J Therm Anal Calorim (2010) 102:469–476
DOI 10.1007/s10973-010-0991-6

Use of DSC and DMA to study crystallization as a possible cause for a glove tear

Neoprene rubber gloves are used as part of a Space Shuttle pressurized astronaut suit

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NATAS2009 Special Issue

Abstract The Advanced Crew Escape Suit (ACES) is a pressurized suit worn by astronauts during launch and landing phases of Space Shuttle operations. In 2008, a large tear (12.7–25.4 mm long, between the pinky and ring finger) in the ACES left-hand glove made of neoprene latex rubber was found during training for Shuttle flight STS-124. An investigation to help determine the cause(s) of the glove tear was headed by the NASA Johnson Space Center (JSC) in Houston, Texas. Efforts at JSC to reproduce the actual glove tear pattern by cutting/tearing or rupturing were unsuccessful. Chemical and material property data from JSC such as GC-MS, FTIR, DSC, and TGA mostly showed little differences between samples from the torn and control gloves. One possible cause for the glove tear could be a wedding ring/band worn by an astronaut. Even with a smooth edge, such a ring could scratch the material and initiate the tear observed in the left-hand glove. A decision was later made by JSC to not allow the wearing of such a ring during training or actual flight. Another possible cause for the ACES glove tear is crystallinity induced by strain in the neoprene rubber over a long period of time and use. Neoprene is one among several elastomers known to be susceptible to crystallization, and such a process is accelerated with exposure of the material to cold temperatures plus strain. When the temperature is lowered below room temperature, researchers have shown that neoprene crystallization may be maintained at temperatures as high as 7.2–10 °C, with a maximum crystallization rate near −6.7 to −3.9 °C (Kell et al. J Appl Polym Sci 2(4):8–13, 1959 [1]). A convenient conditioning temperature for inducing neoprene crystallization is a typical freezer that is held near −17.8 °C. For work at the NASA Marshall Space Flight Center (MSFC), samples were cut from several areas/locations (pinky/ring finger crotch, index finger and palm) on each of two pairs of unstrained ACES gloves for DSC and DMA thermal analysis testing. The samples were conditioned in a freezer for various times up to about 14 days. Some rectangular conditioned samples were unstrained, while most were subjected to strains up to 250% with the aid of two slotted aluminum blocks and two aluminum clamps per sample. Trends were observed to correlate DSC data (heat of fusion) and DMA data (linear CTE and stress for iso-strain testing) with (a) sample location on each glove; and (b) percent strain during conditioning. Control samples cut “as is” from each glove location were also tested by DSC and DMA.

Keywords Pinky/ring finger crotch · Strain-induced crystallization · Freezer conditioning

Introduction

Historical background involving NASA/MSFC

MSFC became involved in this investigation largely because of a previous incident with a torn neoprene latex rubber glove. Non-pressurized neoprene gloves are used in science glove box experiments inside the International Space Station (ISS). In 1999, it was found that some of these gloves stored in a metal cabinet drawer on Earth for 4 years showed significant signs of corrosion. Analysis of the corrosion products by energy-dispersive X-ray spectroscopy (EDS) revealed the presence of free chlorine. It was discovered that the ISS neoprene (polychloroprene) latex

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gloves released small quantities of hydrochloric acid (HCl) with material aging, a process enhanced by the presence of air and light. The HCl not only degraded the neoprene glove material properties (much lower tensile strength and elongation, much higher modulus), but also induced crystallinity in the material. Values of percent crystallinity up to 9.70 were determined by DSC for HCl-affected material, compared with only 0.38 for unaffected material [2].

Literature on crystallization of neoprene (polychloroprene) and other elastomers

Crystallization rate of neoprene

Dilatometric studies were made to determine crystallization and glass transition data for several unvulcanized and vulcanized polychloroprenes, and polychloroprene/styrene-butadiene blends [1]. For five temperatures ranging from −14 to 5 °C, the volume decrease due to crystallization was measured as a function of time. The maximum rate of crystallization of both unvulcanized polychloroprene and the blends occurred near −5 °C. For a crystallization-resistant polychloroprene (Neoprene WRT), the following approximate times were required to reach an equilibrium degree of crystallization: 6.5 days at −5 °C, 11 days at −14.3 °C (lowest temperature measured). Melting temperatures of crystallized samples of several neoprenes ranged from 36 to 43 °C by an optical method. In another paper, a dilatometric application of the Avrami equation was used to study the crystallization kinetics of several grades of polychloroprene [3]. In this study, a curve of crystallization half-period ($t_{1/2}$) versus crystallization temperature for Neoprene W passed through a minimum near −5 °C, indicating the maximum crystallization rate. For crystallization-resistant Neoprene WRT, $t_{1/2}$ was determined to be 175 h (7.3 days), presumably measured at 0 °C.

