Mechanical properties of polymeric fibres exposed to stress in a NO_x environment

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This study explores how a gaseous pollutant affects the long-term mechanical properties of nylon-6 fibres. It will be shown that the high-strength polymeric fibres degrade rather quickly when held under stress in the presence of NO_x, a component of industrial pollution. Studies have been conducted on fibres, both bare and embedded in an epoxy matrix, that clearly demonstrate a synergistic effect of applied stress and NO_x gas. It is observed that the combination of stresses of 50% of the ultimate fibre strength and a NO_x concentration of 0.05% by volume will result in sample failure in less than half a day. This concentration is representative of NO_x emitted in the exhaust of older-model cars. If these high-strength plastics are to be used in industrial or automotive applications where such pollutants would be present, this type of degradation should be taken into consideration for proper design.

(Keywords: mechanical properties; nylon; fibre; stress; matrix protection; nitrogen oxides; pollutants; degradation)

INTRODUCTION

A property associated with many polymers is the ability to resist corrosive attack from many modern chemicals and pollutants. Although some polymers are able to withstand exposure to many chemicals and pollutants for relatively long periods of time, others degrade relatively quickly. Previous research has shown both the deleterious effects of NO_x and the synergistic effects of combined NO_x and stress on bare nylon fibres[1,2]. These fibres are often coated or embedded in a matrix, however, where the material surrounding the fibres might provide protection against corrosive environments. Fibres in this study were examined both bare and embedded in an epoxy matrix to determine how a coating might extend the life in an adverse environment.

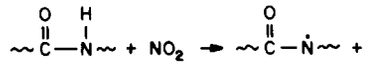
Much of the research dealing with corrosive gases such as NO_x has concentrated on relatively high concentrations. Results from these tests were produced within a relatively short period of time, as compared to degradation resulting from industrial levels of pollution. It is not always clear how such results from these types of accelerated tests would apply to typical industrial levels of pollution. In an effort to understand how degradation changes with concentration, experiments in this study were conducted with varying concentrations. Results obtained from these tests might then be used to extrapolate and help to predict degradation at lower levels, more representative of practical applications.

The mechanisms of degradation under various environmental conditions are generally complex. Accordingly, in most instances, a complete understanding of the mechanism involved is not available. Nitrogen dioxide, or NO_x, was selected as a degradent in this study to isolate its degradative tendencies from other species present in industrial pollution.

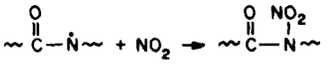
There are, of course, a variety of oxides of nitrogen. Even the terms nitrogen dioxide and NO_x are somewhat ambiguous. They can refer[3] to N_2O_4, NO_2 or NO + O. The exact composition depends on pressure and temperature. At standard pressure and below 21°C, NO_x is mostly liquid N_2O_4 (ref. 4). At standard pressure and 160°C, NO_x is largely gaseous NO_2. Further increases in temperature result in NO_2 breaking down to NO + O. The studies reported here were conducted at room temperature between 22 and 24°C and an atmospheric pressure of approximately 646 mmHg.

If NO_x is allowed to react with air, it can change into yet other species. It can, for example, react with moisture in the air to create nitric acid, which as a vapour can contribute to degradation. On sunny days ultra-violet light from the sun can break apart the NO_2 molecule into NO + O. Monatomic oxygen may then combine with oxygen to form ozone, another reactive and potentially degradative compound.

