

EFFECTS OF CRYOGENIC AGING ON A RAPID PROTOTYPED (RP) POLYMER

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ABSTRACT

Little research has been done on the post-processing (aging) of rapid prototyped (RP) polymers at temperatures below 123K (-238°F). Test specimens of RP thermosetting resin (DSM-Somos 8110) were fabricated and cryogenically aged from 10-25 hours. The tensile strength and impact toughness were measured. This work will study the effect of cryogenic aging on yield strength of Somos 8110. This paper will also discuss our interpretation of the data based on fractography.

INTRODUCTION

As industry continues to increase its use of rapid prototyping (RP) materials, the necessity for enhancing the properties of RP materials is becoming more important. Past studies have concluded that by reducing the temperature below 123K (-238°F), cryogenic processing increased the strength of many materials, particularly metals. But while the strength of the materials increased, the cryogenic treatments also reduced ductility.

Though relatively unstudied, the results of cryogenic tempering on certain polymers will prove highly valuable to industry. This study hopes to increase the usage of RP materials through cryogenic processing by optimizing the combination of strength and ductility for the stereolithography photopolymer epoxy resin, DSM Somos 8110 [1].

The cryogenic test procedure began with the construction of the tensile and impact test samples using the RP materials. In order to increase the mechanical properties, these samples were then subjected to 88K (-300°F) using several different holding and ramping times. Next, the samples were examined using tensile and impact tests. Finally, the data obtained from the tests was analyzed. Based on metals, it was expected that the tensile strength of the RP materials would increase, and the toughness would decrease after cryogenic processing. However, we hoped there would be a combination of cryogenic aging treatments that would improve both the strength and toughness.

The purpose of this paper is to discuss the cryogenic method for post-processing rapid prototyped DSM-Somos 8110 epoxy resin. In addition, this paper will examine the effect of cryogenic aging on the tensile strength and impact energy.

BACKGROUND

Cryogenics

Cryogenics is the science and art of producing a low temperature environment. It started in 1877 when two scientists, Cailletet in Paris and Pictet in Geneva, developed a procedure to liquefy oxygen in the laboratory [2]. Now, liquid nitrogen is one of the most common cooling media. Since the normal boiling points of nitrogen and other permanent gases such as helium, oxygen, and argon is about 84.8K ($\approx -307^\circ\text{F}$), the cryogenic temperature is generally considered to be 84.8K or below [2].

Cryogenic processing is an important field in industry today. For example, an increase of 195% to 817% in wear resistance has been reported for standard steel that was cryogenically treated [3]. The cryogenic process consists of three stages that are time and temperature dependent to the aging temperature. This process starts with the gradual ramping down of temperature for a pre-determined time range, to a specific point. The temperature is then held for a period of time. Finally, a gradual process of temperature ramp-up is executed. As a result of cryogenic processing, some unknown molecular changes occur, modifying the structure of the material [3].

Conventionally, heat treating is used to strengthen steel and other alloys. Upon quenching steel below its eutectoid decomposition temperature, some retained austenite remains [3]. However, cryogenic processing transforms virtually all of the retained austenite to martensite, along with a precipitation of fine carbide particles. These effects have resulted in increased wear resistance [3].

Polymers and Stresses

Polymers can be classified according to their chain structure and chain arrangement. Chain structure of polymers is further characterized by the chemical composition of monomers and their relative arrangement within a chain. The common chain arrangements are linear chains, branched chains, and cross-linked networks (e.g. epoxy resins).

The general characterization of polymers is very difficult due to the complicated structures, the great variety of chemical compositions and the transfer of molecular groups [4]. However, the fracture strength of polymers can be explained from a microstructural point of view. These factors can include molecular stress concentrations and residual thermal stresses [5].

The twisting and kinking of polymer chains contributes to local stress concentrations due to the uneven stress distribution between the molecules. When the entangled polymer chains are under stress, the chain segments in the load direction provide most of the load-carrying capacity. When polymers are cooled too quickly during cryogenic processing, thermal stresses are built up within the polymer, and these act to reduce the tensile strength [4].