Tear strength of neoprene

Tear strength of several elastomers was measured over a range of rates, temperatures, and crosslinking [4]. For neoprene WRT, tear strength was measured for several temperatures from 45 to 150 °C. Even when the amount of curing agent was doubled, tear strength remained high even at a high temperature (150 °C), which could be attributed to strain-induced crystallization along the rough fracture surface upon tearing. The effect of the rough fracture/tear surface was nullified as follows: Two layers of partially crosslinked neoprene were interlinked in contact for a time to achieve the final degree of crosslinking, creating a type of peel specimen. Even with this special specimen to create a smooth fracture surface, data for detachment energy versus reduced rate of crack propagation did not fit on a continuous master curve for temperatures ranging from 0 to 150 °C. The discontinuity in the master curve was attributed to strain-induced crystallization at the high rates and low temperatures.

Mechanical property data to study the crystallization of polyisoprene (natural rubber)

In a 1983 aerospace study, Morton Thiokol found that torques on the natural rubber nozzle flex bearing of the Peacekeeper static test motor were higher than expected for the motor conditioned and tested at 7.2 °C [5]. For unstrained samples of natural rubber conditioned at −3.9 °C, there was a sharp increase in Shore A hardness after 7 days. For strains of 50 and 150%, the rate of increase in hardness increased with increasing strain for 2–7 days of conditioning.

For the test motor study, the shear modulus of natural rubber was also determined as a function of time at temperature, strain rate, cure temperature, and test temperature [6]. These data showed that for several combinations of storage temperature/test temperature, the greatest increase in shear modulus (at 395% strain) was for the 4.4 °C storage/4.4 °C test conditions. For these conditions, the rate of the shear modulus increase slowed between 6 and 13 days. Additional shear modulus data at several temperatures (10–18.3 °C) was compared with previous data at 4.4 and 7.2 °C. From this comparison testing, it was determined that strain-induced crystallization in the natural rubber was formed and retained at temperatures below 10 °C. For several cure temperatures of 137.8–160 °C, shear modulus data also showed that crystallization rate decreased as cure temperature (and crosslink density) increased.

Experimental

Materials and fixtures used

Figure 1 shows one of the ACES gloves used for the testing described in this work. The darker glove material near the palm area and below is Gore-Tex—a fabric containing expanded PTFE. All of the glove material above the Gore-Tex is neoprene. The Gore-Tex was selected to improve glove comfort and breathability. To further improve comfort, the neoprene glove section is “flocked” on the inside with a very thin layer of cotton material. Figure 1 also shows the three primary areas that samples were cut from in the neoprene section for DSC and DMA testing: palm, index finger, and pinky/ring finger crotch.

Fig. 1 Typical ACES glove showing samples cut from the index finger, pinky/ring finger crotch, and palm for the neoprene upper area. The lower (*darker*) glove area below the palm is made of Gore-Tex fabric

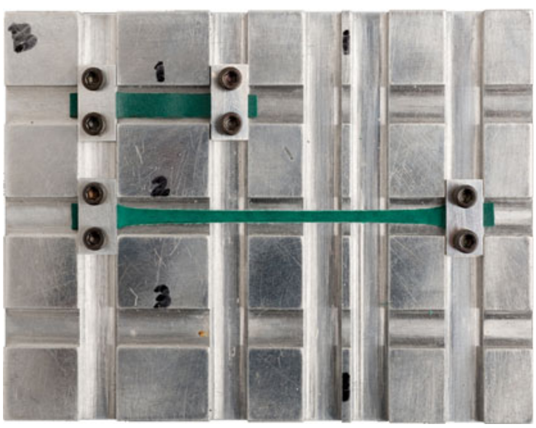

Fig. 2 Aluminum block machined with recessed slots for holding neoprene glove samples at 100, 150 or 250% strain. Sample 1 at the top is unstrained. Sample 2 below is at 250% strain. Such rectangular neoprene samples were tested by DMA, or DMA + DSC after conditioning in a freezer

