespread and has led to greater efficiency in cleaning and sterilisation.

While the utility of NaOCl is thus being constantly improved, deterioration of rubber packings due to residual chlorine has become a problem. To find a solution, the degradation mechanism of the typical rubber packing materials ethylene-propylene-diene monomer (EPDM) rubber [10, 11] and acrylonitrile-butadiene rubber (NBR) [12, 13] has been investigated, as has the behaviour of age-resistors [14, 15]. However, this research has been using aqueous NaOCl solution in the conventional neutral to weakly alkaline pH range, and...
has not hitherto focussed on the state of dissociation of HOCl.

In view of the knowledge gained from elucidation of the NaOCl sterilisation/cleaning mechanism, and the growing popularity of pH-controlled aqueous NaOCl solution in sterilisation/cleaning processes, the authors are attempting to clarify the rubber degradation mechanism with particular reference to the HOCl dissociation equilibrium components. So far we have studied the diffusion of FAC into EPDM as a function of pH and have shown that diffusion of chlorine into the EPDM interior depends on the concentration of undissociated HOCl, not the $C_{\text{FAC}}$, in the aqueous NaOCl solution [16]. In addition, a quantitative comparison of chlorine absorption and diffusion into a pure gum compound and carbon black (CB) compound of EPDM showed that CB increases the amount of HOCl absorbed but suppresses diffusion into the interior, with the result that chlorine is concentrated near the surface in the CB-EPDM compound as compared with a pure gum compound [17]. Information on the initial stages of degradation was obtained by quantitatively evaluating diffusion of chlorine under mild test conditions of low temperature and low FAC concentration, avoiding autodecomposition and carbon black (CB) compound of EPDM showed that CB increases the amount of HOCl absorbed but suppresses diffusion into the interior, with the result that chlorine is concentrated near the surface in the CB-EPDM compound as compared with a pure gum compound [17]. Information on the initial stages of degradation was obtained by quantitatively evaluating diffusion of chlorine under mild test conditions of low temperature and low FAC concentration, avoiding autodecomposition and detachment of rubber particles, etc, from the EPDM surface, and turbidification or discoloration of the aqueous NaOCl solution.

The problems arising from degradation of rubber packings are firstly fouling of the equipment and ingress of foreign matter into the product due to the particulate detachment phenomena known as “kuroko (black speck)” or “bokujuuka (inking)”, and secondly leakage of water due either to rupture or decline in water cut-off performance. As to the time sequence, the latter often follows the former, which may be taken to presage the latter. Our existing studies have shown the importance of HOCl in the dissociated state in the early stage of degradation and pointed to the existence of a degraded layer formed without change in appearance [16, 17]. The next task is to elucidate the mechanism of readily apparent degradation such as cracking or detachment from the EPDM surface, and to identify the risk of insidious degradation.

A powerful means of deducing the degradation mechanism would be to make use of the knowledge already gained systematically on the sterilisation/cleaning mechanism of hypochlorous acid. The parallel between permeation of the cell plasma membrane by FAC, a significant factor in sterilising ability, and the diffusion of FAC into hydrophobic EPDM [16] prompts the notion of EPDM degrading from within. Again, viewed as the ability to elute and disperse oxidised molecules and particles continually into the liquid, cleaning capability determines whether reaction products from EPDM degradation are detached into the liquid or remain on the EPDM surface, and this should be useful when considering changes in morphology and detachment.

The present study used accelerated degradation tests under harsher conditions than hitherto to clarify the effect of dissociation of hypochlorous acid on EPDM morphology and detachment. EPDM was immersed in aqueous NaOCl solution prepared to provide almost 100% of either HOCl or OCI by adjustment of pH, and the changes in EPDM morphology with temperature and FAC concentration were examined. It was discovered that the pattern of degradation of EPDM differed greatly with the state of dissociation of HOCl, and it proved possible to reproduce the characteristic detachment phenomena in the actual deterioration of rubber packing. Surface morphology is referred to simply as morphology in the report below.

**EXPERIMENTAL**

**Preparation of specimens**

The EPDM used was a commercial product (3085, Mitsui Chemical Co.) of ethylene content 62% and diene (ethylene norbornene) content 4.5%. The carbon black (CB) was Tokai Carbon Co. SEAST 3 (HAF, N330). A difunctional peroxide crosslinker (Perbutyl P, NOF Corp.) was used as the crosslinking agent.

