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ROBERT C. CORLEY (Date)
Senior Scientist (Propulsion)
Propulsion Directorate

Degradation of Nylon-6/Clay Nanocomposites in NO_x

J. S. Shelley, and K.L. DeVries*
Air Force Research Laboratory, Propulsion Directorate
AFRL/PRRE, 4 Draco Drive
Edwards AFB, CA 93524-7160

Abstract

Nylon-6 is an important engineering polymer that, in its fully spherulitic (bulk) form, has many applications in gears, rollers, and other long life cycle components. In 1993, Toyota commercialized a nylon-6/clay nanocomposite out of which it produced the timing belt cover for the 1993 Camry. Although these hybrid nanocomposites show significant improvements in their mechanical response characteristics, including yield strength and heat distortion temperature, little is known about the degradation of these properties due to environmental pollutants like NO_x. Nylon-6 fibers are severely degraded by interaction with NO_x and other pollutants, showing a strong synergism between applied load and environmental degradation. While the nanocomposites show a significant reduction in permeability of gases and water due to the incorporation of lamellar clay, their susceptibility to non-diffusional mechano-chemical degradation is unknown. The fracture toughness of these nylon-6/clay nanocomposites increases, not as a function of clay content, but as a function of the volume of nylon-6 polymer chains influenced by the clay lamellae surfaces. Both the clay and the constrained volume offer the nanocomposites some protection from the deleterious effects of NO_x. The time-to-failure at a given stress intensity factor as a function of clay content and constrained volume will be discussed along with fracture toughness of the materials.

Introduction

The emergence of nylon-6/clay hybrid polymer nanocomposites as commercially available materials has incited a flurry of activity in the field of hybrid nanocomposites. The co-polymerization of ε-caprolactam with organically modified montmorillonite clay produces an exfoliated clay habitat intimately bound to a semicrystalline polymer.[1] The resulting nanocomposites have demonstrated improvements in room temperature tensile modulus of 100%, and 75% improvements in yield stress.[2] Increases in Heat Distortion Temperature (HDT) of 87°C and better retention of mechanical properties at elevated temperature[3] have allowed these materials to be used in under-the-hood applications in automobiles.[4] While the impact properties of nylon-6 are only slightly reduced with the addition of clay[5], plane stress fracture toughness of thin sheet increases[6] non-linearly with increasing clay content. The reduced rate of water diffusion and decrease in water absorption imply that the nanocomposites may also be resistant to environmental degradation by pollutant gases.

One ubiquitous environmental pollutant that is known to degrade oriented nylon-6 fibers is NO_x.[7] NO_x refers to the equilibrium mixture of gases that are the nitrogen by products of fossil fuel combustion. NO_2 is the gas that is monitored in our polluted environment; however, at atmospheric temperatures and pressures the NO_x gas mixture contains 70% N_2O_4, NO_2 and nitric acid when water is present.[8] NO_2, being an odd electron molecule, is capable of initiating free radical reactions in polymers.[9] The degradation caused by these reactions are chemical-kinetic rather than diffusion driven in oriented polymer systems.[10] The degradation mechanisms in nylon-6 are deprotonation leading to chain scission or crosslinking, along with the potential for acid hydrolysis and acid solvation when water is present.[11] Smith hypothesized that the balance between chain scission and crosslinking as a free radical termination mechanism in oriented polymer chains is greatly influenced by applied stress: higher stress levels lead to greater chain scission.[12] However, Igarashi has shown that NO_x exposure does not significantly influence the mechanical properties of unoriented nylon-6 rod. The purpose of this research is to investigate the effect of NO_x exposure on extruded sheet of the nylon-6/clay nanocomposites.

Experimental

0, 2, and 5 wt% clay nanocomposites were graciously donated by Ube Industries, Japan, from their commercial materials line. As received pellets where dried in a vacuum oven at 100 °C for several hours then extruded into 0.03 cm thick sheet through a ½ inch Randcastle single screw laboratory scale extruder and a sheet die with a 4:1 draw ratio. The sheet was cooled by circulating air before take-up on a chill roller. No additional draw was induced during take-up. 0.65 cm wide, 7.5 cm long tensile samples were cut longitudinal to the draw direction and 1.25 cm wide, 10 cm long, plane stress fracture toughness and environmental cracking specimens were also cut longitudinal to the draw direction. All samples were stored in a dessicator prior to exposure and tested immediately after exposure.