Figure 2 shows a slotted aluminum block fixture used for conditioning rectangular neoprene samples cut from an ACES glove. Figure 2 also shows the fixture containing two clamped rectangular neoprene samples—one unstrained and one at 250% strain. The slotted block is ~89.2 mm × 69.9 mm, and contains a series of 6.35 mm wide recessed slots. Each rectangular sample was held at each end with an aluminum clamp tightened with Allen screws. The effective sample length held between the two clamps is 15.9 mm. Each rectangular sample was cut from the pinky/ring finger crotch to allow the sample to span that crease. Two aluminum blocks were machined—with accompanying clamps—to allow for freezer conditioning of six glove samples at a time. Each fixture allows for samples to be stretched and held at 100, 150 or 250% strain during conditioning. At least two of the set of six rectangular samples were unstrained (but clamped) during conditioning.

Two pairs of ACES gloves were sent from JSC to MSFC for DSC and DMA testing. The gloves were not previously strained and were within the recommended 78-month (6.5-year) usage life. Both DSC and DMA samples were cut to include the thin layer of cotton flocking on the bottom. Three types/groups of samples were tested in this work, with average weights and dimensions summarized in Table 1. For DSC samples only, each disk sample was weighed, crimped in a standard aluminum pan, and lightly wrapped in aluminum foil. The wrapped samples were placed in a Ziploc bag before freezer conditioning to minimize the effects of condensation from moisture. For DMA samples only, each rectangular sample was also wrapped and stored like the DSC samples. For DMA only or DSC/DMA samples that were cut from the same rectangular specimen; these specimens were mounted in one of two aluminum blocks shown in Fig. 2. Each block plus mounted specimens was also wrapped and stored as described previously, although it was more difficult to keep condensation out during freezer storage.

It is evident in Fig. 1 that the three designated glove areas (especially a crotch area between two fingers) had very limited space from which to cut representative test samples. The number of samples freezer-conditioned at one time was limited to six because of the two positioning blocks (usually 3–4 samples at 150–250% strain and 2–3 samples at 0% strain). With samples removed from freezer conditioning at different times (days), it was not possible to test multiple samples for a given conditioning time so that statistical error bars could be used for the test data. The only multiple samples tested for a given condition were for "as is" glove material that was not strained or freezer-conditioned. Two to three such "as is" samples were usually tested by DSC or DMA for a particular glove area.

Instruments used

The TA Instruments 2920 Differential Scanning Calorimeter (DSC) was used in the standard heating mode. Each disk-shaped neoprene glove sample ("as is" or freezer-conditioned) was equilibrated and held at −20 °C for 5 min, followed by heating at 10 °C/min to 250 °C. Each DSC sample was crimped in a standard aluminum pan, and a steady flow of argon gas was used to purge each sample during heating.

The TA Instruments 2980 Dynamic Mechanical Analyzer (DMA) was also used in this work. Each rectangular sample was equilibrated and held at −22 °C for 5 min, followed by heating at 3 °C/min to 6.5 °C. Missile grade air at 0.41–0.45 MPa pressure was used to operate the DMA

Table 1 Types of tests performed on neoprene glove samples, with average sample weights and dimensions

Sample type tested	Average DSC sample weight/mg	Average DMA sample dimensions/mm		
		Length	Width	Thickness
DSC only	10.1	–	–	–
DMA only	–	11.43	4.05	0.393, 0.428, 0.471 (Pinky/ring, index, palm)
DSC + DMA	6.1	8.62	Same as DMA only	Same as DMA only

drive shaft as well as purge each sample during heating. Each rectangular sample was vertically clamped at each end of the DMA film tension clamp with ~0.45–0.56 N m of torque. Each clamped sample was given some pre-test tension, followed by testing at 22.5% strain in the iso-strain testing mode. For each sample, test data were reported as (a) linear coefficient of thermal expansion (CTE) in μm/m °C from −18 to 0 °C; (b) slope of stress (Pa/°C) from −18 to 0 °C; and (c) stress (Pa) at −18 °C.