EXPERIMENTAL PROCEDURE

Equipment and Process

The following major equipment was used in this research.

1. Northrop Grumman SLA-250 RP Machine
2. Cryogenic Treatment Equipment
3. Instron Tensile Testing Machine
4. Izod Impact Tester
5. Scanning Electron Microscope (SEM)

The experimental setup is shown in **Figure 1**.

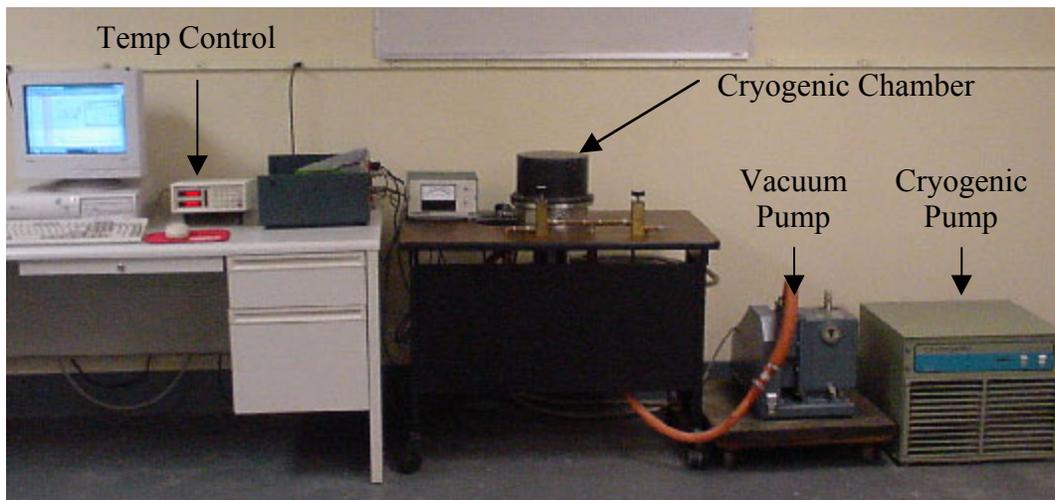


Figure 1. Experimental setup for cryogenic processing.

The following outlines the steps used in the experimental process that was used to design, fabricate, test and analyze the samples.

1. Design Dog Bone and V-Notch Samples
2. RP Machine Builds Parts from Design
3. Expose Parts to Cryogenic Treatment with Liquid He.
4. Tensile and Impact Testing
5. SEM Fractography

Designing and Prototyping the Samples

Drawings of the dog bone and v-notch shaped samples were created using AutoCAD (Figs. 2a and 2b) and these were saved as separate .DWG files. These files were then converted into STL format for use with stereolithography software. SLA-250 (Northrop Grumman) RP machines was then used to rapid prototype the parts.

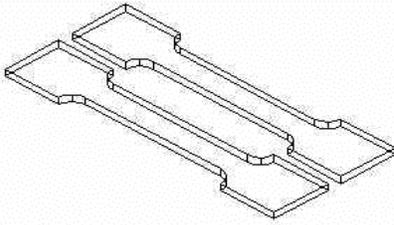


Figure 2a. Two dog bone-shaped samples.

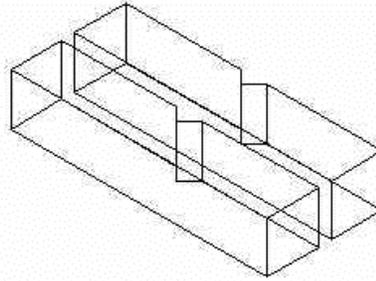


Figure 2b. Two v-notch-shaped samples.

Cryogenic Treatment

The following process was used to cryogenically treat each sample.

