

Diffusion of Sulfuric Acid Solutions in Nylon 6,6 Monitored by Neutron Activation Analysis

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ABSTRACT: Nylon 6,6 is an excellent material for the study of the diffusion mechanism and associated mechanical performance of polymers saturated with aqueous solutions of varying pH at different temperatures. The diffusion profile was studied for samples saturated at temperatures ranging from 20 to 90°C in solutions decreasing in pH from distilled water to 1.0M sulfuric acid. The presence of sulfuric acid molecules within the diffusing solutions acts to promote hydrolysis of the polyamide molecules. The degree of hydrolysis is dependent on saturation temperature and solution pH. The extent of degradation was evaluated via changes to mechanical performance and inherent viscosity and often results in a reduction of the stress at yield, flexural modulus, and inherent viscosity on increasing temperature

and decreasing pH. The use of neutron activation analysis allowed for an evaluation of the sulfur content within the samples as a function of diffusing time. This demonstrated that although the mechanical performance decreases rapidly on initial exposure to the aqueous medium, this is likely due to plasticization. As diffusion time progresses, the sulfur content within the sample continues to rise to a level where the acid/water molar ratio is much higher in the sample than that of the bulk. This results in an enhancement of the degradation process as time progresses. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2476–2487, 2005

Key words: polyamide (Nylon); diffusion; sulfuric acid; viscosity; neutron activation analysis

INTRODUCTION

As part of the quest to find a solution for the disposal of Canada's radioactive waste, the Royal Military College of Canada has been conducting research on the use of polymeric materials for the design of radioactive waste storage containers. Previous work has determined that these materials exhibit the required mechanical strength and resistance to radiation to make them viable alternatives to the titanium containers currently proposed by Atomic Energy Canada Ltd. in the Environmental Impact Statement on the Concept of Disposal of Canada's Nuclear Fuel Waste.¹

Bonin and colleagues demonstrated that composite materials such as those based on polyamide 6,6, polycarbonate, and polyurethane would perform well in the radioactive environment produced by low and intermediate level wastes.^{2,3} Miedema investigated the use of polymer composites such as

polyether ether ketone/graphite in the radioactive environment that is expected in the storage and disposal of spent nuclear fuel and high-level radioactive waste.⁴ Both determined that these types of materials, in combination with a packing material such as ThO₂, which acts as a radioactive shield, would have the required mechanical strength to be viable alternatives to the titanium containers currently proposed.

As the titanium containers' mode of failure is electrochemical corrosion, it is important to evaluate the corresponding barrier properties of the polymeric materials. This will allow for an assessment of the lifetime of a polymer container based on its ability to restrict the flow of groundwater in and subsequently the leaching of radionuclides out of the container.

The diffusion properties that govern the mass transport of materials such as water, acidic, or alkaline solutions through the container walls are the key to the evaluation of the lifetime of these materials. Due to the complex nature of the environment into which these containers will be placed (for several centuries), this diffusion process will be equally as complex. Initial studies have focused on the effects of temperature (20–90°C) and pH 0–7 on this diffusion process. The use of sulfuric acid solutions of varying pH was based on groundwater studies performed at possible burial locations.⁵

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There exist many references to diffusion processes in polyamides. The majority of the work has focused on water diffusion and hydrolysis.^{6–8} Others have focused on acidic solution diffusion such as acetic acid,⁹ sulfuric acid,¹⁰ and hydrated salts.¹¹ However, these studies are often limited to a single concentration or temperature. This work required that a complete series of data for a range of pH and temperature be produced. Also important was the determination of the acid molecules diffusion profile within the sample. Neutron activation analysis (NAA) was utilized to monitor the ingress of the sulfuric acid molecules into the sample as a function of diffusing time.

Polyamide 6,6 has been utilized as the initial test material due to its sensitivity to radiation exposure compared to other thermoplastic materials such as polyethylene or polypropylene. It is also hydrophilic and will absorb relatively high amounts (>9%) of solution over a time period that is acceptable for the experimental timescale. Previous work at RMC has focused on the assessment of mechanical performance to determine whether materials studied would maintain properties under conditions expected over the container lifetime. The focus of this work is to begin with the worst case scenario (polyamide 6,6) and establish a complete set of data, which can then be used to form the basis for evaluation of other materials that would be more suitable for this application. Beginning with materials that perform well in radioactive environments and do not intake appreciable groundwater over the experimental timeframe does not provide any detail as to the degradative mechanisms that may be active over long storage times.

EXPERIMENTAL

Materials

For the present work, pelletized polyamide 6,6 (Dupont Zytel 101L Nylon 6,6, $T_m = 263^\circ\text{C}$, $\rho = 1.18 \text{ g cm}^{-3}$) was selected for use. The material was first dried at 80°C for 24 h and then injection molded, using an ENGEL EC88 injection molder, with nozzle temperature ranging from 275 to 280°C and mold temperature of 80°C . Flexural bars measuring $3.1 \times 12.7 \times 127 \text{ mm}$ were formed in accordance with ASTM D3641–02¹² for flexural testing. To ensure that samples remained dry, all samples were vacuum packaged in aluminum-lined bags or stored in an air-free environment. This allowed for use without the requirement for further drying.

Diffusion experimental setup

Figure 1 presents the experimental setup, which is based on the weight gain method of determining moisture uptake in polymeric materials, ASTM D570–95.¹³ Flex-

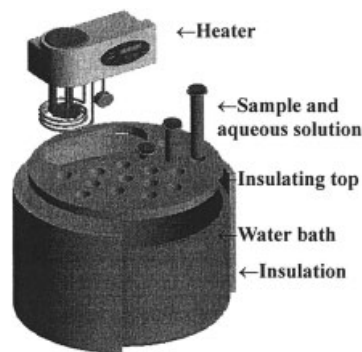


Figure 1 Experimental setup

ural bars were placed in each of the 100-mL test tubes. These tubes were then filled with the diffusing solution and lowered through the insulating top into the water bath. The water bath was entirely insulated with flexible foam sheets to minimize heat loss and to maintain the system at the experimental temperature ($\pm 1^\circ\text{C}$). Periodically throughout the experiment, the test tubes were opened, pH was measured, and the samples were dried and weighed. Samples were removed from the test tube, dried well with absorbent paper to remove the surface moisture, and allowed to air dry for 5 min at room temperature. Samples were then weighed to the nearest 0.0005 g on an analytical balance and, finally, returned to the test tube.