The fracture toughness and environmental cracking specimens were pre-notched into the single edge notch tension (SENT) sample geometry by cutting a notch approximately 0.5 times the width of the sample with a razor blade and extending the notch by pressing a new razor blade into the notch tip. While the fracture toughness samples where too thin to meet the plane strain conditions outlined in ASTM D 5045, the recommended procedure was followed to determine a plane stress fracture toughness, K_{Qc}. A sample thickness of approximately 4 cm was calculated as necessary to meet plane strain conditions using a literature value of 3 $MPa(m)^{1/2}$ for the K_{1C} of nylon-6.[13] Acceptable thick samples could not be manufactured. Similarly, the SENT sample geometry is not recommended by the ASTM D 5054, however, it was a convenient geometry for testing the extruded sheet and permitted geometric comparability between the fracture toughness and environmental cracking samples. Environmental cracking under sustained load was conducted on samples of the same SENT geometry used in the fracture toughness experiments. These samples were exposed to 1 vol% NO_x introduced into a sealed chamber from a "lecture bottle" of NO_2 and loaded by a cantilevered weight. While attempts were made to minimize the amount of water present by purging the chamber with dry air prior to introduction of the

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* University of Utah, Department of Mechanical Engineering, 50 South Campus Drive, Salt Lake City, UT 84112

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NO_x, the exposure environment was not rigorously anhydrous. The time to failure was recorded by video taping the samples during loading.

For the tensile and fracture toughness experiments, samples where either tested immediately or exposed to 1 vol% NO_x for a specified period of time. Fiberglass packing tape protected the grip ends of the samples both during exposure and during testing to prevent premature breakage in the grips. The tensile and fracture toughness samples were loaded to failure at a rate of 5 cm/min in an Instron load frame with a 25kN load cell. Yield was taken at the point of zero slope in the stress-strain curve, modulus was taken as a best-fit line through the initial portion of the curve, after the load take-up region, and strain was derived from crosshead displacement.

Results and Discussion

The improvements in tensile properties with clay content and constrained volume for dry, unexposed, samples are shown in Table 1. Both the yield stress and the room temperature modulus increase by over 100% with the addition of 5 wt% clay, without severely impacting the strain-to-failure of the materials. This improvement in mechanical response characteristics has been attributed to a reduction in mobility of the nylon-6 polymer chains in the nanocomposite materials. Chain mobility is reduced by both end-tethering of the chains through ionic interactions with the clay lamellae and complexation of the mid-chain carbonyl groups with the clay surfaces.[2,6] The volume of polymer chains exhibiting reduced mobility is estimated as the constrained volume. The constrained volume is calculated from dynamic mechanical analysis data following the method developed by Oka and Chikahisa[2,14] for determining the crystallinity of semi-crystalline polymers.

The constrained volume is calculated as the ratio of the lost work fraction of a material to the fraction of work lost in a sample of known constrained volume, or crystallinity. The lost work fraction is the ratio of the magnitude of the loss modulus to the total material response at the peak of the alpha relaxation, or glass transition, of the loss modulus versus temperature profile. The reference constrained volume for the nanocomposite materials was taken as the crystallinity of the 0% clay nylon-6 as determined by differential scanning calorimetry, approximately 15%.

While the improvements in modulus and yield stress are nearly linear with the clay content, the fracture toughness improvement is nearly linear with constrained volume. This linearity suggests that the reduction in mobility of the polymer chains has a strong influence on the resistance to crack propagation in the nanocomposites. However, this reduced mobility does not appear to protect the nanocomposite materials from the effects of NO_x degradation.

The mechanical properties of the nylon-6 and nanocomposite materials after 70 hours of exposure to 1 vol% NO_x are shown in Table 2. The moduli decrease by 60% and the yield strengths decrease by over 70% for all three materials, while strain-to-failure remains roughly constant. When normalized by their dry air moduli, it is evident that the properties of the nanocomposites decay at the same rate regardless of clay content or constrained volume, as illustrated in Figure 1.