1. All samples except the baseline went through cryogenic treatment before testing. The samples were prepared at Northrop Grumman, and cryogenically aged at Loyola Marymount University.
2. The cryogenic process is characterized by three parameters: ramp-down time from room temperature to 88K (-300°F), hold time at 88K, and ramp-up time from 88K to room temperature.
3. Preliminary experiments were performed on cryogenic treatment. The ramp-down time of 14 hours was used. Three holding times of 10, 15 and 20 hours, and ramp up times of 14 hours were used.
4. Samples are labeled as follows: XX-XX-XX. The numbers represent the ramp-down time, holding time and ramp up time, respectively, in hours. (e.g: 14-10-14 means that the samples were ramped-down in 14 hours, cryogenically aged 10 hours, and then ramped-up in 14 hours.)

Tensile Testing

The yield and ultimate strengths of the samples were measured using the Instron Universal Testing Instrument 4500. The cross-head speed of the test machine was 0.0212 mm/s. The interface with the machine was performed using the front panel and a software program running on a desktop computer. The test specimens were designed in the shape of a dog-bone, similar to ASTM D638-97. The end pads of the specimen were tightened and aligned between the two grips of the frame unit. A computerized load cell located inside the frame unit measured the force applied to the gauge section of the sample. The software calculated the tensile stress in the gauge section. Strain was measured with an extensometer, and the stress vs. strain curves were plotted as the specimen was continuously loaded. The yield stress was measured at 0.2% offset strain, and the ultimate strength was measured at the maximum stress the material could withstand. Four to six specimens were tested for each cryogenic aging treatment (0-20 hours). The tensile strength data were statistically analyzed to determine the effect of aging treatment on the yield and ultimate strengths.

Izod Impact Testing

Izod impact testing is performed to determine the toughness of a material. The sample is made

with a centered v-shaped notch. During the impact testing, the sample is subjected to a quick and intense blow by a hammer pendulum. The impact test evaluates the material's resistance to crack propagation. The impact energy absorbed by the sample during failure is determined by calculating the difference in potential energy of the hammer [5].

SEM Fractography

The fracture surfaces of the failed tensile samples of Somos 8110 resin were examined under a scanning electron microscope (SEM). SEM fractography was used to interpret the results of the tensile strength data for both the untreated (baseline) and cryogenically treated samples [6]. The SEM used an acceleration voltage of 1.2kV. The fracture surfaces were observed sequentially at magnifications of 15x, 40x and 150x.

The stretching of the polymer chains and fracture initiation were correlated with the yield strength data. Here critical-size cracks were initiated from defects and propagated when the yield strength of the polymer was exceeded. The propagation of the crack front was correlated with the ultimate strength. Then the crack propagation patterns could be observed on the fracture surface of the failed specimens.

RESULTS AND DISCUSSION

Tensile and Impact Testing

The results of the yield strength and ultimate strength vs. cryogenic treatment time (0-20 hours) are shown in **Figures 3A, 3B**. In both cases, the strengths appear to be affected by aging time. To verify these results, the data were statistically analyzed using multiple t-testing, which compared the means of two treatments at-a-time at a 0.05 level of significance [7]. A one-way analysis of variance (ANOVA) could not be used, because the variances of the treatments were unequal. For the yield strength data (**Figure 3A**), it was determined with 95% confidence that the means of the treatments were statistically insignificant. Due to the large variances at 15 and 20 hours, we can say that there was no significant increase in the yield strength with aging time.

For the ultimate strength (**Figure 3B**) vs. aging time, the data were analyzed in the same way. Again, one-way ANOVA could not be used. Multiple t-testing on the treatment means showed that for 95% confidence two conclusions were reached: (1) the mean strengths at 0, 10 and 20 hours were equivalent, and (2) the mean strength at 15 hours was significantly lower than that at 10 and 20 hours. Hence, aging time produced a drop in the ultimate strength between 10 and 15 hours. Otherwise, there was no significant effect of cryogenic aging on the ultimate stress.

When the impact energy data vs. aging time (**Figure 3C**) were statistically analyzed, the large variance at 10 hours indicated that the treatment means were insignificant with 95% confidence. Hence, there was no effect of cryogenic treatment time on the impact energy.