Neutron activation analysis

Neutron activation analysis was performed after exposure to the thermal neutron flux from the SLOW-POKE-2 research nuclear reactor. The sulfur content in the samples was compared to that of the sulfur-free samples, allowing for a determination of the quantity of sulfur in the samples. The sensitivity for the analysis of trace elements using NAA is both element and technique specific, but is in the range of 0.001 ppm.¹⁴ A cross section of the samples was utilized for this analysis.

Flexural testing

Flexural testing was carried out with an Instron testing apparatus according to the ASTM D790–02¹⁵ three-point bending test. The crosshead speed was maintained at 13.65 mm/min for all experiments. Measurements were taken with a 5-kN tension/compression load cell. Tests were run until break occurred or until the maximum displacement was reached.

Dilution viscometry

Dilution viscometry was completed on a Lauda Intrinsic Viscosity Measurement system with Ubbelohde

viscometers. Initial sample concentrations were approximately 0.005 g cm^{-3} . A series of dilutions was carried out for each sample at intervals of 0.0005 g cm^{-3} beginning at 0.0045 g cm^{-3} and finishing at 0.0015 g cm^{-3} . Nylon 6,6 samples were dissolved in *m*-cresol at room temperature prior to testing with a Type II viscometer. The kinematic viscosity of *m*-cresol at 25°C was determined to be $13.1 \text{ mm}^2 \text{ s}^{-1}$.

RESULTS AND DISCUSSION

Neutron activation analysis

NAA was used to determine the concentration of sulfur within the samples as a function of diffusing time. The technique is based on the radiative capture of neutrons into the nuclei of stable isotopes. These neutrons are produced by the SLOWPOKE-2 nuclear research reactor at RMC. Following this nuclear reaction, the resulting atoms have an additional neutron within their nuclei, with these atoms being either stable isotopes of the original nuclear species or radioactive isotopes (radioisotopes). Neutron bombardment of a sample results in a number of radioisotopes being created, such that the analysis technique is then based on the detection and measurement of the radiation emitted by these radioisotopes. Although emitted particles, such as α and β particles, or Auger electrons, can be used for the analysis, NAA is traditionally based on the analysis of the spectra of the γ rays emitted by the radioisotopes. In the present work, the interest is focused on the sulfur isotopes that are among the constituents of the sulfuric acid diffusing into the polymer matrix. This element is thus used in the following paragraph to describe the method in greater detail.

Natural sulfur consists of the following four stable isotopes: ^{32}S (92%), ^{33}S (0.75%), ^{34}S (4.21%), and ^{36}S (0.02%). The percentages represent the natural atomic composition. At RMC, NAA is based on the absorption of slow (thermal) neutrons into the target nuclei, since the capture possibilities are much higher for thermal neutrons than those for fast neutrons, and because the SLOWPOKE-2 is a thermal reactor with more than 90% of the neutron population being made of thermal neutrons. The capture of a thermal neutron into the nucleus of ^{32}S and ^{33}S leads to the formation of stable ^{33}S and ^{34}S , respectively, both useless for NAA since they are not radioactive. However, two radioisotopes can be formed from the absorption of a thermal neutron into ^{34}S and ^{36}S , resulting in ^{35}S and ^{37}S , respectively. ^{35}S is a long-lived radioisotope that decays into stable ^{35}Cl by β emission without emitting γ rays. Therefore, it cannot be used for NAA. Finally, ^{37}S decays rapidly into stable ^{37}Cl by β decay, but also includes the emission of γ photons with an energy spectrum displaying several energies, the most impor-

tant being 3103.36 keV (this photon is emitted 100% of the time). It takes 5.05 min for a given quantity of ^{37}S to decay to half its original value (half-life). This has two beneficial effects for NAA: a short irradiation provides a maximum activity for the samples, and the short half-life means high activities, thus high counting rates for better counting statistics and higher accuracy. Despite the low natural content of the ^{36}S isotope, there are still sufficient amounts of sulfur in the samples to guarantee high activity levels. The high energy of the main γ photon emitted makes its detection easy and the measurement nonambiguous, since few radioisotopes have γ energies with comparable intensities within their γ spectra.

This nonambiguity represents the main asset of NAA as a qualitative analysis technique, but it is in the quantitative analysis that NAA is most advantageous. The quantitative assessment of the content of an element within a sample is made by comparing the intensity of key photon peaks to those of standard samples irradiated and counted usually under the same conditions as those for the unknown sample. A simple rule of three is then used to determine the mass of the element of the unknown sample, which is commonly done in the parts per million range, or even in the parts per billion range, with an accuracy usually better than 1%. The success of NAA does, however, come with a cost: the method provides information only on the elemental content of the analyzed samples, without providing any knowledge of the molecular structure. In addition, there are some elements for which NAA is not well suited because the neutron capture probability is too small, such as the noble gases, elements with a magic number for their Z or A number (such as lead), and a few other elements for which the absorption of a neutron has a small probability or leads to the formation of stable isotopes (carbon, nitrogen, oxygen).