Results and discussion

DSC data at NASA/JSC

NASA/JSC in Houston, Texas, performed DSC testing in late 2008 on samples of ACES gloves for six different cure dates from 1995 to 2005. One of the six cure dates represented a control for the gloves (no flight or flight training use). The samples were cut from three areas for each glove (pinky/ring finger crotch, index finger and palm). Each sample was heated in a TA Instruments Q Series DSC. Since NASA/MSFC had previous experience with an issue concerning crystallinity in neoprene gloves [2], they performed an independent evaluation of the DSC data from JSC. The small endothermic peak attributed to neoprene crystallinity was calculated for each glove cure date and glove area. The heat of fusion was plotted versus cure year (from 1995 to 2005) for the three glove areas in Fig. 3. Between 2004 and 2005, it appears that the heat of fusion has a rather sharp increase. The last two data points on the time scale in Fig. 3 are from a glove in which the actual tear occurred (cured 1st qtr. 2005). These data indicate that between 2004 and 2005, at least two cure dates of ACES gloves showed an increase in crystallinity compared with previous years. For the torn glove, samples from the pinky/ring finger and index finger had higher than normal values of heat of fusion. A sample from the palm area of the torn glove did not give meaningful results and was not included in Fig. 3.

DSC data at NASA/MSFC

Figure 4 is a DSC plot of heat flow versus temperature for "as is" and strained glove samples cut from the palm area of a right-handed glove (RH2). The strained sample was stretched 250% during freezer conditioning for 4.9 days. The strained sample shows a clear increase in crystallinity compared with the "as is" sample.

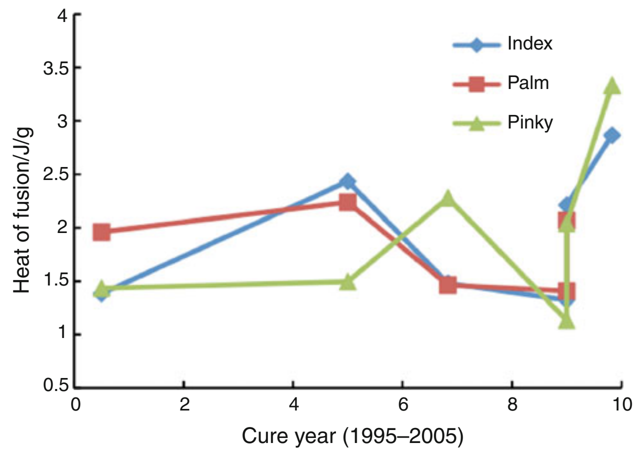

Fig. 3 DSC heat of fusion vs. cure year for samples from ACES gloves with six different cure dates. For each glove, samples were cut from three different areas: pinky/ring finger crotch, index finger and palm

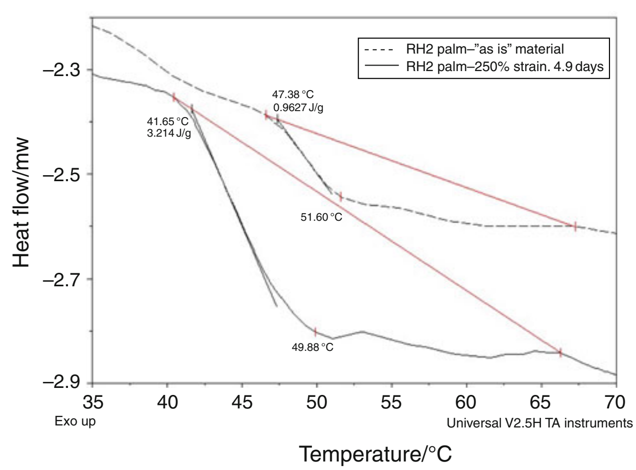

Fig. 4 DSC plot of heat flow vs. temperature for two neoprene samples cut from a right-handed glove (RH2): "as is" sample, and a sample strained at 250% for 4.9 days in a freezer

Figure 5 is a plot of DSC heat of fusion versus time in freezer (days) for samples cut from the pinky/ring, index