SEM Fractography

Since all of the tensile specimens failed near the fillet radius, failure analysis was performed on the tested specimens. The fracture surfaces of the tensile specimens were examined under three different treatment conditions: (1) Sample A, treated for 15 hours and having the highest yield strength (**Figure 3A**), (2) Sample B, treated for 15 hours and having the lowest yield strength (**Figure 3A**) and (3) Sample C, untreated.

The following findings were made from observing the fracture surfaces of Samples A, B, C in **Figures 4A, 4B** and **4C**, respectively. In all cases, the fracture originated from surface defects on the fillet radius (between the gauge length and grips) of the tensile specimens. Fracture propagated from left to right, as shown by the 'river markings' on the fracture surface [6]. Samples B and C showed similar fracture patterns that consisted of mixed mode I and III fracture [6]. Here, fracture initiated from the stepped fillet radius in **Figures 4B, 4C** and **5B**, which was formed during stereo-lithographic processing. Sample A exhibited primarily mode I fracture from the fillet surface, and fracture did not originate from steps on the fillet radius (**Figures 4A** and **5A**).

Samples B and C had low yield strengths and similar fracture patterns. The low strengths were interpreted as being caused by the stepped fillet radius. The steps probably caused a high stress concentration at the fillet surface. In addition, the steps appeared to have surface defects on the fillet radius (**Figures 4B, 4C** and **5B**). Sample A had the highest yield strength, and there were no steps or surface defects on the fillet radius where fracture originated. Hence, the stepped fillet surfaces with their associated surface defects probably caused the specimens to fail prematurely at lower strengths. The steps and surface defects in Samples B and C also accounted for the higher variance (scatter) in the data.

The differences in the fracture patterns between Sample A and Samples B, C could have also accounted for their difference in yield strength. In Samples B and C, it appeared that the crack front propagated at slower velocities than in Sample A. The crack had more time to separate on to different levels and develop mode III shear lips (**Figures 4B** and **4C**). In Sample A, there were no steps and surface defects at the fillet radius. Consequently, a critical-size crack had to be nucleated on the fillet surface, and this required extra stress, which caused the strength to be higher. Once a critical-size crack was formed, the extra stress caused the crack to propagate catastrophically at a higher velocity. The higher velocity fracture in Sample A is indicative of primarily mode I fracture patterns with little mode III shearing (**Figure 4A**).

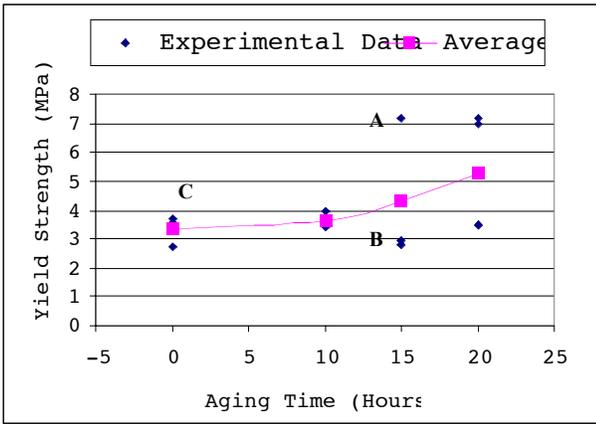


Figure 3A. Yield Strength vs. Cryogenic Aging Time.

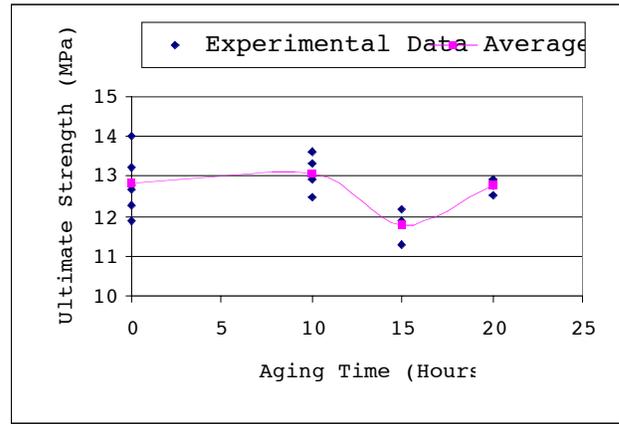


Figure 3B. Ultimate Strength vs. Cryogenic Aging Time.