The use of NAA in the elemental analysis of diffused species in polymeric materials does not require chemical alteration or dissolution of the sample and thus is extremely valuable. Impurities within the samples are sometimes present in large enough quantities to interfere with the specific element of interest. But, there are techniques to cope with this problem, such as adjusting the neutron flux, the irradiation times, or the decay times, or changing the analysis method to include cyclic or pseudocyclic NAA techniques. In the case of interferences in the recorded γ spectra when multiple elements are studied in the polymer matrix, techniques such as spectra-stripping or computer aided analysis programs may be used to deduce the spectra for the elements of interest.¹⁶

Figure 2 illustrates the results obtained for the NAA studies on Nylon 6,6 samples at various stages during the diffusion process. Measurements of the sulfur content in the dry sample indicate that there exist low

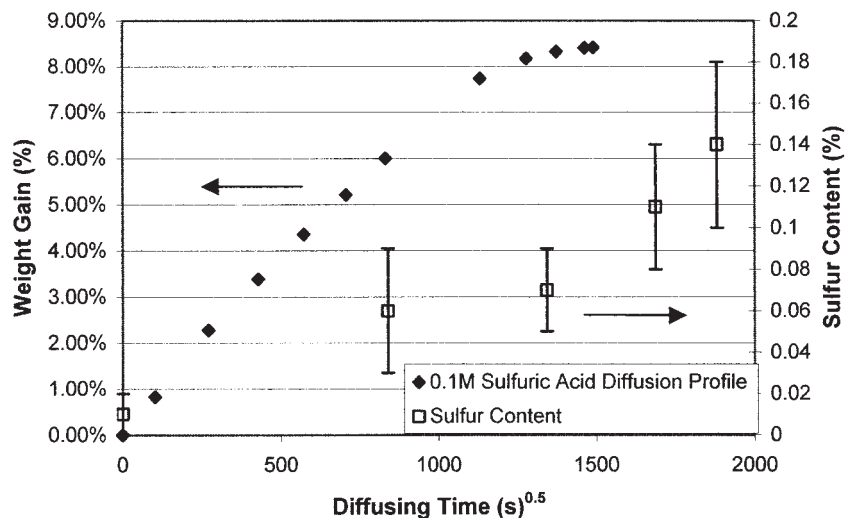


Figure 2 Neutron activation analysis of the sulfur content through the cross section of the sample as exposure time is increased for Nylon 6,6 exposed to 0.1M sulfuric acid at 40°C.

levels of sulfur within the polymer matrix in the form of impurities. The increase in sulfur content that occurs during the initial stages of diffusion exhibits a slower ingress profile than that after saturation is achieved. Upon saturation, the sulfur content increases more rapidly.

A brief quantitative analysis was performed based on the NAA data presented in Figure 2. It is assumed that each molecule of sulfuric acid, once dissolved in water, will be dissociated into one solvated proton H_3O^+ and one sulfate ion HSO_4^- . When one sulfuric acid molecule diffuses into the Nylon 6,6 sample, it effectively consists of a single unit of two ions due to the requirement for charge neutrality. The total molecular weight of one diffusing sulfuric acid molecular unit becomes 116 Da. This value can now be used to deduce the molar ratio of the diffusing unit into the sample and then compare it with the molar ratio of the bulk solution used, which is 0.1/55 or 0.18%, for the 0.1M sulfuric acid solution.

Take, for example, a point of 3% weight gain from the left side of the curve in Figure 2, which corresponds to a sulfur content of about 0.07%, from the right side of the curve representing NAA data. The latter value yields a diffusing sulfuric acid content of 0.27%, which corresponds to a molar ratio of about 1.53%. With the assumption that all sulfur present is contained in the diffusing sulfuric acid molecular unit, given that dry samples were found to contain 0.0096% sulfur, this molar ratio is significantly higher than that of 0.18% obtained for the bulk concentration as cited above. Table I presents the calculated values for this and two other data points from Figure 2. From these results, it can be concluded that the sulfuric acid content absorbed into the Nylon 6,6 sample is about 7 or 8 times larger than the bulk acid concentration.

The amine groups have a higher attraction to the protons of the diffusing sulfuric acid unit than those of water, therefore causing the acid concentration to be higher at the surface of the sample than in the bulk solution. This is evidenced upon visual inspection of the samples, in that when dried, white patches are present on the surface of samples. The amine groups within the sample may also ease the diffusion of the larger diffusing sulfuric acid groups within the sample and result in less water ingressing due to space limitations. The size of the sulfuric acid group is estimated to be five or six times that of water; therefore, the higher the number of acid groups within the sample, the less space available for water molecules. As the diffusion progresses past saturation, the molar ratios remain constant at around 1.3%.

These results provide support to results presented in later sections, which illustrate a decrease of mechanical performance and inherent viscosity over time, specifically samples saturated with 0.1M sulfuric acid solution at long aging times. These NAA results demonstrate that the ingress of dissociated sulfuric acid molecules into the polymer matrix is significantly enhanced after saturation is achieved when monitored by gravimetric methods.

TABLE I
A Quantitative Analysis of Neutron Activation Analysis Results

Weight gain (%)	Sulfur content (%)	Diffusing acid (%)	Acid/water molar ratio (%)
3.0	0.07	0.27	1.53
5.0	0.11	0.43	1.46
7.0	0.15	0.58	1.40

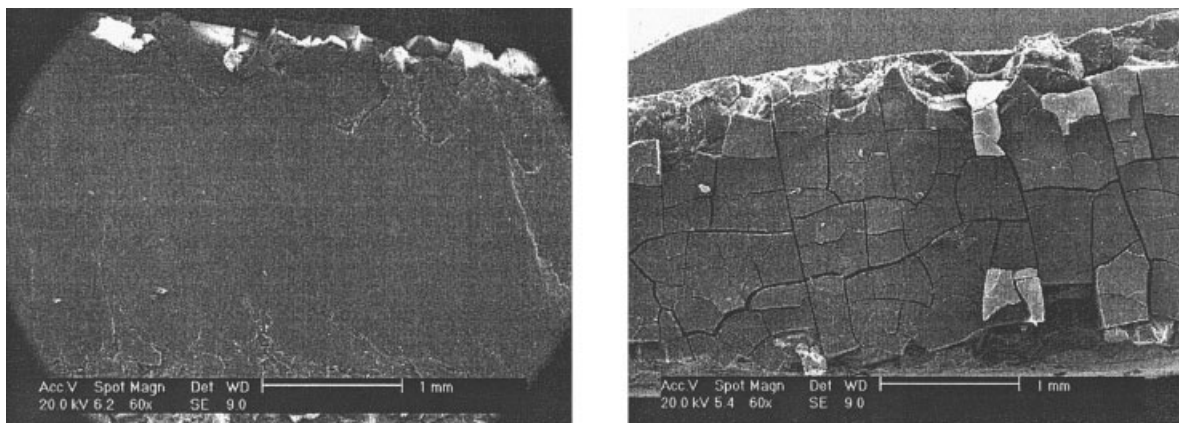


Figure 3 Scanning electron microscope image (60 \times) of 1.0M sulfuric acid exposure at 60°C.