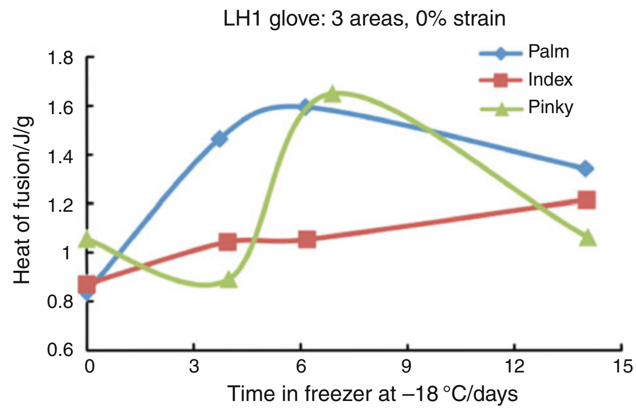

Fig. 5 DSC heat of fusion vs. time in freezer (days) for samples cut from three areas (pinky/ring finger crotch, index finger and palm) of a left-handed glove (LH1). All samples were unstrained

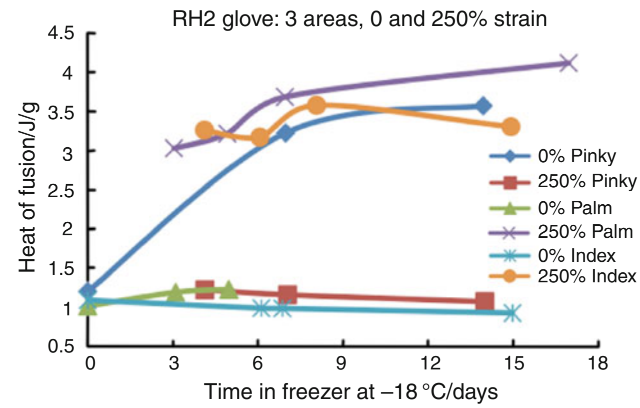

Fig. 6 DSC heat of fusion vs. time in freezer (days) for samples cut from three areas (pinky/ring finger crotch, index finger and palm) of a right-handed glove (RH2). Samples were strained 0 and 250%

and palm areas of a left-handed glove (designated LH1). Each of these samples was weighed and crimped in a standard aluminum DSC pan before being conditioned in the freezer. Since each sample was sealed in a DSC pan during conditioning, no sample was subjected to strain. Figure 5 indicates that the degree of crystallization goes through a maximum at ~6–7 days in conditioning for the pinky/ring crotch and palm areas, a finding that has some validity based on literature data. Kell et al. [1] showed that for crystallization-resistant neoprene WRT, a maximum/equilibrium degree of crystallization was reached at about 6–8 days for conditioning temperatures ranging from −9 to 0 °C. For conditioning temperatures of 5 and −14.3 °C, the maximum degree of crystallization occurred at about 9–11 days. In Fig. 5, samples from the index finger appeared to crystallize less than samples from the pinky/ring crotch or palm. Samples in Fig. 5 ranged in estimated crystallinity from 0.88 to 1.74%. Percent crystallinity by DSC was estimated based on the heat of fusion of 95 Joules/gram for the crystalline phase of unvulcanized polychloroprene [7, 8].

Figure 6 is a plot of heat of fusion versus time in freezer (days) for samples cut from the three previously designated areas of a right-handed glove (designated RH2). Each of these samples was cut as a rectangular strip, clamped at each end, and mounted in the slotted aluminum block in Fig. 2. For each set of samples conditioned from a specific glove area, most samples were strained 250%, while a few samples were unstrained. After a DSC sample was cut from each rectangular strip, the remainder of the same strip was used as a DMA sample. Probably the most significant information from Fig. 6 is that for 250% strain, palm and index finger areas showed considerably higher heat of fusion (and percent crystallinity) than for the pinky/ring finger crotch area. This is not in clear agreement with data from Fig. 5, even though freezer-conditioned samples in Fig. 5 were unstrained. In Fig. 6, heat of fusion and crystallinity for freezer-conditioned samples from pinky/ring samples at 0% strain were high and similar to that of index finger and palm samples at 250% strain. Samples from the index finger and palm at 0% strain, and pinky/ring samples at 250% strain, had the lowest heat of fusion and crystallinity. Palm samples showed the highest crystallinity in Fig. 6 (4.33%) compared with as low as 1.07% for "as is" material. One study yielded percent crystallinity as low as 5% by DSC for Neoprene W and WHV [9]. Plateaus/inflections in most of the curves in Fig. 6 also seem to indicate that the maximum degree of crystallization occurs at ~6–7 days of freezer conditioning.

