Evaluation of the Chemical Resistance of High-Density Polyethylene Geomembranes

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ABSTRACT: The chemical resistance of high-density polyethylene geomembranes (GMs) with smooth and textured surfaces in notched and unnotched forms at different pH values and in the range of 20–80°C was examined with stress crack resistance testing. Surface microcracks in GMs were observed in scanning electron microscopy images. Smooth and textured GMs did not show significant differences in their mechanical behaviors. The yield strength decreased with the temperature, pH, and exposure time. The yield strain increased with the temperature, but there were no good correlations with pH values. The break strength also decreased with the temperature and showed no significant correlation with pH variations. The break strain did not show a good correlation with the temperature and pH variations. The stress crack resistance was independent of pH variations but significantly depended on the temperature. It was negatively correlated with the exposure time. J Appl Polym Sci 117: 2575–2582, 2010

Key words: mechanical properties; structure-property relations

INTRODUCTION

Geomembranes (GMs) have been used mainly in environmental, geotechnical, and transportation applications, and their primary function is acting as a liquid or gas barrier. In general, high-density polyethylene (HDPE) is used as a raw polymer to manufacture GMs because of its excellent impermeability (e.g., lower water vapor transmission property).[1,2] In Korea, most waste landfills contain waste leachate solutions that are either acidic or alkaline.[3] When HDPE GMs are damaged and exposed to these waste leachate solutions, it is possible for them to decompose, and their mechanical performance will be reduced.[4] Therefore, the chemical resistance and durability of GMs are decreased, and this will influence the stability of waste landfills. Refuse in landfills can make leachate solutions with pH values ranging from 3 to 12 within 3 months, and pH values of 4.4–7.5 and 6.6–7.5, respectively, have been recorded.[3,5,6] Also, the temperature variation ranges of 25–43 and 50–70°C within several months have been mostly recorded in waste landfills.[3,5,7,8] However, there are not enough reports available to observe the chemical resistance of HDPE GMs via mechanical property variations under different temperatures. In this study, the chemical resistance of HDPE GMs with smooth and textured surfaces was investigated at pHs 4, 7, and 8 and at 20, 40, 60, and 80°C to reflect long waste landfill periods and real leachate conditions. To investigate the chemical resistance of HDPE GMs, notched constant tension load (NCTL) tests were adopted.

EXPERIMENTAL

Preparation of the GM samples

Commercially available smooth and textured HDPE GMs were used for this study. The GM specifications are given in Table I.

Tensile testing of GMs was used to compare the mechanical properties before and after damage by NCTL testing. For tensile and NCTL testing, GM specimens were cut into dumbbell dimensions with a blanking die apparatus as specified by ASTM D 638 and ASTM D 5379, respectively. Samples made for tensile and NCTL tests are illustrated in Figure 1 with notch marks on only 2 samples. These notch marks were made in the middle area of each

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TABLE I
Specifications of the GMs

Property	ASTM	Surface type of HDPE GMs	
		Smooth	Textured
Thickness (mm)	D 751	2.5	2.5
Density (g/cm^3)	D 1505	0.948	0.948
Tensile properties	D 669		
Yield load (kg)		30	30
Break load (kg)		50	50
Yield elongation (%)		10	10
Break elongation (%)		700	700
Stress crack resistance (h)	D 5397	250	250

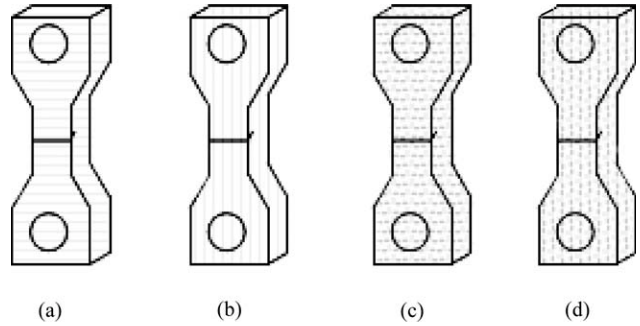


Figure 2 GMs used for NCTL testing: (a) smooth in CMD, (b) smooth in MD, (c) textured in CMD, and (d) textured in MD.

specimen to 20% of the thickness of its cross section. Thus, samples for tensile testing were classified as unnotched smooth (UNS), unnotched textured (UNT), notched smooth (NS), and notched textured (NT).