EPDM 100 parts by weight was mixed with CB 60 parts by weight and crosslinking agent 2 parts by weight on a 6-inch open roll and then pressed for 20 min at 438 K to obtain crosslinked rubber sheet of approximate thickness 1.2 mm. Test pieces measuring 20 cm x 20 mm were cut by razor from the crosslinked sheet and used for immersion testing in aqueous NaOCl solution.

**Immersion testing in NaOCl solution**

To provide the solution for immersion testing (NaOCl test solution), NaOCl reagent of FAC concentration (C_{FAC}) 60,000 ppm (Lot DWF2416, Wako Pure Chemical Industries) was diluted to the prescribed C_{FAC} with ultrapure water and adjusted to pH 10 or 4.5 by addition of NaOH or HCl solution. The EPDM test piece was immersed in a test tube holding 20 mL of NaOCl test solution, the tube was tightly stoppered, protected from light with aluminium foil, and left to stand for 7 days in a thermostatic tank at the prescribed temperature (277-323 K). On withdrawal from the test solution, the test piece was rinsed with ultrapure water, air-dried and then dried in vacuo for 24 hours at 323 K.
Morphological examination

An Olympus Lext OLS4000 confocal laser scanning microscope (CLSM) was used with a x50 objective lens to examine the morphology in the middle of the test piece. The arithmetic mean roughness ($S_a$) was computed from the three-dimensional data obtained over an area of 260 µm × 260 µm.

To study the fine structure of the specimen, the secondary electron images at low magnification ($×1000$) and high magnification ($×5000$) from a field emission scanning electron microscope (FE-SEM, JEOL Ltd. JSM-7500FA) were observed. The accelerating voltage was set at 2 kV and no vapour deposition or other electro-conductive treatment was applied to the specimen.

RESULTS

Changes in test piece morphology at pH 4.5

**Figure 1** shows the three-dimensional CLSM image (**Figure 1a**) and FE-SEM secondary electron images (**Figure 1b** and **c**) of a test piece (control) that had not been immersed in the test solution. The striped pattern running left to right in (**a**) and from upper right to lower left in (**b**) and (**c**) has been transferred from the polishing marks on the die surface during press forming. The $S_a$ of the control found from **Figure 1a** was 0.06 µm.

**Figure 2** shows three-dimensional images of the central part of a test piece immersed 7 days in the test solution of pH 4.5. When the immersion temperature was varied at a $C_{FAC}$ of 500 ppm, almost no change was seen at $×303$ K (**Figures 2a-2d**) and $S_a$ was about the same as for the control. Some surface irregularity became visible at 313 K (**Figure 2e**) and the morphology was clearly different from the control at 323 K (**Figure 2h**), at which the value of $S_a$ also increased. When the immersion temperature was set at 323 K and the $C_{FAC}$ was varied, changes in morphology accompanied by increase in $S_a$ were clearly identifiable even at the low concentration of $C_{FAC} = 125$ ppm (**Figure 2f**). The morphology changed markedly with increase in $C_{FAC}$, and the value of $S_a$ at $C_{FAC} = 1000$ ppm (**Figure 2j**) was about 10 times that of the control. Regardless of whether or not morphology was affected, test pieces immersed in the pH 4.5 test solution were never tacky to the touch.

**Figure 3** shows the secondary electron images from the FE-SEM of test pieces immersed for 7 days at different temperatures. Although almost no difference from the control (**Figure 1b**) was evident at low magnification in **Figures 3a-e**, the striped pattern transferred from the die gradually became fainter above 296 K in the high magnification images (**Figures 3f-j**), at the same time, a particulate structure attributable to CB became clearly discernable. **Figure 4** shows the secondary electron images from FE-SEM of test pieces immersed for 7 days at 323 K in pH 4.5 test solutions of different $C_{FAC}$. The striped pattern seen in the specimen series for which the temperature was varied in **Figure 3** was only faintly identifiable in the low magnification image at $C_{FAC} =$...
125 ppm, revealing a major change in morphology. Crack-like structure was visible at $C_{\text{FAC}} = 125$ ppm and 250 ppm, though in the case of a crack the geometry on both sides of the channel should match, as with adjacent puzzle pieces. However, as the structure looks like a string of holes (Figure 4f) at high magnification, and the geometry of opposite sides of the channel does not match (Figure 4g), the structure appears to be pits formed by localised degradation rather than a crack. The pits are small and round at $C_{\text{FAC}} = 500$ ppm, become even smaller at $C_{\text{FAC}} = 750$ ppm and all but vanish at 1000 ppm. Examination at high magnification revealed a particulate fine structure of clearly defined outline at 125 ppm and 250 ppm but the particles are no longer prominent at 500 ppm, and at $\times750$ ppm the particulate structure was no longer identifiable. Cracks like that visible on the left of Figure 4h were seen at $\times500$ ppm, and were more prominent at the margins of the specimen.