Apparent diffusion coefficient and activation energy

Initial experiments were completed to determine the apparent diffusion coefficients and apparent activation energies for the diffusion of distilled water, 0.1, 0.5, and 1.0M sulfuric acid in Nylon 6,6. Experiments were conducted at 20, 40, 60, 70, and 90°C. Experiments at high temperatures (70 and 90°C) and acid concentration (1.0M) were found to cause extreme degradation to the samples, as can be seen in the scanning electron microscope images shown in Figure 3.

Apparent diffusion coefficients

Experiments were carried out at temperatures ranging from 20 to 90°C and acidic conditions ranging from distilled water (pH of approximately 6.5) to 1.0M (10 wt %) sulfuric acid solution (pH of approximately 0). The pH was measured during the diffusion process and remained constant throughout the experimental

time period. Figure 4 presents a typical plot for the diffusion of distilled water into Nylon 6,6, representing the percentage weight gain (which is shown in Eq. (1) below) as a function of the square root of time.

$$\% \text{ weight gain} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \quad (1)$$

The curves shown in Figure 4 are representative of Fick's diffusion curves, and according to Ishak and Berry,¹⁷ the apparent diffusion coefficients may be calculated based on the initial linear portion of the curve. Equation (2) shows the details of the relationship between the above graph and the apparent diffusion coefficient, D ,

$$D = \frac{\pi}{16} \left[\left(\frac{M}{t^{1/2}} \right) \frac{h}{M_m} \right]^2, \quad (2)$$

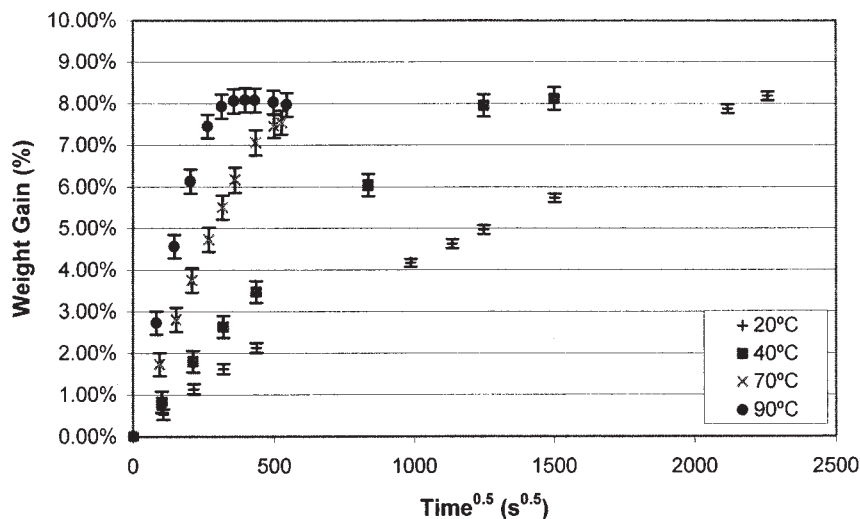


Figure 4 Water diffusion in Nylon 6,6 for various temperatures.

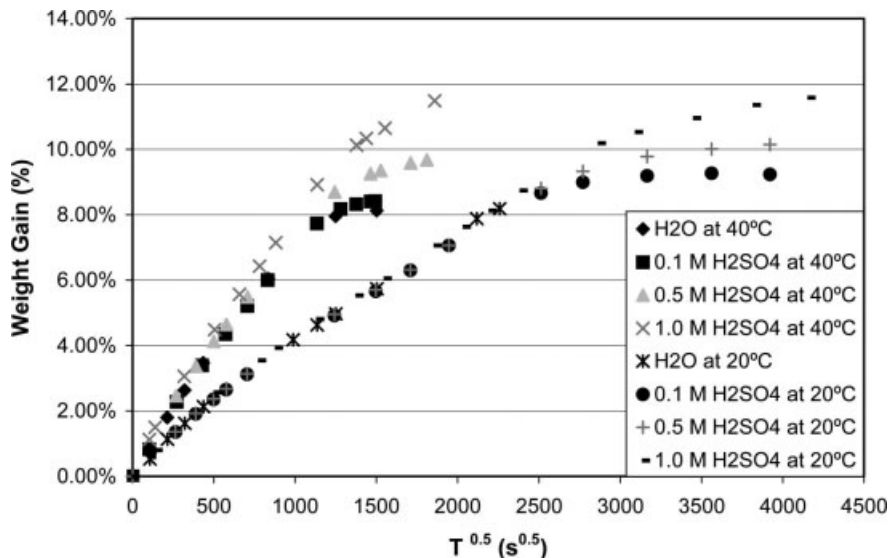


Figure 5 Diffusion in Nylon 6,6 at 20 and 40°C.

where $\frac{M}{t^{1/2}}$ is the slope of the initial linear portion of the curve, h the thickness of the sample, and M_m the maximum weight gain.