For NCTL testing, samples were cut in the machine direction (MD) and cross machine direction (CMD), and notches were marked on all the samples. Thus, two holding holes were made on each of these samples as specified in ASTM D 5379. The samples used for NCTL testing are illustrated in Figure 2.

NCTL tests

To observe the chemical resistance, tensile testing was performed to measure the changes in the mechanical properties. HCl, NaOH, and distilled water were used to control and keep the pH values of 4, 7, 8, and 12 on the basis of previously published reports.[3,5,6] Testing conditions are given in Table II. Five specimens from each treatment were tested for the load and elongation at yield with a constant rate of loading on a tensile testing machine every 30 days. In this experiment, the load and elongation at yield were examined. To observe the chemical resistance of GMs, NCTL testing was carried out for the original and treated samples: we measured the crack resistance in unnotched and notched GMs. For NCTL tests used to examine the chemical resistance, GM samples were treated with pH 4 and 8 solutions at 40 and 60°C. The test conditions are given in Table III. The rupture time of stress crack resistance was measured for five GM specimens with each treatment at the end of the test. The applied stress levels ranged from 25 to 60% of the yield stress in increments of 5%. The morphology of the surfaces of the notched and unnotched GM specimens was examined with scanning electron microscopy (SEM) before and after the tensile and NCTL tests.

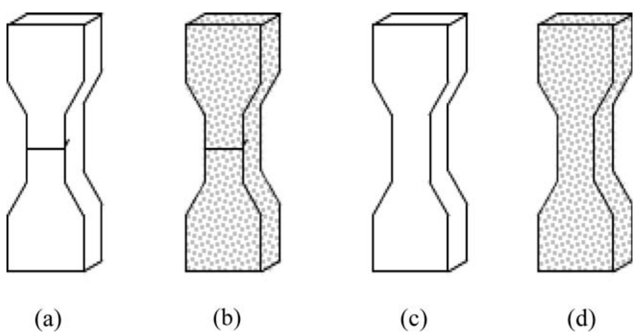


Figure 1 GMs used for tensile testing: (a) NS, (b) NT, (c) UNS, and (d) UNT.

RESULTS AND DISCUSSION

Tensile properties

To analyze the tensile property variations of GMs under various pH and temperature conditions, we used smooth and textured GMs that are generally used in waste landfill construction as water barriers. However, according to our statistical analysis, they do not show significant differences below the 95% significant level. Therefore, we used the data obtained from smooth-type GMs. Figures 3 and 4 show the load and elongation at yield for notched and unnotched GM samples at different temperatures and pH values for 120 days. According to Figure 3, there was no significant reduction of the load at yield for 120 days at 20°C. However, the load at yield was more sensitive to temperature, and higher temperatures such as 60 and 80°C produced a greater reduction of the load at yield. This reduction amounted to 20–68% after 90 days. Thus, acidic and

TABLE II
Testing Conditions for the Tensile Tests

pH	Temperature (°C)	Test duration (days)
4	20, 40, 60, and 80	30, 60, 90, and 120
7		
8		
12		

TABLE III
Test Conditions for the NCTL Tests

pH	Temperature	Test duration
4 8	40 and 60°C	Up to 1200 h

alkaline pH values such as 4 and 12 showed a higher reduction of the load at yield than pH values of 7 and 8, especially at 60 and 80°C. On the basis of these findings, it is hypothesized that a pH change from 3 to 12 in waste landfills within 3 months is the main cause of lower yield loads, and this