Figure 5 shows the surface at the outer edge of a test piece immersed for 7 days at 323 K in test solution of pH 4.5, $C_{\text{FAC}} = 1000$ ppm, together with the threedimensional measurement data. Figure 5a is a brightness image from CLSM (brightness mapping of the reflected laser light), the position $x = 0$ on the left of the diagram denoting the edge of the test piece. A zone of low brightness extends about 0.5 mm into the test piece from the edge, and islands of low brightness are present a little towards the centre. The secondary electron image from

**Figure 3.** SEIs of surfaces of carbon black filled EPDM from CLSM after being immersed in NaOCl solutions of pH 4.5 for 7 days

**Figure 4.** SEIs of surfaces of carbon black filled EPDM after being immersed in NaOCl solutions of pH 4.5 at 323 K for 7 days

**Figure 5.** Morphologies and line profiles of the outer edge portion of carbon black filled EPDM after being immersed in NaOCl solutions of pH 4.5 containing 1000 ppm FAC at 323 K for 7 days. (a) Brightness image from CLSM, (b) SEI at point 1, (c) SEI at point 2, (d) height profiles of line 1 and line 2
FE-SEM of the peripheral low brightness zone (point-1 in Figure 5a) is shown in Figure 5b. Degradation has proceeded very vigorously, giving a structure in which particles presumed to be CB are clearly identifiable as pores. The secondary electron image of the boundary zone between an island of low brightness and area of high brightness (point-2 in Figure 5a) is shown in Figure 5c. The left half is the low brightness zone, where degradation similar to that as in Figure 5b has clearly occurred. The right half is the high brightness zone and has a morphology similar to the middle of the test piece (Figure 4j).

Figure 5d shows the profile of the horizontal height of the surface on line-1 and line-2 in Figure 5a versus the distance x from the edge. The height was small near the edge, increasing with a sharp change in level of roughly 20 µm at around x = 0.5 mm, the height then decreased gently towards the centre. The low brightness areas seen as islands were almost 20 µm lower than the high brightness zone.

**Changes in test piece morphology at pH 10**

Figure 6 shows three-dimensional CLSM images of test pieces immersed for 7 days in a test solution of pH 10. When the immersion temperature was varied at C_FAC = 500 ppm, almost no change in morphology was seen up to 313 K (Figure 6a-e). When the immersion temperature was set at 323 K and the C_FAC was varied, morphology was affected irrespective of C_FAC across the range 125-1000 ppm. In contrast with the results at pH 4.5, however, S_a showed no tendency to increase with increase in C_FAC, on the contrary, the surface roughened at the lowest concentration of 125 ppm (Figure 6f), which gave a large value of S_a.

Figure 7 shows the FE-SEM secondary electron images for test pieces immersed 7 days at different temperatures in a test solution of pH 10, C_FAC = 500 ppm. Although change in morphology at 313 K or above was seen at low magnification, the pattern transferred from the die persisted. At high magnification the surface appears to have dissolved at ×296 K, the structure presented at 313 K being a mixture of zones where particles presumed to be CB are distinctly visible and zones where the particles are indistinct.

Figure 8 shows the secondary electron images of test pieces immersed for 7 days at 323 K in pH 10 test solutions of different C_FAC. The striped pattern deriving from the die was completely invisible at 323 K. At low magnification the surface was roughest at C_FAC = 125 ppm as in the CLSM results and flat at high concentration. At high magnification numerous pits appeared at C_FAC = 125 ppm, and presumed CB particles were clearly identifiable. The surface flattened somewhat at C_FAC = 250 ppm, but as at 125 ppm, pits...
and presumed CB particles were identified. At $C_{\text{FAC}} \times 500$ ppm the surface was flat with no evidence of pits but there was some difference in the appearance of the presumed CB particles, which were most clearly delineated at 1000 ppm, ill-defined at 750 ppm, and intermediate between the two at 500 ppm.