Diffusion coefficients were determined to be temperature dependent with slight variations noted due to changes in the diffusing solution toward more acidic conditions. Maximum weight gains were also noted to increase under acidic conditions. As can be seen in Figure 5, the initial sections of the diffusion curves are closely overlaid; however, increasing acid concentration produces increased maximum weight gain. This can be explained simply in that the molecular weight of the dissociated sulfuric acid molecule is approximately five times higher than that of the water molecule. An increase in concentration of sulfuric acid

(decrease in pH) likely provides a larger number of dissociated sulfuric acid molecules within the diffusing solution to diffuse into the material, resulting in an increase in the maximum weight gain.

Figure 6 illustrates the relationship between the apparent diffusion coefficients and temperature. An Arrhenius-type relationship is evident from these results and as such can provide a valuable means of determining the apparent activation energy for the systems.

Apparent activation energy

Plots such as the one shown in Figure 6 presenting the natural logarithm of the apparent diffusion coefficient, $\ln D$, as a function of the inverse of the temperature,

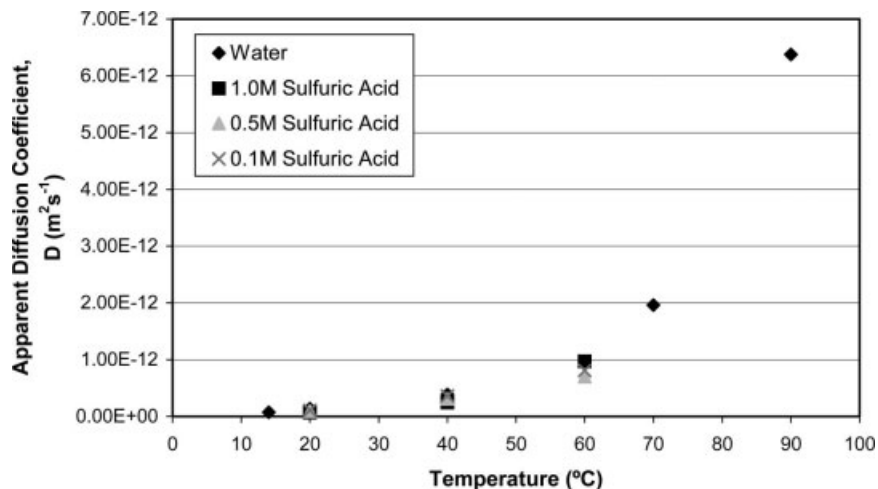


Figure 6 Apparent diffusion coefficients versus temperature for Nylon 6,6 diffusion of distilled water and acidic solutions of various molarities.

TABLE II
Apparent Activation Energies for Various Systems

Diffusing species	Activation energy (kJ mol ⁻¹) ± 10%
Distilled water	48.5
0.1M sulfuric acid	40.8
0.5M sulfuric acid	41.0
1.0M sulfuric acid	53.6

T^{-1} , can be generated and confirm the Arrhenius relationship between the diffusion coefficient and the temperature, where D is the diffusion coefficient (m² s⁻¹) and T is the temperature, (K).¹⁸

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

This Arrhenius-type relationship allows for the calculation of the apparent activation energy, E_a , for each of the experimental conditions. Table II is a summary of the apparent activation energies for the systems studied. Ishak and Berry¹⁹ have obtained a value of 55.6 kJ mol⁻¹ for the activation energy of unreinforced Nylon 6,6. Differences may be attributed to experimental uncertainties and differences in the characteristics of materials used, such as molecular weight and percentage crystallinity.

From Figure 7, it can be noted that the slopes of the lines for the 0.1 and 0.5M solutions are similar in slope but shallower than that of water. For the high-concentration solution (1.0M), the slope is steeper than that of water. These results indicate that more energy is required for the diffusion process when the sulfuric acid molecules are in high concentration. However, at the intermediate concentrations of 0.1 and 0.5M, it would appear that the sulfuric acid molecules present in solution actually facilitate the diffusion process, result-

ing in a lower apparent activation energy for these processes.

Assessment of the effects of diffused water and sulfuric acid solutions on nylon 6,6

Mechanical performance

Testing was performed once it was determined that the samples had reached the point of saturation. This was determined from the weight gain plots and corresponded to the point where a steady plateau was reached, indicating that weight measurements remained constant. Results presented are averaged over three to five specimens tested.

As previously mentioned, the samples exposed to higher temperatures and higher acid concentrations exhibited a more severe surface degradation, which was visible to the eye and resulted in a significant decrease in the mechanical performance. This is evident in the higher standard deviations of the flexural testing results for those samples. Figures 8 and 9 are representations of these results. It can be seen that, as the saturation temperature increases, the maximum stress at yield also increases in the case of distilled water. This is due to a slight increase in the maximum percentage weight gain with increased saturation temperatures. The higher the saturation temperature, the higher the maximum percentage weight gain, indicating that a larger amount of water has penetrated the polymer matrix, thus resulting in an increase in the maximum stress at yield, due to an increase in plasticization resulting from the water molecules within the polymer matrix.

Similarly, the ingress of 0.1M sulfuric acid at lower temperatures also results in an increase in the stress at yield and can be seen to provide an increase over that of water. However, at higher temperatures, this is no longer true. As the temperature is increased,

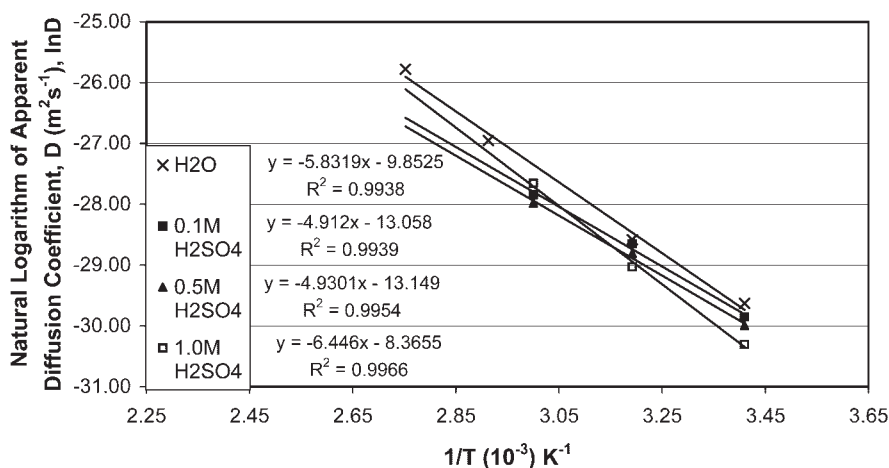


Figure 7 Arrhenius plots for Nylon 6,6 saturated in distilled water and various sulfuric acid solutions.