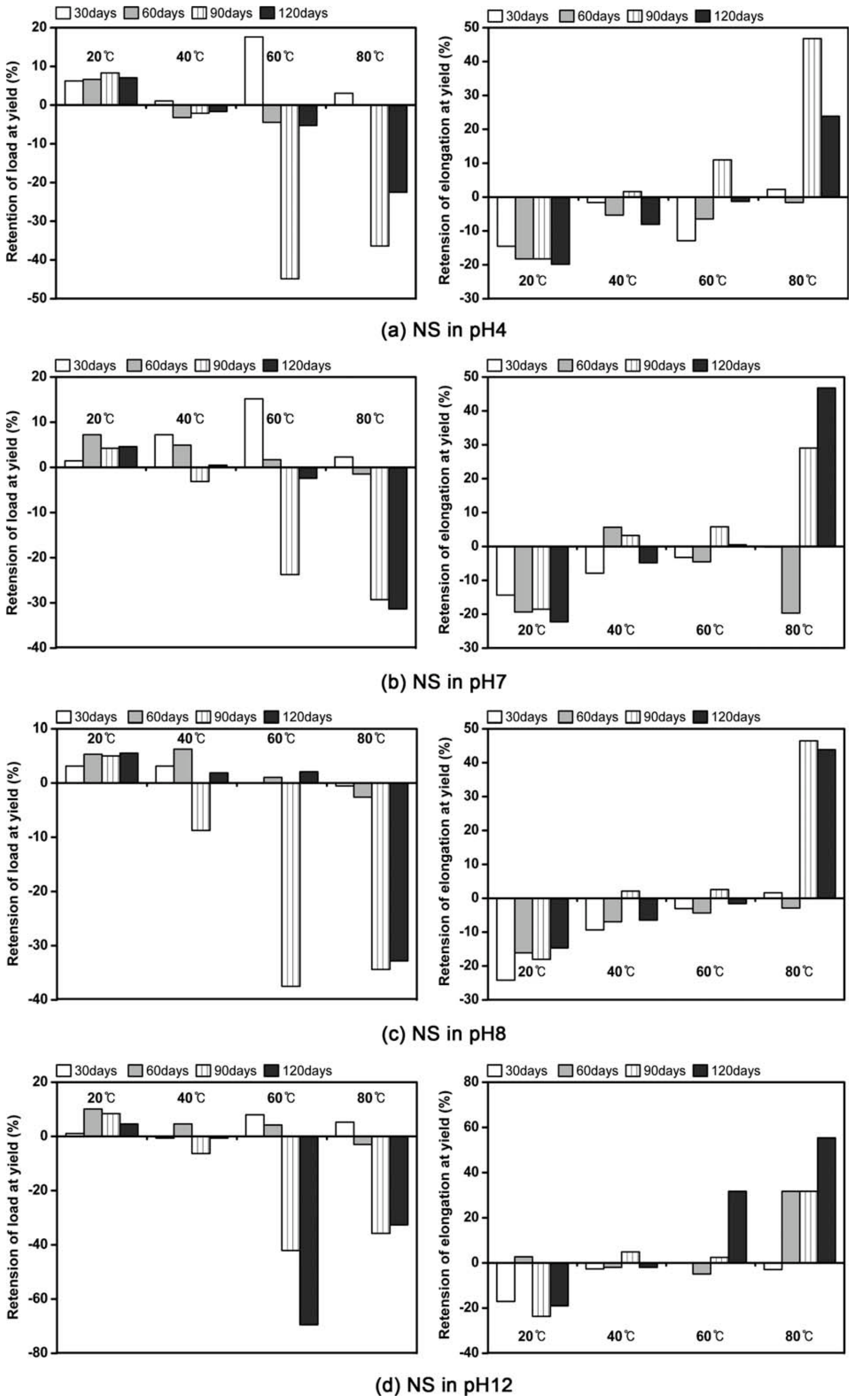


Figure 3 Load and elongation at yield of notched GMs at different temperatures and pH values.