The ability of NO_x to degrade the mechanical properties of nylon is clearly a result of a chemical reaction. The process is generally accepted as NO_2 attacking the hydrogen–nitrogen bond in the nylon chain as[5–7]:



Once the hydrogen–nitrogen bond has been broken, the remaining nitrogen atom may react in any of the following forms:



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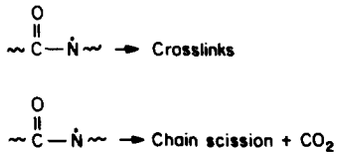

Nylon can, therefore, do three things when exposed to NO_x: absorb NO_2, crosslink, or undergo chain scission. It could be postulated, therefore, that stressing the nylon while being exposed to NO_x might allow more chain scission to occur than would otherwise take place. If placing the nylon under stress did allow the reaction to change in such a manner, the synergistic effect of stress and NO_x could be explained. It is expected, after all, that increased chain scission, particularly of the load-carrying chains, should result in a lower fibre residual strength.

EXPERIMENTAL

Material

The material used in this study was in the form of high-strength, small-diameter (0.027 mm) nylon-6 fibres provided by Dr D. Prevorsek of Allied-Signal Inc. The fibres were manufactured for use as tyre yarns. From standard buoyancy measurements, using the techniques described by Nelson[8], the fibres were found to be 80–85% crystalline.

The purpose for which these fibres were manufactured provides excellent justification for this study. In a pressurized tyre the fibres would be under continuous stress and exposed to engine exhaust gases, a primary source of NO_x. Tyre yarns would also be embedded in a material (rubber) that should provide some protection from the reactive gases found in engine exhaust. It is important to note, however, that this study was not intended specifically to represent accelerated testing methods for yarns in tyres. The epoxy coating used in this study, for example, has mechanical properties and perhaps protective properties that are very different from those of the rubber found in tyres. This study was intended to analyse the protective nature of epoxy coatings in general, rather than a specific application. Fibres are also sometimes used in ropes and cords where they are not protected. For this reason, fibres in this study were investigated both bare and embedded in an epoxy.

Bundled fibre samples were manufactured by wrapping yarn around two pegs. Loops were formed at the ends of the samples by applying epoxy near each end and wrapping nylon around the uncured epoxy area. The epoxy was then allowed to cure. Loops formed in this manner were used to apply uniaxial loads to the fibres both in and out of the NO_x environment. After the epoxy had cured, a few yarns were cut from the centre of each specimen to induce failure in the centre region rather than the loops. This effectively made a 'dog bone' fibre sample – larger (stronger) at the ends than in the centre. As a further aid to prevent the loops from premature failure, they were covered with 3 inch wide transparent packaging tape from 3M. In spite of these precautions, loops occasionally failed before the centre section. When such anomalous failure occurred, it was not included in the test results.

Some of the samples were tested bare, while others were embedded in a bisphenol A epoxy and hardened with a polyamine hardener before testing. The embedded samples were of two types, referred to as flat and round. During cure of the epoxy, the centre section of the flat samples was pressed between two plates as the epoxy cured. Visual and microscopic examination of the cross-sectional areas revealed that the cross-sections were quite reproducible. These had cross-sections of either 0.10 mm thickness and 13 mm width or 0.15 mm thickness and 6 mm width, depending on the fibre volume fraction. Sample dimensions were controlled by plate pressure, where increased pressure resulted in thinner and wider samples with a higher fibre volume fraction. The two types of flat samples studied are referred to as 'narrow' and 'wide'. Wide flat samples had a fibre volume fraction of 65%, while narrow flat samples had a fibre volume fraction of 55%.

Round samples were allowed to cure without pressure, leaving the cross-section of these samples nearly round in shape. If degradation of embedded samples is dominated by surface-area effects, samples with round cross-sections would be expected to withstand degradation better than flat samples.

Ultimate sample strength was determined by loading the samples in tension to failure at 50 mm min^{-1}, and is the fibre stress at failure. Bare and flat samples had nearly equivalent ultimate strengths of 954 MPa, while the ultimate strength of the round samples was 10% higher at 1059 MPa.

Environment

Chambers of approximately 20 litres volume were manufactured from 6.35 mm thick acrylic and used to expose the fibres to gaseous NO_x. Some samples had no load, while others were simultaneously placed under stress by positioning the samples in a load frame that fit inside the chamber.