The temperature onset of heat of fusion ranged from ~41–48 °C as a function of freezer conditioning time (days) and % strain, for all gloves and areas tested. This temperature onset averaged 46.5 ± 0.82 °C for "as is" material (no freezer conditioning, no strain), taken from all three glove areas of two different gloves. These onset temperatures are just outside the high end of the range of optical melting temperatures reported in the literature for grades of neoprene—36–43 and 39–44 °C [1, 9].

DMA data

Figure 7 is a DMA plot of dimension change and stress versus temperature for a strained glove sample cut from the index finger of a right-handed glove (RH2). The strained sample was stretched 250% during freezer conditioning for 6.1 days. In the DMA, the sample was tested at 22.5% strain. Figure 6 shows the calculations of: (a) linear CTE from −18 to 0 °C (slightly negative for this sample); (b) slope of stress from −18 to 0 °C; and (c) stress at −18 °C.

Figure 8 is a plot of linear coefficient of thermal expansion (CTE) versus time in freezer (days) for samples cut from the three previously designated areas of a right-

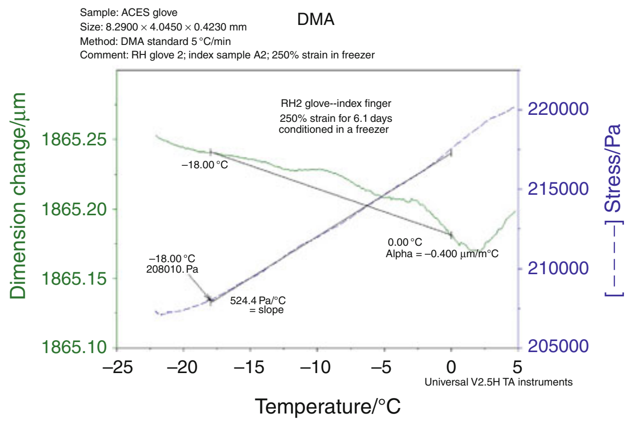

Fig. 7 DMA dimension change and stress vs. temperature for a rectangular neoprene sample tested in the iso-strain mode. Calculations show linear CTE (−18 to 0 °C), slope of stress (−18 to 0 °C), and stress at −18 °C

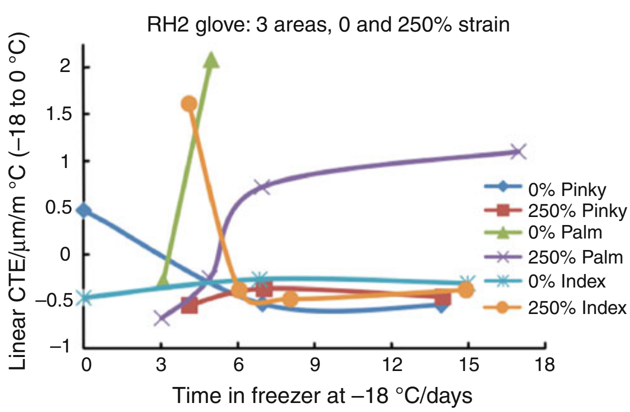

Fig. 8 Linear coefficient of thermal expansion (CTE) vs. time in freezer (days) for rectangular DMA samples cut from three areas (pinky/ring finger crotch, index finger and palm) of a right-handed glove (RH2). Samples were strained at 0 and 250% in the freezer, then 22.5% in the DMA

handed glove (RH2). Of the three glove areas tested, the palm shows the steepest increase in CTE for about 3–6 days in the freezer. Most of the index and pinky/ring areas at 0 and 250% strain show a slightly negative CTE (shrinkage) for about 6–15 days in the freezer. Both the index finger (250% strain) and palm (0% strain) show one data point with much higher positive values of CTE, but the reasons for this are not clear. Each rectangular sample tested in the DMA at a constant strain yielded a small dimensional change versus temperature. However, such a dimensional change is not a true linear expansion (because of constant strain), but likely indicates more of a lateral expansion in the sample.