**Material detached from test pieces**

A change in the appearance of the test solution was noted after immersion at $C_{\text{FAC}} \times 500$ ppm at 323 K, at pH 4.5 the test solution assumed a transparent yellow colour and a black sediment was seen. The change at pH 10 was very different, the test solution developed a turbid black colouration and no sediment was seen. The turbid solution cleared on acidification with hydrochloric acid, and a black coagulum was obtained. The test piece immersed under conditions giving rise to black turbidity became tacky to the touch, and black foreign matter readily lifted from the surface before drying.

**Figure 9** shows the FE-SEM secondary electron image of solid matter obtained from the test solutions after a test piece had been immersed for 7 days at 323 K, $C_{\text{FAC}} = 1000$ ppm. **Figure 9a** shows the sediment recovered from the pH 4.5 test solution, a size of around several tens of µm predominating. One surface of each particle is flat, mostly with the same structure as the immersed test piece surface. Apart from the flat surface, the particle is irregularly shaped and although porous, resembling the low brightness zone in **Figure 5**, the presumed CB particles are poorly delineated. **Figure 9b** shows material filtered off from the pH 10 test solution, the morphology is essentially the same as for particles of the CB filler used.

**DISCUSSION**

**Acceleration of changes in morphology by heat**

The change in morphology of the test pieces was more marked the higher the temperature of immersion, decrease in temperature requiring observation at high magnification to ascertain any change, below room temperature it was impossible to identify change in morphology even on the high magnification FE-SEM secondary electron images (**Figure 3, Figure 7**). Rubber is three-dimensionally crosslinked and does not usually dissolve in solvents, unlike plastics, moreover, it is incapable of plastic deformation by heat or stress. Morphological change therefore necessitates scission of molecular chains by chemical reaction. The effect of heat in oxidation with hypochlorous acid has been studied in detail in evaluating sterilisation and cleaning properties and the reaction is known to exhibit temperature dependence of Arrhenius type [7]. Hence acceleration of change in EPDM morphology by heat is to be expected.
Analysis of morphological change also requires consideration of the effects of elution or detachment of the degradation reaction products on spatial organisation. In the case of rubber, changes to functional groups through chemical reaction do not necessarily alter the morphology. It could therefore be a change in spatial organisation due to elution or detachment that greatly impacts on morphology. The interfacial phenomenon of elution or detachment of reaction products is presumably due to the effect of hypochlorous acid in removing solid surface deposits (cleaning), and once again the resultant morphological change would be accelerated by heat.

Change in morphology at pH 4.5

At pH 4.5, when the hypochlorite is almost 100% HOCl, degradation with accompanying change in appearance of the test solution occurs under test conditions of high temperature (323 K) and high concentration ($C_{\text{FAC}} \times 500$ ppm). No change in either the test solution or the high magnification secondary electron image of the test piece is evident after immersion at low temperature (Figure 3f and g). However, it may be inferred from the test conditions that chlorine diffuses at least tens of µm into the EPDM [18], and the initial stages of degradation by HOCl will clearly be difficult to track from change in morphology. Even if the test solution is unaffected, the high magnification secondary electron image of the test piece reveals morphological change at $C_{\text{FAC}} = 500$ ppm and $\times 296$ K (Figure 3h-j) or when the temperature is 323 K at low concentration (Figure 4f-g). In either case, the change is in the direction in which the presumed particles of CB become clearly observable, suggesting that oxidised EPDM molecules are eluted from the surface. As the pits form locally, it is clear that elution from the EPDM surface does not proceed uniformly. Under high temperature-high concentration conditions, severe changes occur (Figure 5) at the periphery of the test piece (i.e. close to the cut surface), suggesting degradation readily proceeds from defects such as scratches in the surface.

The shape of the particles (Figure 9a) and the form and shape of the perimeter of the test piece (Figure 5) would indicate that the sediment forming at high temperature and concentration comprises rubber fragments shed by the test piece, presumably replicating the “black speck” phenomenon. Shedding of rubber fragments was more prominent the higher the concentration $C_{\text{FAC}}$, but although the macroscopic irregularities increase in size with increase in $C_{\text{FAC}}$ at the centre of test piece where little material is shed (Figure 2h-j), the fine structure at the microscopic level due to pits and presumed CB particles is no longer visible, the surface appearing smooth (Figure 4). The reason why fine structure is no longer visible could be that organic matter sediments onto the surface, pointing to reprecipitation of eluted EPDM molecules or migration of EPDM of much reduced molecular weight to the surface. Preferential detachment of CB from the surface layer is another possibility but since there is no evidence of CB becoming suspended in the test solution, this can be discounted. The development of cracks in the EPDM precipitated or transferred onto the surface (Figure 4h) and absence of cracks suggest embrittlement of the surface.