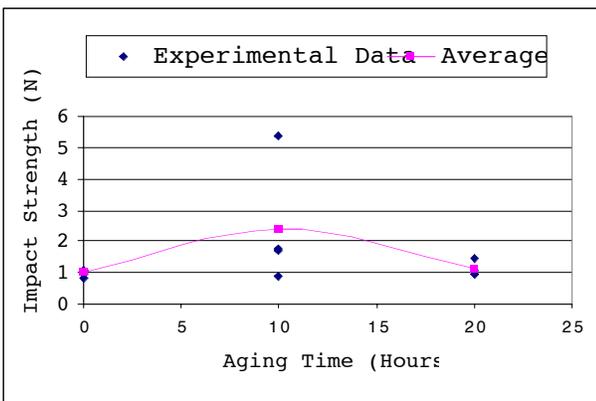


Figure 3C. Impact Energy vs. Cryogenic Aging Time.

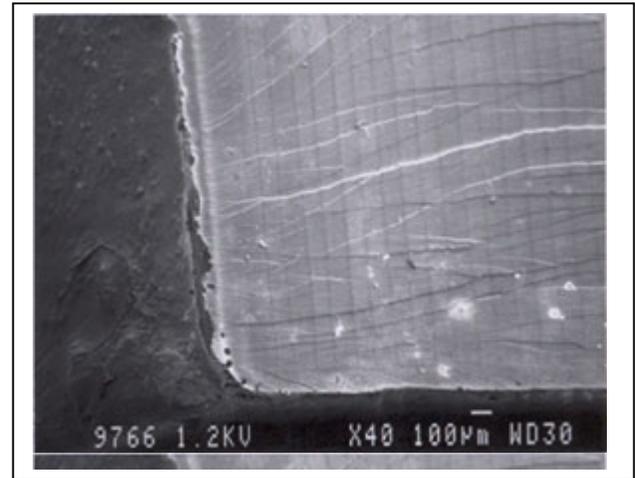


Figure 4A. 40x SEM micrograph of Sample A in Figure 3A.

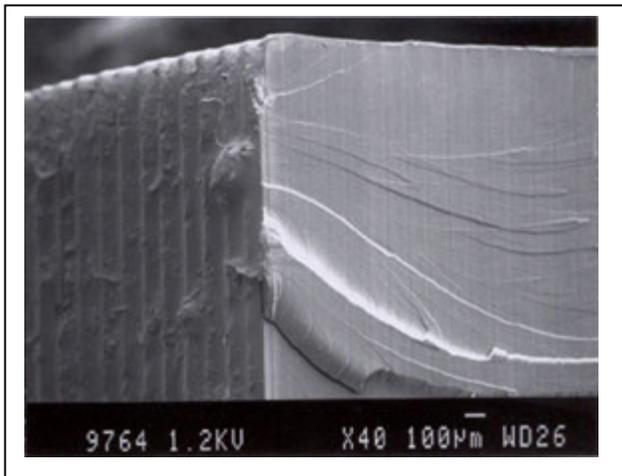


Figure 4B. 40x SEM micrograph of Sample B in Figure 3A.