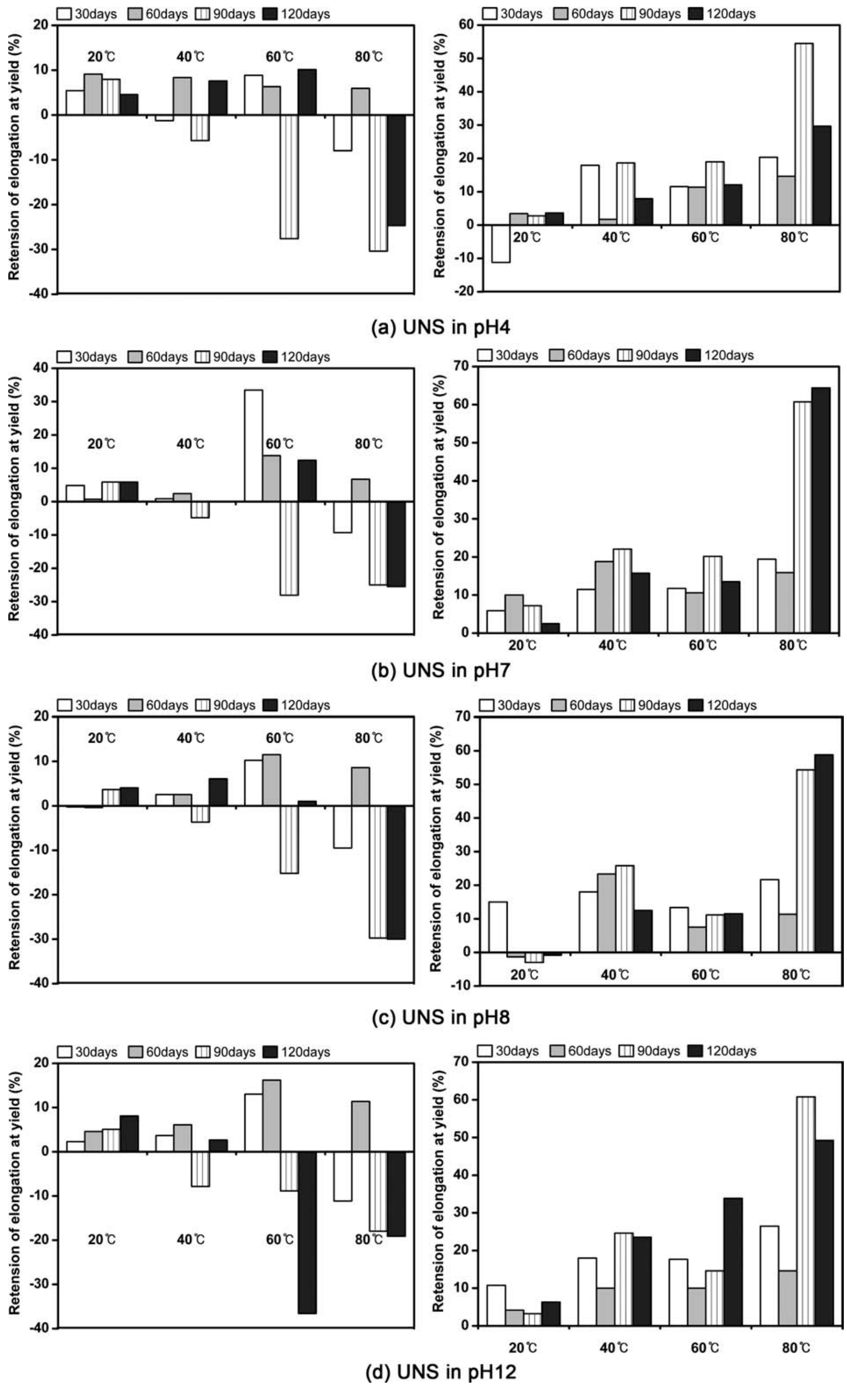


Figure 4 Load and elongation at yield of unnotched GMs at different temperatures and pH values.

negative effect may decrease with time. In Figure 3, N-S GM samples show a reduction of the elongation at yield from their original values at all tested pH values at 20°C. This does not mean any significant effect of the exposure time at this temperature. However, with increasing temperature, there was a tendency of increasing elongation at yield (versus reductions at 20°C), and this was also positively correlated to the exposure time. In comparison with load and elongation figures, the load at yield decreased with increasing elongation. The highest elongation at yield appeared at 80°C, especially after