The plane stress fracture toughness, however, decays to a greater extent for the nanocomposite materials than for nylon-6 when exposed to NO_x. The K_{QC} of the nylon-6 decreases by only 8% after 70 hrs of exposure, while the K_{QC} of the 5 wt% clay nanocomposite decreases by 19%. While this increase in the degradation of plane stress fracture toughness may indicate an increased sensitivity to NO_x degradation, it more likely indicates an increased sensitivity of the crack propagation mechanism in the nanocomposites to the results of NO_x induced chain scission.

The time dependant NO_x exposure results under the influence of concentrated stress show that the nanocomposites are protected from the synergy of NO_x degradation and applied stress. The results of sustained load environmental cracking experiments are shown in Figure 2. The stress intensity factors for samples exposed to dry laboratory air decay asymptotically with failure time to a long duration value that are higher for the nanocomposites than for nylon-6. However, the decay of the stress intensity factor with NO_x exposure time is linear for all materials. A linear decay of K_{Qi} with exposure time indicates that the mechanism of NO_x degradation is not diffusion limited. The free radical initiation mechanism of NO_2 attack is chemical-kinetic rather than diffusion driven; therefore non-exponential behavior of the property degradation should be expected.

While the decay rate of the stress intensity factor with exposure time is linear for all three materials, the influence of the constrained volume shifts the line to higher values and decreases its slope with increasing clay content. For any failure time, the K_{Qi} value of the NO_x exposed nylon-6 is less than that of the dry air exposed nylon-6. However, for the 5 wt% clay nanocomposite, the K_{Qi} of the NO_x material is significantly higher than for the dry air exposed material for all exposure times recorded. (The approximately 13 hours maximum failure time recorded in this sustained load experiment are significantly shorter than the 70 hours of exposure time used in the exposed fracture toughness experiments.) Since the post-exposure mechanical property data do not indicate that either the reduced diffusion rate in the nanocomposites, or the presence of the clay reduces the rate of decay of the nylon-6 polymer, the toughening of the nanocomposites with NO_x exposure can not be attributed to the presence of the clay. However, the reduction of polymer chain mobility within the constrained volume may contribute to a reduction in the stress/degradation synergy in the nanocomposite materials.

The degradation in mechanical properties of highly oriented nylon-6 fibers in NO_x depends upon the stress applied during exposure.[10] Since, the initiation of free radicals by NO_2 attack of the polymer chains can lead to either chain scission or crosslinking, stress applied to highly oriented polymer chains shifts the balance of the chemical degradation reaction towards chain scission. Therefore, if the constraint of the polymer chains by the clay lamellae in the nanocomposites prevents the polymer chains at the crack tip of the environmental cracking specimens from orienting and reacting the intensified stress levels, then the free radical termination reactions in the nanocomposites would favor crosslinking rather than chain scission. This shift in free radical termination mechanisms would protect the nanocomposites from environmental cracking by NO_x.

Estimations of the state of orientation of the polymer chains at the crack tip can be made by applying the Dugdale-Barenblatt strip yield zone model[15] to the plane stress fracture toughness data. The length of a yielded region extending from the tip of a notch can be estimated from the square of the ratio of the critical fracture toughness to the yield stress. Assuming that this yielded region is triangular and that the apex angle is constant between materials, then the length of the yield zone is proportional to the height of the base of the yield triangle. The height of the base of the yield triangle can be assumed to be a measure of the polymer chain orientation at the crack tip. Figure 3 shows the calculated length of the strip yield zone as a function of clay content in the nanocomposite materials. The nylon-6 and nanocomposite fracture toughness and environmental cracking specimens displayed a roughly triangular yield region extending from the tip of the cut notch during loading. While the measured size of this region is more that twice that calculated using the Dugdale-Barenblatt equation, the trend in the data is consistent. The smaller yield zone length in the nanocomposites indicates that the polymer chains at the crack tip are less well oriented in the 5 wt% clay nanocomposite than in the nylon-6 at the same stress intensity level. Therefore, the environmental crack propagation behavior of the nanocomposites is less significantly influenced by the stress/degradation synergy of NO_x attack than the nylon-6. The nanocomposites are thereby protected from the effects of NO_x attack.