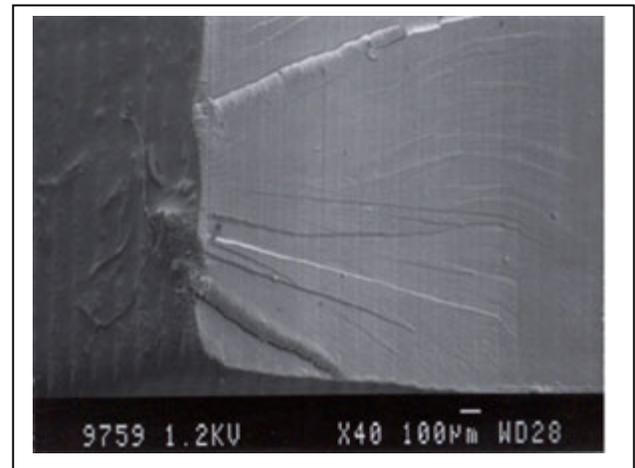


Figure 4C. 40x SEM micrograph of Sample C (Baseline) in Figure 3A.

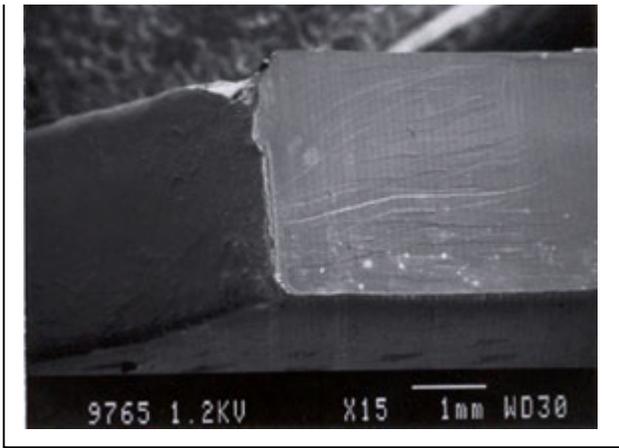


Figure 5A. 15x SEM micrograph of Sample A from **Figure 4A**.

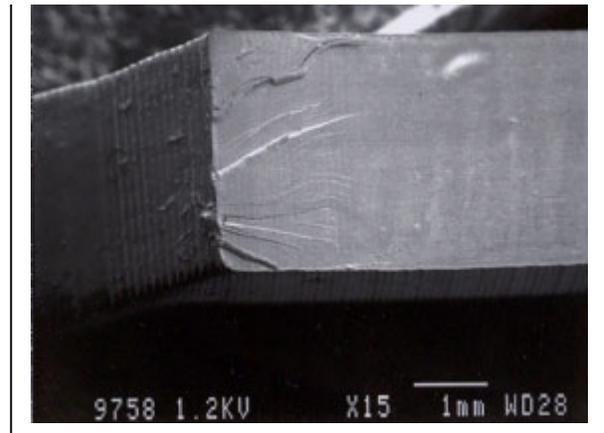


Figure 5B. 15x SEM micrograph of Sample C (Baseline) from **Figure 4C**.

CONCLUSIONS AND RECOMMENDATIONS

Based on the findings from our research, the following conclusions and recommendations can be made:

1. DSL-Somos 8110 test specimens were fabricated by stereo-lithography using SLA-250 RP equipment. The specimens were laser cured by pulling the specimens parallel to the tensile axis.
2. The test specimens were cryogenically treated by a ramp-down cycle from room temperature to 88K in 14 hours, a hold cycle of 10 - 20 hours, and then a ramp-up cycle from 88K to room temperature in 14 hours.
3. Due to large data scatter, the yield strength and impact energy were not affected by cryogenic aging treatment. Only the ultimate strength exhibited a significant decrease with aging treatment from 10 to 15 hours.
4. It was expected the wide data scatter was caused by microscopic steps and their associated defects at the fillet radius of the tensile specimens. Samples with steps and defects had lower strengths, and those without steps and flaws had high strengths. The variability in the surface texture of the fillet radius caused a wide variability in the tensile strength and impact energy.
5. For future work, it is recommended that the SLA specimens be rapidly prototyped normal to the face of the dog-bone specimen. This will hopefully reduce the data scatter, which currently masks any potential effect of cryogenic aging time on the tensile strength and impact energy.

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