Figure 9 is a plot of stress (at −18 °C) versus time in freezer (days) for samples cut from the three previously designated areas of one right-handed glove (RH2). Samples

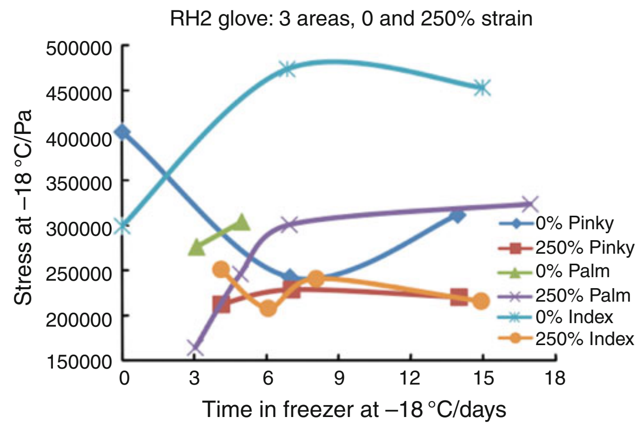

Fig. 9 Stress (at −18 °C) vs. time in freezer (days) for rectangular DMA samples cut from three areas (pinky/ring finger crotch, index finger and palm) of a right-handed glove (RH2). Samples were strained at 0 and 250% in the freezer, followed by 22.5% strain in the DMA

were conditioned in the freezer at 0 and 250% strain. Unstrained index finger samples showed a much higher stress (for ∼7–15 days in the freezer) than any other samples tested. Samples from the pinky/ring finger crotch and index finger with 250% strain showed the lowest values of stress for ∼4–15 days in the freezer—data curves for both sample areas were very similar. At 250% strain, the stress was almost 25% higher in the palm area than in the pinky/ring and index finger areas for ∼7–15 days in the freezer. These data show that for 250% strain, glove material in the pinky/ring and index finger areas would be more likely to tear than in the palm area.

Figure 10 is a plot of stress slope (from −18 to 0 °C) versus time in freezer (days) for samples cut from the three designated areas of one right-handed glove (RH2). Samples

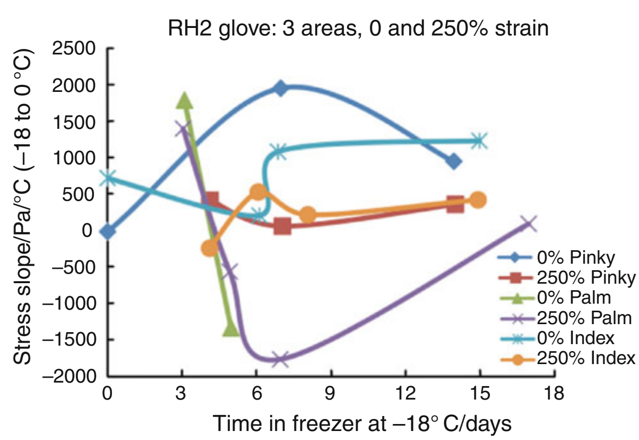

Fig. 10 Stress slope (from −18 to 0 °C) vs. time in freezer (days) for rectangular DMA samples cut from three areas (pinky/ring finger crotch, index finger and palm) of a right-handed glove (RH2). Samples were strained at 0 and 250% in the freezer, followed by 22.5% strain in the DMA

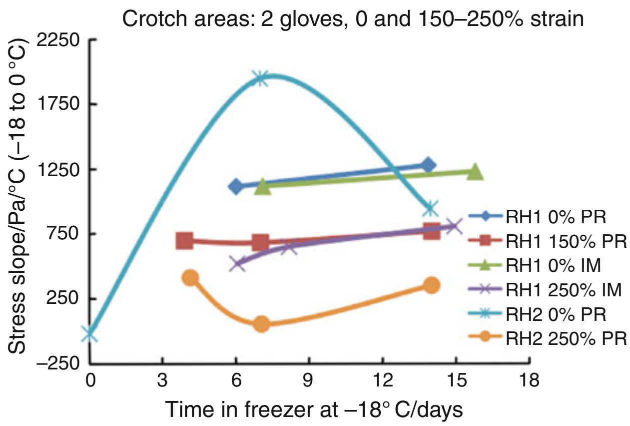

Fig. 11 Stress slope (from −18 to 0 °C) vs. time in freezer (days) for rectangular DMA samples cut from crotch areas (between two fingers) of two different gloves. Crotch areas were between the pinky and ring fingers (PR) and index and middle fingers (IM). Samples were strained at 0 and 250% in the freezer, followed by 22.5% strain in the DMA

were conditioned in the freezer at 0 and 250% strain. Stress slope data appear to show a clearer difference between different areas of the same glove than for stress at a single temperature (−18 °C) in Fig. 9. At 250% strain, stress slope was similar for the pinky/ring and index finger areas. At 250% strain, stress slope was partly negative for the palm area, followed by steeply positive values for freezer conditioning times ≥7 days.