Conclusions

The copolymerization of nylon-6 with organically modified montmorillonite clay results in a hybrid nanocomposite that exhibits impressive improvements in mechanical properties over nylon-6. 100% improvements in tensile modulus and yield stress are possible with the incorporation of 5 wt% clay. The plane stress fracture toughness of extruded sheet of the 5 wt% clay nanocomposite increases by nearly 50% over that of nylon-6. While post exposure tensile experiments indicate that the mechanical properties of the nanocomposites decay at the same rate as nylon-6 with NO_x exposure, the nanocomposite materials are more resistant to environmental cracking under sustained load than nylon-6 due to a decrease in polymer chain orientation at the crack tip.

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Clay Content (wt%)	Constrained Volume (vol%)	Modulus (GPa)	Yield Stress (MPa)	Failure Strain (%)	Plane Stress Fracture Toughness (MPa*m$^{0.5}$)
0	15	1.57 ± 0.3	48.0 ± 1.5	264 ± 38	5.21 ± 1.25
2	28	2.37 ± 0.7	73.3 ± 2.2	292 ± 49	7.29 ± 0.57
5	36	3.22 ± 0.3	101.4 ± 7.9	255 ± 10	7.60 ± 1.49

Table 1: Thin sheet longitudinal tensile properties at room temperature

Clay Content (wt%)	Modulus (GPa)	Yield Stress (MPa)	Failure Strain (%)	Plane Stress Fracture Toughness (MPa*m$^{0.5}$)
0	0.59±0.1	10.5±2.9	375±94	4.80±2.1
2	1.20±0.3	29.9±9.9	277±35	4.46±2.1
5	1.36±0.2	31.7±4.8	243±46	6.12±1.2

Table 2: Post-exposure tensile properties, 70 hrs in NO_x at room temperature

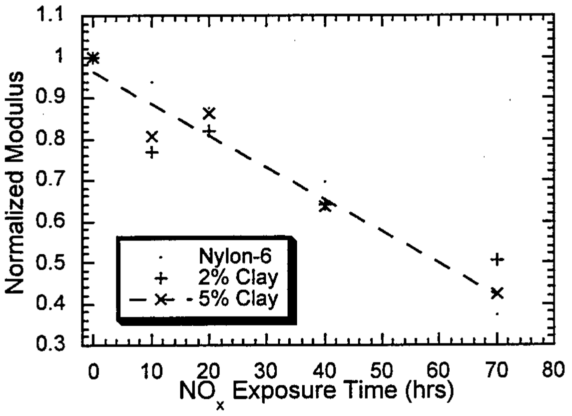

Figure 1: Normalized initial tensile modulus as a function of 1 vol% NOx exposure time.

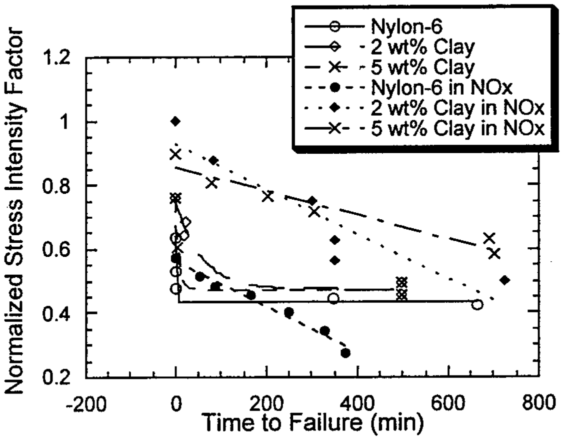

Figure 2: Sustained load environmental cracking results: normalized initial stress intensity factor as a function of failure time.

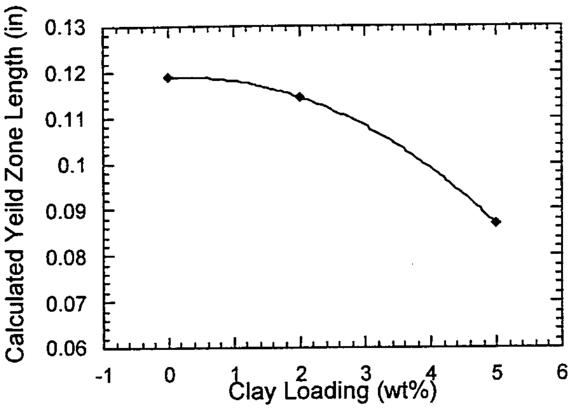

Figure 3: Dugdale-Barenblatt strip yield zone length as a function of clay content.

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