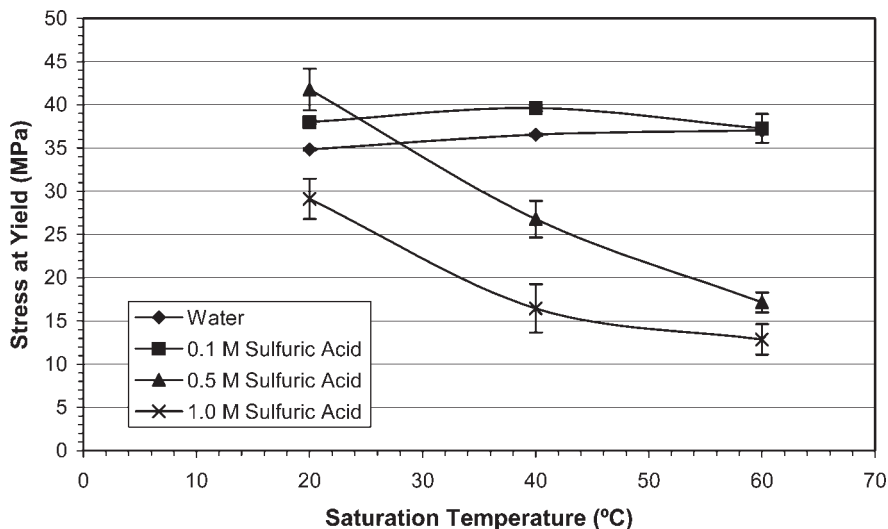


Figure 8 Maximum stress at yield as a function of saturation temperature.

the sulfuric acid has a much more damaging effect on the polymer molecules leading to degradation of the long polymer chains and a reduction in the stress at yield. This is also evident in the results for 20°C, 0.5M sulfuric acid saturation resulting in an increase in yield stress, but due to the increased concentration of sulfuric acid, the degradative effect becomes much more prevalent at intermediate and higher temperatures. Also seen in the 1.0M sulfuric acid results is that even at low temperatures, the concentration of sulfuric acid molecules is sufficient by itself to result in a decrease in the stress at yield. With increasing temperature, the degradation is amplified. The polymer molecules are no longer able to support a load. It is in these cases where fracture was noted to occur.

Results obtained for the flexural modulus follow a similar trend to that discussed for stress at yield. Once

again, the resistance of the sample to deformation is enhanced by the presence of sulfuric acid molecules at lower temperatures. It is likely that the larger sulfuric acid molecules provide some restriction to the movement of the polymer molecules without causing degradation of the long polymer chains. However, this increase, over that of water, is no longer significant at higher temperatures. The polymer chains then have more energy available for movement, resulting in the degradative effects of the sulfuric acid becoming more pronounced at elevated temperatures and higher concentrations.

Of interest is the case of high temperature (60°C) and high concentration (1.0M). Due to the extreme conditions and the advanced degradation of the samples at saturation, it was no longer possible to obtain accurate weight measurements due to the embrittle-

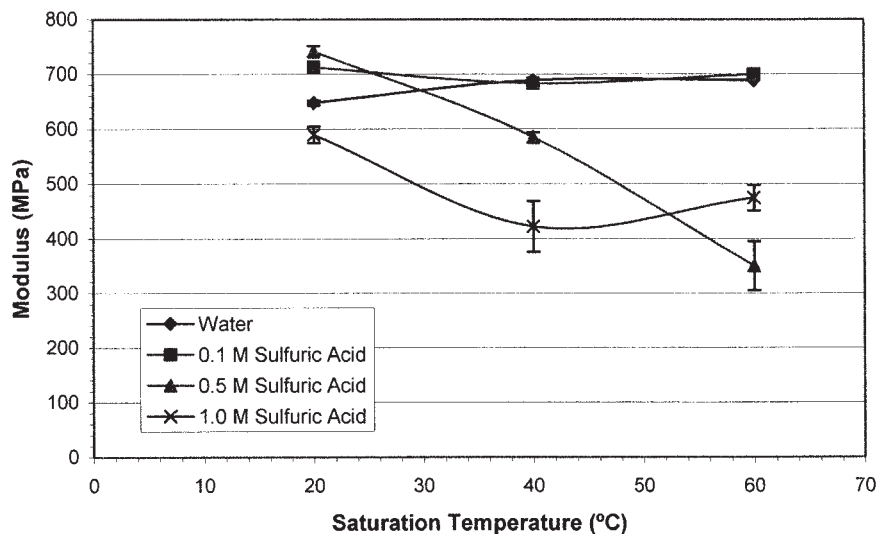


Figure 9 Modulus as a function of saturation temperature.