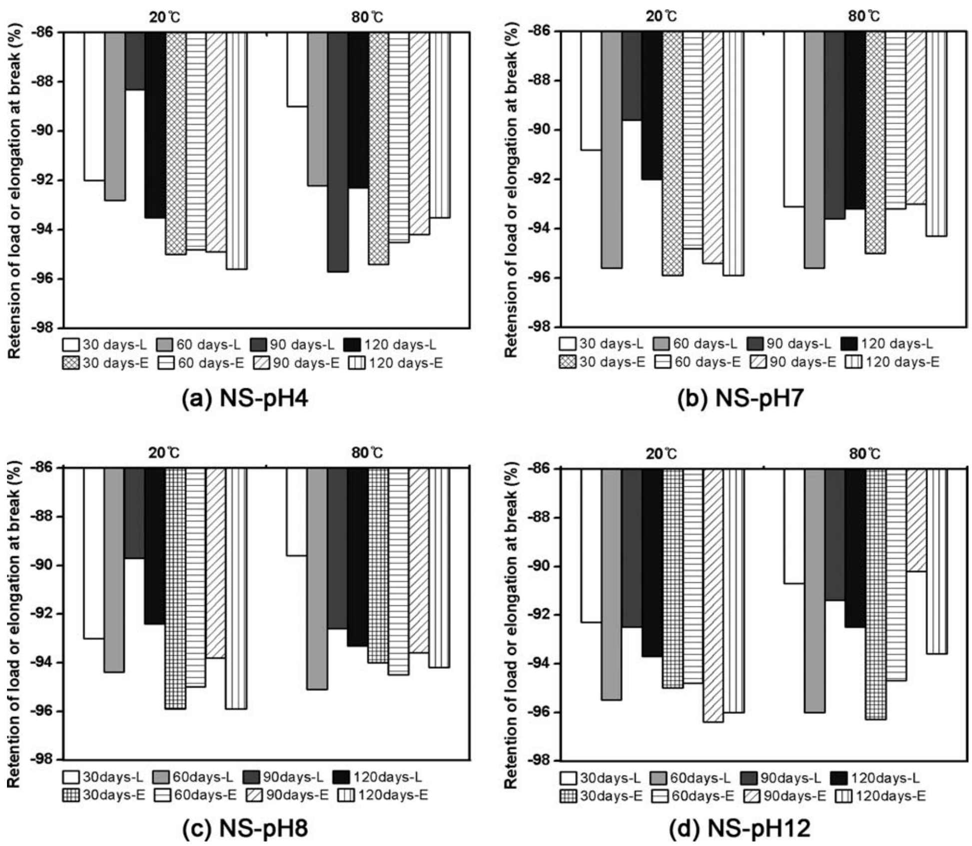


Figure 5 Load (*L*) and elongation at break (*E*) of notched GMs at different temperatures and pH values.

90 days. Thus, this was about 30–45% higher than the original value.

As displayed in Figures 3 and 4, unnotched GM samples showed higher loads at yield than notched samples. The reduction of the load at yield for unnotched GM samples amounted to 4–35%. Thus, the yielding phenomena started with lower loads at higher temperatures after 90 days. Moreover, alkaline and acidic pH values affected lower yield loads for the unnotched GM samples. According to the yield elongation graphs presented in Figure 4, the unnotched GM samples at the yield point showed significantly higher elongations (mostly with a positive retention of elongation) in comparison with the notched samples. Thus, the yield elongation for the unnotched GM samples showed a positive tendency of increasing with the temperature. This means that at higher temperatures the unnotched GM samples yielded under higher elongation. Hence, in certain cases, a tendency could also be observed with increasing pH values, especially at 80°C.

Figure 5 shows the load and elongation behaviors at the break point for notched GM samples at pH values of 4, 7, 8, and 12 with different temperatures. Load retention values were calculated with reference to the original breaking values given in Table I. In this experiment, we compared the load and elongation values at 20 and 80°C because, according to the analysis, data obtained at 20 and 40°C and at 60 and 80°C did not show significant differences. As shown in Figure 5, the breaking load and elongation were reduced much more in the notched GM samples. These reductions amounted to more than 88% for the load and more than 90% for the extension at break. This implies the effect of damage on the load and elongation at rupture of GMs. At 20 and 80°C, an increasing tendency of breaking of notched GM samples at much lower loads was shown for the first 60 days, and after this period, this tendency was reduced (except in a pH 4 solution). However, between 60 and 90 days, notched GM samples ruptured at higher loads than in other tested periods. Thus, in most of the cases, the load at break decreased at the higher temperature (80°C). Significant correlations were not found between the variation of the breaking load and the pH value for notched GM samples. Thus, in most of the cases, increasing the temperature and changing the pH value did not have a significant effect on the variation of the elongation at break for notched GM samples. However, some cases showed slight significance, such as samples treated at pH 12 and 80°C and tested with respect to the breaking elongation after 90 days. However, the reason is hard to determine.

Figure 6 shows the load and elongation at break for unnotched GMs at different temperatures and