Change in morphology at pH 10

As at pH 4.5, the change in appearance of the test solution under test conditions of high temperature (323 K) and high concentration ($C_{\text{FAC}} \times 500$ ppm) at pH 10 when the hypochlorite is almost 100% dissociated to OCI indicated stable suspension of black microparticulate matter. From its colour and shape (Figure 9b), the floating matter is presumably CB or composite CB-rubber particles detached from the test piece, reproducing the “inking” phenomenon. Although no change is seen at temperatures up to 288 K under the present observation conditions, particles presumed to be CB are clearly observable, pointing to elution of EPDM, at $\times 296$ K and $C_{\text{FAC}} = 500$ ppm (Figure 7h-j) or at 323 K and low concentration (Figure 8f-g). Thus, under conditions leaving the appearance of the test solution unchanged at pH 10, the change in morphology seems greater than at pH 4.5, and at 323 K, $C_{\text{FAC}} = 125$ ppm, the surface roughness increased to a level detectable by CLSM. Under conditions where the test solution blackens, the surface flattens, this may be attributed to the capacity that CB has for detachment and reorganisation. Since the dissociated form OCI does not diffuse significantly in EPDM [16, 17], degradation reactions remain at the surface, this means that, if the reaction products detach from the surface as in this case, the degradation mechanism is difficult to discern from analysis of the degraded test piece. Nevertheless, detachment effects like surface tackiness and blackening of the test solution would indicate rupture of EPDM molecular chains by OCI.

Elution or dispersal of reaction products

Elution or dispersal of reaction products goes no further than elution of EPDM molecules at pH 4.5, but at pH 10 proceeds to suspension of CB and “inking”. This may be attributed to the aforementioned difference in cleaning effect of hypochlorous acid on organic contaminants at different pH values. The diffusion process whereby the dissociated form OCI adsorbs and substitutes at the solid-liquid interface is rate-determining in cleaning with hypochlorous acid and the cleaning characteristics are dependent on the OCI concentration [7, 8, 19].
At pH 10, therefore, a strong cleaning effect due to hypochlorous acid is operative, promoting detachment of reaction products into the liquid. At pH 10, moreover, the carboxyl groups introduced by oxidation dissociate, acquiring a negative charge. As a result, hydration of reaction products is promoted, while electrostatic repulsion occurs at the oxidised surface, elution or dispersal of reaction products into the test solution would therefore be promoted. Coagulation of the floating matter on acidification of the blackened test solution arises precisely because electrostatic repulsion is lost. Coagulation of the “ink” with change in pH suggests the possibility that material originating from “ink” is involved in incidents reported as “black speck”, and it should be possible to confirm this based on the situation in which it occurs and the morphology.

CONCLUSIONS

With particular regard to the state of dissociation of hypochlorous acid, EPDM test pieces were immersed in NaOCl test solutions adjusted in pH to give almost 100% of undissociated HOCl and almost 100% of its dissociated form OCl⁻, respectively, and the changes in surface morphology were evaluated. The findings were as follows.

1. At pH 4.5, with HOCl almost 100% undissociated, localised degradation gave rise to pits, blisters and cracks and the roughness of the EPDM surface increased noticeably. The test pieces were never tacky to the touch. Rubber fragments of at least tens of µm, detectable with the naked eye, became detached and settled in the test solution, though the solution retained its clarity, free from suspension of CB.

2. At pH 10, with almost 100% dissociation to OCl⁻, pits formed and the roughness of the EPDM surface increased, though blisters and cracks were absent. The test pieces were tacky to the touch. The test solution developed a black turbidity due to suspended CB but no solid matter precipitated.

3. Accelerated degradation in which the state of dissociation of the hypochlorous acid was controlled produced very different changes in morphology at the EPDM surface. The detachment seen in accelerated degradation at pH 4.5 and pH 10 appeared to reproduce the “ink speck” and “inking” phenomena, respectively. Defining the conditions for their occurrence would be useful for evaluating endurance in this respect.

REFERENCES