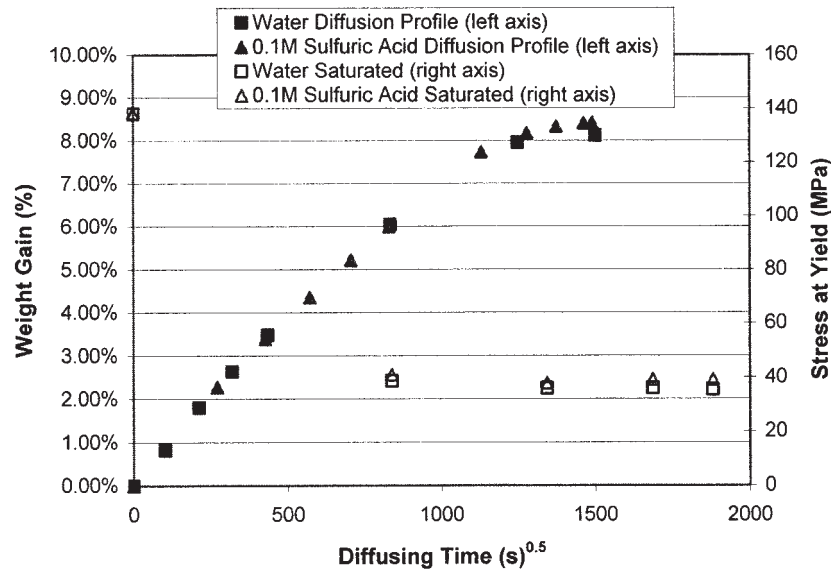


Figure 10 Stress at yield versus diffusing time for Nylon 6,6 in water and 0.1M sulfuric acid at 40°C.

ment and cracking of the samples. Therefore, samples were removed and tested “earlier” in the diffusion process than those in which the saturation plateau was well established prior to testing. The higher temperature (60°C) resulted in a faster diffusion process than the 40°C process; therefore, less time was available for the degradation of the long-chain polymer molecules.

It is often difficult to determine the exact time of saturation due to slight variations in weight measurements. It was determined that it was optimal if saturation was assured prior to testing. Therefore, initial flexural testing results may be occurring at times slightly greater than those for the exact point of saturation. Figures 10 and 11 present the flexural

yield stress and modulus for Nylon 6,6 as a function of diffusing time in distilled water and 0.1M sulfuric acid at 40°C.

The loss of mechanical performance (decrease in stress at yield and flexural modulus) occurs early on in the diffusion process with the maximum loss realized much in advance of saturation. Initial uptake of solution results in plasticization of the polymer matrix such that further ingress of solution into the void spaces within the sample does not significantly alter the mechanical performance. The initial loss of performance, prior to the plateau, may be associated with the diffusion front progression through the sample. Further weight gain after this point may be attributed

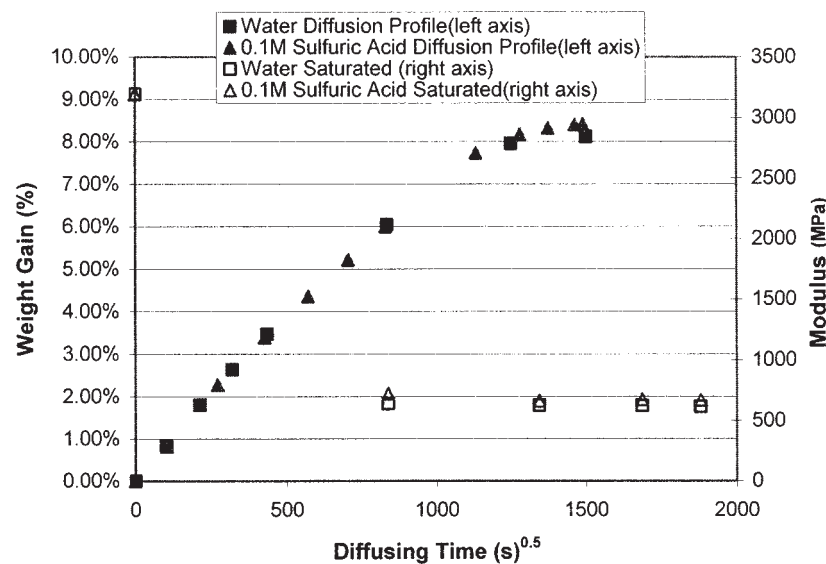


Figure 11 Flexural modulus versus diffusing time for Nylon 6,6 in water and 0.1M sulfuric acid at 40°C.

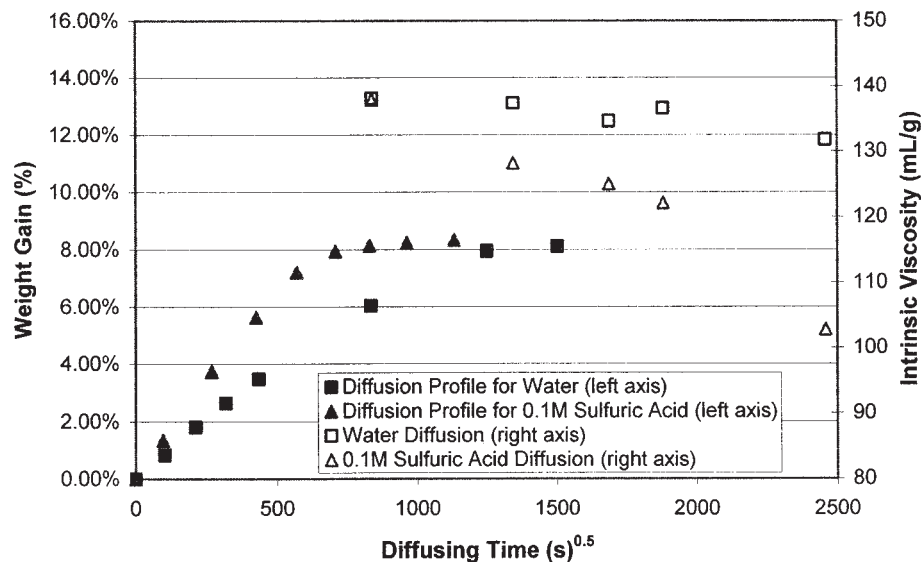


Figure 12 Intrinsic viscosity as a function of diffusing time at 40°C.

to the continued filling of void spaces with solution. It can be concluded that the initial plasticization of the polymer results in the loss of mechanical performance, and saturation of all void spaces does not result in further loss of performance.