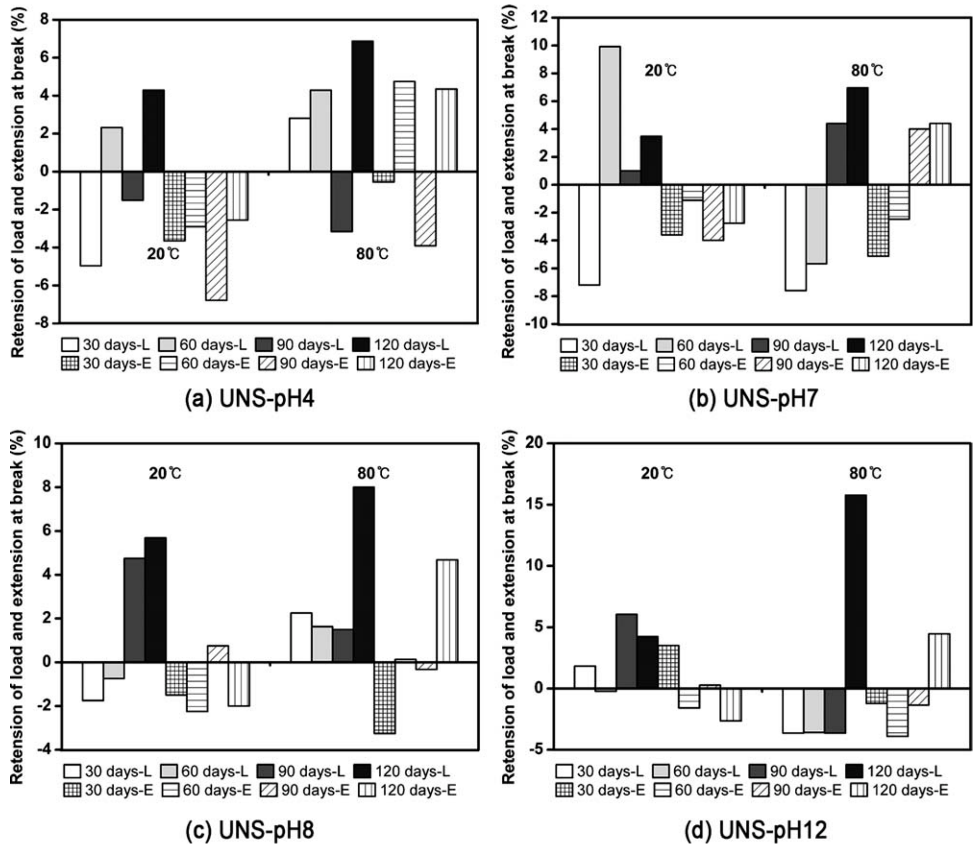


Figure 6 Load (*L*) and elongation at break (*E*) of unnotched GMs at different temperatures and pH values.

pH values. Unnotched GM samples ruptured at significantly higher loads in comparison with notched GM samples under the same test conditions. The maximum reduction of the breaking load amounted to 8% of their original values in unnotched GM samples. Certain samples showed even positive retention of breaking loads up to 15% of their original values. Thus, it is very hard to find correlations between the breaking load and temperature or pH values. After 120 days, a positive increasing tendency of breaking loads for unnotched GM samples was shown with temperature, especially with respect to each pH value. Meanwhile, higher breaking loads were indicated at 80°C with the pH value. With respect to each pH value, the elongation at break was higher at 80°C versus 20°C in each test period. However, exceptions were found in alkaline pH solutions (e.g., pH 12) only at 30, 60, and 90 days. Thus, higher positive retention of breaking elongation was reported at 80°C after 120 days, regardless of pH variations. This shows that GM samples with notch marks ruptured at much lower loads and elongations than samples with unnotched marks. The reason is that the notch-type mark damage was made into the relevant samples. Therefore, damage occurring to GMs is the most important factor to be considered with respect to their durability. After the yield point, noncrystalline and uncrosslinked polyethylene chains of unruptured GM samples broke, and thereafter, semicrystalline polymer chains bore the applied load until the GM structure broke.

Stress crack resistance

To measure the chemical resistance of GM samples, we performed more appropriate and stringent stress crack tests such as NCTL testing.[1] Figure 7 shows NCTL test results for GMs at pHs 4 and 8 and 40 and 60°C. A yield stress of 30% was reported after a failure time of 250 h for the original materials. As shown in Figure 7, the yield stress (%) was negatively correlated with the time. When we compare the graphs in the two diagrams of Figure 7, no significant difference can be observed for the pH 4 and 8 solutions. This implies that the stress–crack behavior was independent of pH variations. However, temperature variations were more sensitive to stress crack behavior, as shown in Figure 7. The higher the temperature was, the lower the stress crack resistance was. Thus, no significant difference between CMD and MD or between S and T samples was found. However, according to the graphs, GMs at pH 8 and 60°C showed very minimal deviations in the yield stress percentages of S and T samples and