Gaseous NO_x was introduced into the chambers from a pressurized 'lecture bottle' of liquid N_2O_4, purchased from Aldrich Chemical Co. Upon releasing N_2O_4 from the 'lecture bottle' to atmospheric conditions in the chamber, a rapid gaseous equilibrium of mostly NO_2 and N_2O_4 was observed. Qualitative observations were made both visually, since NO_2 is reddish-brown in colour, and by testing small samples of gas (100 ml) using Draeger concentration tubes purchased from Lab Safety Supply Inc. Results thus obtained were qualitatively consistent with the predicted equilibrium of pure NO_x, which is approximately 30% NO_2 and 70% N_2O_4 at standard conditions[9].

Gas volume was measured by displacing a column of water in a graduated cylinder with the NO_x gas. The NO_x gas was observed to react with the water being displaced. To separate the gas from the water, the layer of mineral oil was added to the water column. NO_x reacted to a lesser extent with mineral oil but significant absorption was qualitatively observed, as indicated by a yellowing of the oil. The most accurate volumetric measurements were achieved using a mylar bag to separate the NO_x and water. This method also had its drawbacks, however, since it was required to replace the mylar bag every few measurements. *Figure 1* is a schematic drawing of the apparatus described above.

Gas samples were taken randomly from experiments to verify NO_x concentrations using the gas concentration tubes described above. Although the chambers were

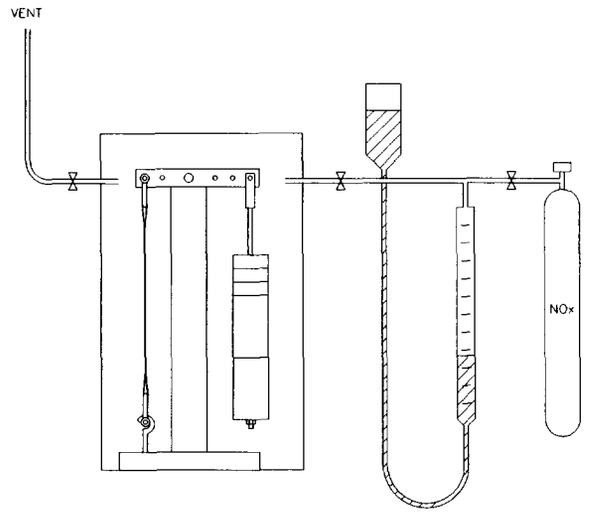

Figure 1 Apparatus for exposing samples to NO_x and/or stress

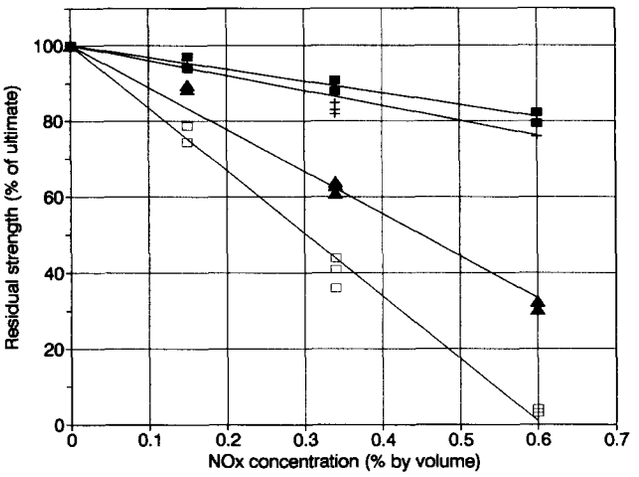

Figure 2 Degradation of unstressed, bare fibres *versus* NO_x concentration: (■) 30 min, (+) 60 min, (▲) 120 min, (□) 240 min exposure

air-tight, the concentration of NO_x decreased slightly with time. This was probably due to NO_x absorption into the samples and chamber, as well as reactions with the air in the chamber. To provide experiments with a nearly constant concentration of NO_x, the chamber was purged and new gas was introduced every 30 min.