Intrinsic viscosity

As a means of gaining insight into the relative lengths of the polymer molecule chains after exposure to the various environments, dilution viscometry was used as a comparative method between samples. Lower intrinsic viscosities can be related to decreases in molecular weight, whereas increased viscosities can be correlated to increases in molecular weight. This is assuming that the polymer chains do not undergo any configuration change.

As with flexural testing, it was important to investigate the intrinsic viscosity as a function of diffusion time. The results reported here have been corrected for increased sample weight due to the ingress of solution into the sample. Figure 12 shows the molecular weight changes that are occurring as diffusion progresses. Intrinsic viscosity remains essentially constant throughout the diffusion process for both distilled water and 0.1M sulfuric acid diffusion. However, once saturation is reached and aging begins, it is clear that the sulfuric acid acts to enhance the hydrolysis process. Samples in distilled water at 40°C do not show an appreciable change in intrinsic viscosity over time, which is in agreement with flexural testing results previously described.

The diffusion of 0.1M sulfuric acid at 40°C results in a marked reduction in the intrinsic viscosity and associated decrease in chain length. This is due to the

greater cleavage “power” of the 0.1M sulfuric acid solution than that of water. The sulfuric acid molecules within the polymer matrix also act as a catalyst to accelerate the cleavage of the long chains, thus accelerating the reduction of the intrinsic viscosity.

Further increases in temperature or acid concentration result in further reduction of the intrinsic viscosity. Figure 13 shows that there is a greater intrinsic viscosity increase for the samples saturated in 0.1M sulfuric acid at 40°C than for those at 20 or 60°C for the same solution. There also exists a similar increase for samples saturated with distilled water at 40°C. This result is in agreement with results previously presented for the stress at yield under the same conditions. Once again, it may be suggested that the lower concentration of sulfuric acid molecules present in the 0.1M solution provides some protection to the polymer molecules at 40°C. Also important to note is the difference in diffusion times and temperatures for these samples. Samples saturated at 20°C require approximately 1 year to reach saturation, thus providing more time for polymer chain degradation (hydrolysis). Those saturated at 60°C require much shorter times, but due to higher temperatures, they experience a higher degree of degradation. Samples saturated at 40°C in 0.1M solution are not at temperatures significant to the degradation process and are not required to remain in the acidic solution for such long times; therefore, the higher intrinsic viscosities (and flexural results) are likely due to the more “ideal” conditions to which the samples are exposed.

Similar results with samples exposed to water are recorded, as water is much less degradative to the samples, the increase noted at 40°C is lower in mag-

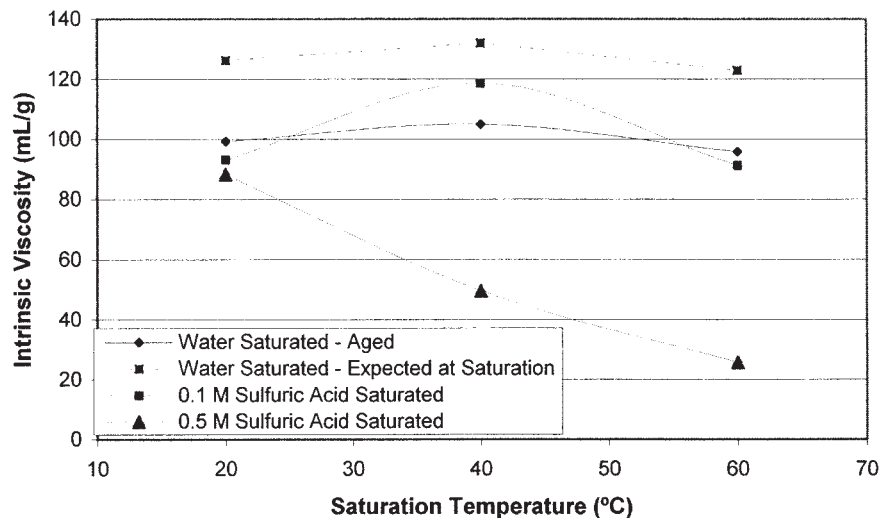


Figure 13 Intrinsic viscosity as a function of temperature.

nitude; however, the same principles are expected to be true. Samples allowed to age in water at room temperature for extended periods of time show a decrease in intrinsic viscosity from those tested at or near the time of saturation. Given longer periods of time the water molecules present within the polymer matrix continue to cleave the polymer chains via hydrolysis of the amide group, thus resulting in a decrease in the intrinsic viscosity.

Finally, as with the flexural results, samples saturated in 0.5M sulfuric acid show a steadily decreasing trend with increasing temperature. This is due to the damaging effects of the stronger acid concentrations and is magnified by the increase in temperature.

CONCLUSIONS

Neutron activation analysis seems to be a useful technique for monitoring the diffusion of sulfuric acid in Nylon 6,6, both qualitatively and quantitatively. NAA has been used to demonstrate that the diffusion of dissociated sulfuric acid continues after the weight gain diffusion plateau has been achieved.

Diffusion in Nylon 6,6 has been shown to be not only temperature dependent, but also pH dependent. As the pH is increased, the apparent diffusion coefficient is also increased, which may be attributed to the decrease in concentration of the sulfuric acid molecules in solution. The mechanical performance (stress at yield and flexural modulus) of Nylon 6,6 was found to decrease with increasing water uptake until a time at which it is assumed that the diffusion front has progressed through the material; however, the saturation plateau was not yet reached as the void spaces had not yet been filled with solution. Higher temperatures and higher acid concentrations resulted in a marked decrease in performance over time. Dilution

viscometry results demonstrate the reduction in polymer chain length that is occurring and its dependence on both temperature and pH.

Experimental conditions studied in this work have been much more severe than those expected within the container storage environment. Results confirm that even hydrophilic materials, such as Nylon 6,6, will not show appreciable degradation in the low-acid-concentration environments (approaching that of distilled water), which are expected within the storage environment.

Scanning electron microscopy and neutron activation analysis were performed at the Department of Chemistry and Chemical Engineering at the Royal Military College of Canada.

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