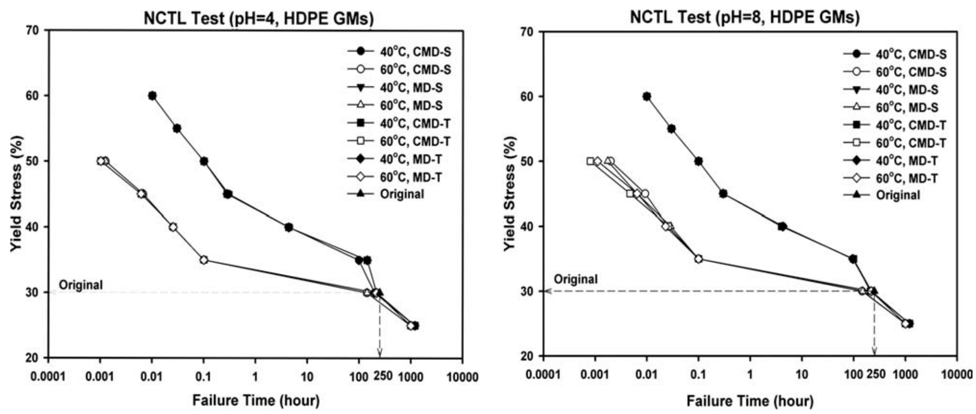


Figure 7 Yield stress (%) variations with the failure time (in hours) for HDPE GMs in acidic (pH = 4) and alkaline solutions (pH = 8) at 40 and 60°C (CMD-S = cross machine direction smooth HDPE GM; MD-S = machine direction smooth HDPE GM; CMD-T = cross machine direction textured HDPE GM; MD-T = machine direction textured HDPE GM).

in CMD and MD up to about 0.5 h. After the yield stress was lowered to 30% at 250 h (the same as the original yield stress percentage), all tested GM samples treated under 40 and 60°C came to the same line, and the yield stress percentage was further reduced below 30%. This is a common feature, as indicated by both diagrams presented in Figure 7.

Morphologies

At higher temperatures after 120 days, most of the GM samples showed higher variations of their rupture loads and elongations. Therefore, we captured SEM images of notched and unnotched GM samples under 80°C. Figure 8 shows the surface appearance of notched and unnotched GM samples under 80°C

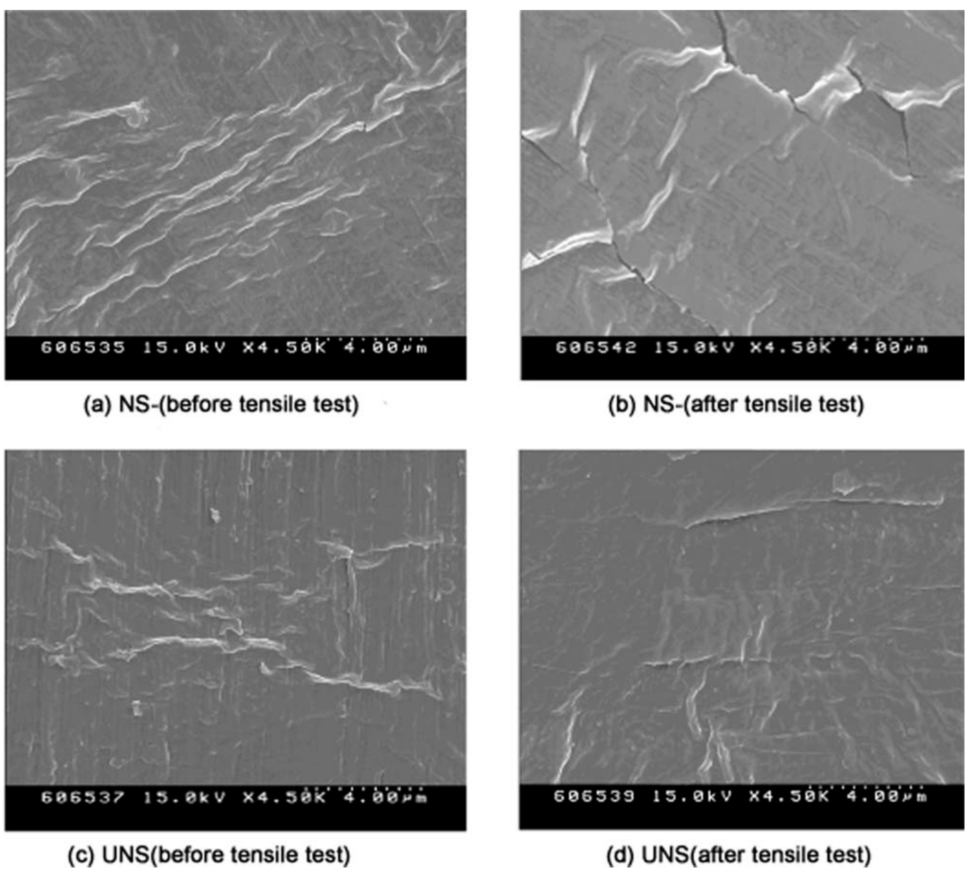
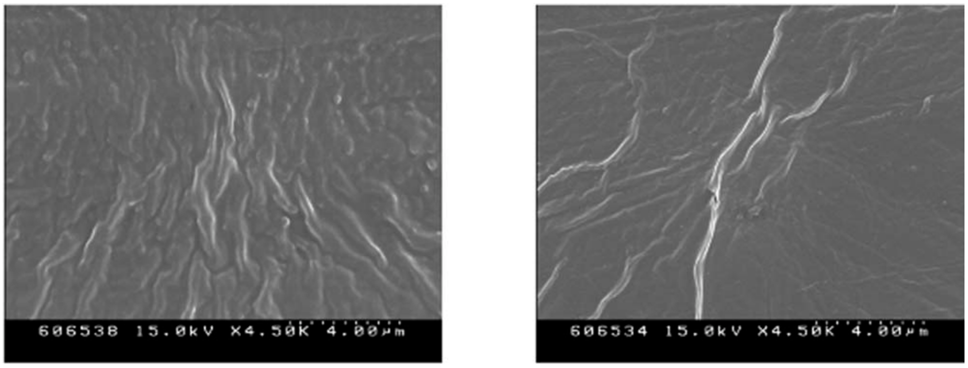