RESULTS AND DISCUSSION

NO_x without stress

To study the relationship between NO_x concentration and degradation of oriented nylon-6 fibres, concentrations of 0.15, 0.34, 0.60 and 0.84% were studied. Bare and embedded samples were placed in these environments for 30, 60, 120 and 240 min. To investigate the effect of the environment on the residual strength of the fibres, the samples were loaded to failure at 50 mm min^{-1}.

For the exposure times and concentrations considered, bare and embedded fibres exhibited a nearly linear decrease in residual strength with both concentration and time. The straight lines shown in *Figures 2* and *3* are the least-squares fits of the data. The slopes of the lines fitting the data provide comparison between experiments, and will be referred to as the rate of degradation. The ordinate of *Figures 2* and *3* represents a normalized residual strength. This was determined by dividing the residual strength of each sample exposed to the environment by the average ultimate strength of that type of sample without the environmental exposure.

All the samples embedded in an epoxy exhibited higher residual strengths than bare fibres when exposed to identical environmental conditions. Both fibre volume fraction and fibre geometry were experimentally observed to affect the degradation of the samples. Flat samples, for example, had twice the residual strength of bare fibres after 4 h in identical NO_x environments. Protection was observed to increase further for these flat samples as the fibre volume fraction was decreased. The narrow flat samples, for example, had 10% more residual strength than the wide flat samples, for the exposures considered in this study.

Degradation of samples made with nearly round cross-sections was so small that it was difficult to distinguish degradation from the data scatter. These

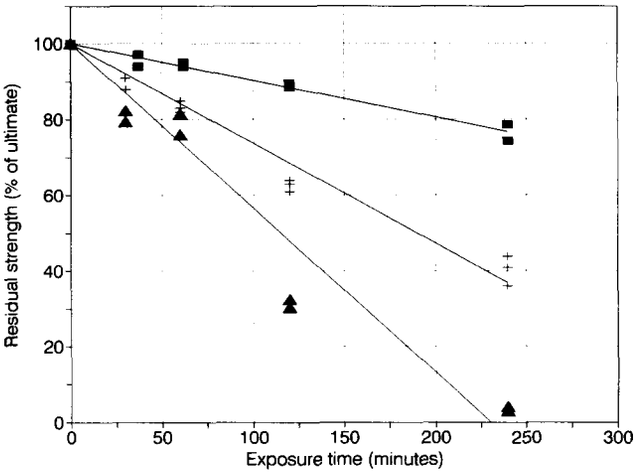

Figure 3 Degradation of unstressed, bare fibres *versus* time: (■) 0.15%, (+) 0.34%, (▲) 0.60% NO_x by volume

samples, for example, degraded only 9% after 4 h in 0.86% NO_x (the longest exposure time and the highest concentration considered in this study). Bare and flat samples, however, had virtually no residual strength after 4 h in 0.86% NO_x. Although no pressure was applied to the round samples during cure, their fibre volume fraction was only 5% below that of the narrow flat samples. It was therefore observed that, for the test conditions considered in this study, reducing the surface area exposed to the hostile environment significantly extended the life of the fibres.

NO_x with stress

Bare samples and samples embedded in an epoxy were stressed between 20 and 50% of their ultimate strength while exposed to 0.86% NO_x. The time required for the samples to fail in the combined environment of NO_x and sustained stress was recorded. Since the majority of these samples failed within 30 min, the gas was not replenished for these tests. As can be seen from *Figure 4*, the amount of protection that the epoxy matrix provided for the flat samples was only just measurable. There was a more significant effect for the round samples, but the epoxy matrix still provided little protection when compared to unstressed bare samples.