Figure 11 is a plot of stress slope (from −18 to 0 °C) versus time in freezer (days) for samples cut from the crotch areas (between two fingers) for two different gloves (RH1 and RH2). Samples were conditioned in the freezer at 0, 150, and 250% strain. Stress at −18 °C was lower for the pinky/ring (PR) finger area in glove RH2 at 250% strain than for glove RH1 at 150% strain, a trend also evident from the stress slope in Fig. 11. The index/middle (IM) finger area in glove RH1 at 250% strain had about the same stress slope as the PR finger area at 150% strain in the same glove.

Summary and conclusions

The Advanced Crew Escape Suit (ACES) is a pressurized suit worn by astronauts during launch and landing phases of Space Shuttle operations. In 2008, a large tear between the pinky and ring finger in the ACES left-hand glove made of neoprene latex rubber was found during training for Shuttle flight STS-124. An investigation to help determine the cause(s) of the glove tear was headed by the NASA Johnson Space Center (JSC) in Texas. One possible cause for the ACES glove tear suggested by the NASA/Marshall Space Flight Center (MSFC) in Alabama was crystallinity induced by strain in the neoprene rubber over a long period of time and use.

Thermal analysis testing (DSC and DMA) was performed at MSFC on two pairs of ACES gloves with no previous flight or flight training use. Test samples were cut mostly from three areas in each glove: pinky/ring finger crotch, index finger, and palm. Crystallinity was induced by stretching and holding rectangular samples at strains of 150–250%, followed by conditioning in a freezer at −18 °C for up to 14 days.

For unstrained freezer-conditioned circular samples tested by DSC only, the pinky/ring and palm areas had higher crystallinity than the index finger area. Rectangular specimens were freezer-conditioned at 0–250% strain, and samples were cut from each specimen for both DSC and DMA testing. For 250% strain, DSC crystallinity was considerably higher for the palm and index finger areas than for the pinky/ring finger area.

With increasing freezer conditioning time, DMA stress at −18 °C and 250% strain was lower for both pinky/ring and index finger areas than for the palm area. Similar trends were observed for the stress slope from −18 to 0 °C. Stress is proportional to the modulus, which is an indicator of material stiffness. With each DMA test on a rectangular specimen performed at 22.5% strain, a "lateral" coefficient of thermal expansion (CTE) from −18 to 0 °C was considerably higher for the palm area than for the pinky/ring and index finger areas (all freezer-conditioned at 250% strain).

DMA data indicated that the pinky/ring and index finger areas of the glove could be more likely to tear/rip than the palm area due to strain-induced crystallinity. This same conclusion was not as clear-cut based on DSC data. The DSC and DMA data generally showed maxima, minima, or plateaus in percent crystallinity for 6–7 days of freezer conditioning. This latter finding is in general agreement with some literature data for crystallization-resistant neoprene that reached a maximum/equilibrium degree of crystallization at several isothermal temperatures [1].

NASA/MSFC supported an investigation in 1999 in which a slow release of hydrochloric acid from neoprene gloves significantly increased the DSC heat of fusion (and percent crystallinity) of the material. Based on that historical knowledge, further examination of DSC data from NASA/JSC on ACES glove samples revealed a rather sharp increase in the DSC heat of fusion (and percent crystallinity) for gloves with cure dates of 2004–2005. The tear during flight training occurred in a glove with a cure date of the first quarter of 2005. These increased values in heat of fusion from JSC data generally agreed with the largest heat of fusion values produced at MSFC by strain-induced crystallinity in the glove material from freezer conditioning. It is possible that a crotch area like the pinky/ring finger is more likely to tear (perhaps due to lower stress/modulus) than areas such as the index finger or palm. Yet, the rather sharp increase in DSC crystallinity from JSC data applied to all three glove areas examined for a particular glove and did not indicate that a specific area would be more likely to tear.

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