Figure 8 SEM images of notched and unnotched HDPE GMs at 80°C in alkaline solutions (pH = 12) after 120 days before and after tensile testing.



(a) before NCTL test (b) after NCTL test

Figure 9 SEM images of HDPE GMs at 60°C in alkaline solutions (pH = 8) before and after NCTL tests.

and after 120 days. They were taken before and after the tensile tests. Figure 8 presents SEM images of notched HDPE GMs at 60°C in an alkaline solution (pH 12) before and NCTL testing.

A comparison of Figure 8(a,b) shows that the surface nature changed after the application of tension during testing. The same feature can be seen in Figure 8(c,d). Visible surface microcracks can be seen in Figure 8(b). These were due to the notches made on these GM samples. Also, they cracked and failed under applied loads, but unnotched GM samples did not show these types of cracks after the tensile test. The visible cracks indicated in Figure 8(b) may have caused linear failures in the GMs. As shown in Figure 9 also, the surface nature was changed by NCTL testing, but no visible surface microcracks were found after stresses were applied. Therefore, damage to the GMs should be considered a very important factor influencing the durability of GMs. It leads to severe problems in the load and elongation at yield and break and produces microsurface cracks that will bring the GMs to a poor performance state.

For Figure 9, we selected HDPE GMs at 60°C and pH 8 because, on the basis of the observations made during stress crack resistance testing (Fig. 7), 60°C yielded lower stress crack resistance properties than 40°C, and so we assumed that it might be possible for microsurface cracks to occur at 60°C. Thus, the stress crack resistance property variations are independent of the pH values. However, it was not possible to observe any microcracks on the surface at that temperature. This implies that temperatures between 40 and 60°C do not create any cracks in the GM structure in acidic or alkaline pH solutions, and this results in good crack resistance under the aforementioned conditions. One reason is the high degree of crystallinity of HDPE, which is composed of a greater number of tie molecules with greater molecular weights and longer polymer chains.[7]

CONCLUSIONS

Smooth and textured GMs did not show significant differences in their mechanical behavior under the tested conditions. The loads at yield for notched GM samples decreased with temperature, and higher reductions occurred with acidic and alkaline pH values and after 90 days. Elongations at yield for unnotched GM samples were also positively correlated to the temperature, and no good correlations were found with pH variations. Significantly higher breaking loads and elongations were found with unnotched GM samples, and no significant correlations were found with the breaking load, temperature, and pH value in most cases. However, higher loads and elongations at break were found at 80°C after 120 days for unnotched GM samples, regardless of pH variations. Stress crack resistance was independent of pH variations but significantly depended on the temperature. Notched GM samples showed microcracks on their surface, and unnotched GM samples did not show any microcracks under tensile loads. Thus, temperatures between 40 and 60°C did not create any cracks in the GM structure in acidic or alkaline pH solutions and resulted in good crack resistance under the aforementioned conditions.

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