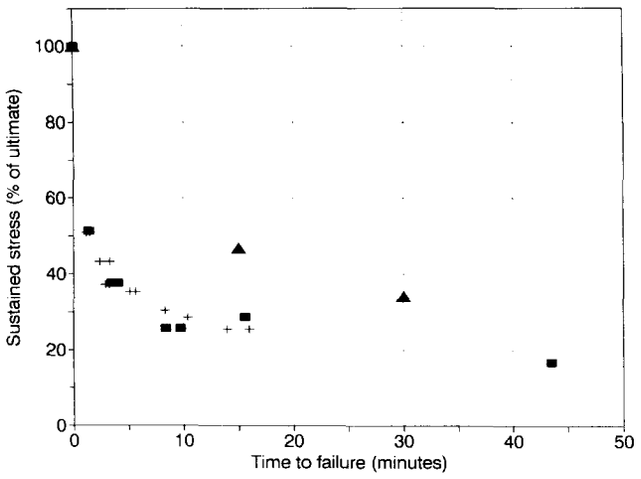

Figure 4 Time to failure of bare and embedded samples exposed to 0.86% NO_x at various stress levels: (■) bare bundled, (+) embedded flat, (▲) embedded round. The unexposed failure stress, represented as 100% in this figure, was 954 MPa for the bare and flat samples, and 1059 MPa for the round samples

Initially, it was suspected that the large difference between stressed and unstressed samples was a result of matrix cracking. Cracks of this type would remove the coating from the fibres in the area of the crack, allowing the hostile environment to attack the bare fibres. Since the effect was largest in the flat samples, the following tests were conducted on flat samples to check this hypothesis.

Virgin samples were first inspected visually under a microscope for cracks. When cracks were not visually detected, the relative strain of the matrix and fibre was explored. Strain of the nylon fibres at the maximum load applied in the environmental chamber (50% of ultimate strength) was experimentally determined, from total cross-head movement, to be of the order of 9%. Standard dog-bone specimens were manufactured from the neat epoxy and tested to failure. These were found to strain on the order of 75% before failure occurred. These tests were repeated for samples exposed to 0.86% NO_x for 60 min, without stress. Although absorption was qualitatively observed by a yellowing of the samples, the failure strain of the matrix and fibre samples was similar to that reported above. Residual strength, likewise, did not change significantly for the matrix samples. There was, however, a marked decrease in residual strength for fibre samples, as reported previously.

One might anticipate that matrix cracking would be most likely to occur if the failure strain of the matrix is less than that of the fibres. In the study reported here, the matrix could experience strain nearly an order of magnitude greater than the fibres. Consistent with this, no visual or other evidence was found for cracking perpendicular to the direction of loading.

On the other hand, there was evidence for cracking parallel to the direction of applied load. Fibres were stressed to 50% of their ultimate strength outside the environmental chamber and observed visually. Fibre–matrix separation was visually detected as white lines parallel to the direction of the fibres. These samples were cut in half, so that the cross-section could be examined under a microscope.

Two modes of fibre–matrix separation were observed. First, sample cracking parallel to the direction of loading was seen, where a crack traversed the sample thickness. The crack path could be the boundary between two yarns of nylon. Such a crack might form as the two yarns deformed differently under load. Secondly, fibre pull-out was observed under the microscope, where a single fibre or group of fibres would pull out of the matrix. Fibres near the surface of the sample that were displaced by the matrix flow during cure might pull away under load in this manner. In either case, the observed fibre–matrix separation effectively removed the coating from the fibres in the area of the longitudinal cracks.

While the exact origin of these longitudinal cracks is not known, the authors do not find their presence surprising. It is well known, after all, that the fibres in the samples are not all equally stressed, despite efforts to obtain homogeneous samples. Furthermore, epoxy does not typically form a strong adhesive bond to nylon-6. The combination of non-homogeneous stress distribution with the relatively weak adhesion could well initiate such cracks. Once the longitudinal slippage allows the ingress of the environment to the fibres and breaks or seriously weakens some of the fibres, the stress distribution in the fibres becomes more non-homogeneous, thereby aggravating the problem. Furthermore, some of the fibres lie very near the surface of the sample, where the amount of coating decreases sharply. This would again weaken and cause failure of these fibres, resulting in further stress inhomogeneity. This might in fact help to explain the difference in the round and flat specimens, where the flat specimens had a surface area of nearly four times that of the round specimens.

If one compares the rate of degradation between stressed and unstressed samples, the importance of the synergism between stress and the environment becomes clear. First, samples of the type used in these experiments, not exposed to NO_x, could sustain stresses of 50% of their ultimate strength for over a month with no measurable change in their residual strength, i.e. they had the same ultimate strength as the virgin sample. On the other hand, bare fibres maintained in a 0.86% NO_x environment unstressed for 30 min experienced a decrease in residual strength of 55%. The same type of samples in the same environment without stress but embedded in an epoxy matrix experienced a decrease in residual strength of only 0.6% for the round specimens and 28% for the flat specimens. These encapsulated specimens failed after 30 min exposure to the 0.86% NO_x environment and sustained stress of only 27% of the ultimate strength for round samples and 20% of the ultimate strength for flat samples. In summary, we see that embedded samples in identical environments have 52–72% more residual strength when unstressed than samples stressed to 20–27% of the ultimate fibre strength.

It was observed that stress had a pronounced effect on the rate of degradation down to stresses of approximately 20% of the ultimate fibre strength. There was an apparent threshold at this point, in that below it the degradation rate was indistinguishable from that for unstressed material. A few samples tested at lower NO_x concentrations clearly demonstrated the synergistic interaction between stress and the environment. At 0.15% unreplenished NO_x, samples held at a stress of 50% of the ultimate fibre strength always failed after only a few hours even when encapsulated. Bare samples exposed to the same environment but not under stress retained 90% of their ultimate strength. A few tests with 0.05% NO_x

showed similar trends but with proportionately lower rates of degradation.

CONCLUSIONS AND RECOMMENDATIONS

The most salient features of this research were as follows.

Stress and NO_x interact synergistically to degrade highly oriented nylon-6 fibres. Concentrations studied here varied from 0.05 to 0.86% by volume, while sustained stresses varied from 0 to 50% of the material's ultimate tensile strength.

The rate of this degradation is very large for the concentrations, stress levels and exposure times investigated. The parameters were purposely selected to give rapid rates so that effects could be easily observed in laboratory timescales. Nevertheless, the lower concentration of 0.05% NO_x is at least approaching what might be found in some exhaust gases. The authors feel that future research should emphasize studies in which there are lower gas concentrations, albeit that this would be more difficult experimentally, but would provide a base for more reliable extrapolation to usual service conditions. The environments, described above, can have catastrophic effects as evidenced by studies on both bare and encapsulated specimens. Samples in both groups lost almost all their strength in a matter of hours.

Encapsulating the samples in epoxy had a smaller effect than had initially been anticipated. While relatively thick epoxy coatings provided significant protection for unstressed samples, the epoxy became progressively less protective under sustained mechanical stress. For example, as shown in *Figure 4*, samples held under sustained loads varying from 18 to 50% of their ultimate strength failed in times varying from a few minutes to less than an hour.

While the exact mechanism for the rapid degradation in strength noted above is not known, a few observations might be helpful. It is well known that epoxies typically do not form strong bonds to nylon. The interface region between the epoxy and nylon might provide a path for ingress of the environment that is aggravated by stress-induced slippage. Microscopic investigation of the samples subsequent to the stress–environmental treatment did not reveal any cracking perpendicular to the fibre direction (i.e. on the plane of maximum tensile stress). There was, however, cracking evident parallel to the fibre direction, perhaps due to slippage induced between fibres of different lengths. These effects may aggravate the phenomena associated with the adhesion problem.

These observations may have important ramifications in design with these materials for applications in environments that might contain NO_x.

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