

## Preliminary evaluation of the use of elevated pressure to accelerate thermo-oxidative aging in composites

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### Abstract

A study was conducted to evaluate the use of elevated pressure to accelerate the rate of thermo-oxidative degradation in polymeric composite materials. The motivation for this work was based on earlier studies by Tsotsis [1,2], Kerr and Haskins [3] and by Ciutacu, et al. [4] which demonstrated that higher pressures of air or oxygen tended to increase the rate of degradation of polymeric composites. Moreover, accelerated aging methods are needed to evaluate materials which are to be used under long-term exposure to elevated temperature in oxidative environments such as the High-Speed Civil Transport (HSCT). The methodology proposed herein augments elevated temperature aging with elevated pressure to accelerate the rate of thermo-oxidative degradation. Temperatures below those used by previous workers were employed in order to avoid anomalous non-linear effects which can occur near the glass-transition temperature of polymeric materials. In the present work, Hexcel AS4/3501-6 [ $\pm 45^\circ$ ]<sub>2s</sub> shear and [ $+45^\circ/0^\circ/-45^\circ/90^\circ$ ]<sub>2s</sub> quasi-isotropic Hexcel IM7/8552 open hole compression specimens were aged at 121°C (250°F) at pressures of 0.101, 0.345, 1.03, and 1.72 MPa (14.7, 50, 150, and 250 psi). Three pressure vessels were designed and built to contain the prescribed pressures. These vessels were placed inside an oven and used an air bleed to recycle the air inside the vessels. For the open hole testing, a test method was derived from Boeing BSS 7260 to reduce the material required for each specimen. Specimens were tested as-made and after 1000 h exposure to each of the pressures. Results show up to a 20% reduction in tensile shear strength for the [ $\pm 45^\circ$ ]<sub>2s</sub> specimens but show no decrease in open hole compression strength though weight losses and visible discoloration of the specimens are present in both materials. Differences are attributed to the different lay-ups used as well as the different materials systems of the two specimen types. © 1999 Elsevier Science Ltd. All rights reserved.

### 1. Background and objectives

Future high-speed commercial aircraft (HSCT) applications will likely require polymeric composites able to withstand long-term (60,000 h) exposures at elevated temperatures between 177°C and 232°C (350 and 450°F). In such applications, the long-term stability of the polymeric material system is essential. The long-term performance of polymer composites at elevated temperature is dictated by thermal and oxidative degradation of the materials. When considering composites for long-term applications, it is necessary to know how the materials will behave during the intended service life. The underlying degradation processes leading to material structure changes are not well known, however, it has been observed [1–4] that elevated pressures

increase the degradation rate of polymeric composites. Furthermore, it has been noted [2] that aging at too high a temperature leads to erroneous calculations of material lifetimes because the mode (or relative modes) of degradation change from what would occur at normal usage temperatures.

Therefore, the present work is intended to evaluate the potential of using elevated pressures in conjunction with a “realistic” use temperature. The pressures chosen were atmospheric (0.101 MPa or 14.7 psi) pressure and the elevated pressures of 0.345, 1.03, and 1.72 MPa (50, 150, and 250 psi) at a temperature of 121°C (250°F). Because the intent of the present work is to accelerate the rate of degradation, no reduced pressures were considered. The temperature of 121°C was selected as an acceptable use temperature for the materials considered which typically have glass transition temperatures in the range of 160–190°C (320–370°F). Although aging at 121°C is known to age these resin systems [1], the aging

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temperature is far enough below the unaged  $T_g$  that non-linear effects which occur near  $T_g$  should be avoided.

The lay-ups used were selected because they are highly sensitive to matrix properties: the  $\pm 45^\circ$  to matrix shear strength and modulus and the open hole compression coupons to matrix yield point and modulus. Previous work [1] has shown that compressive and shear properties show much greater decreases in strength than other properties.

The chief reason for the high dependence on matrix properties is that elevated temperature aging tends to post-cure and degrade polymers causing increased cross-linking or chain scission, respectively. The matrix properties thus change as a consequence of long-term exposure. The rate of degradation as determined by a reduction in strength or stiffness properties is a result of the chain scission reaction taking precedence over the cross-linking reaction. Furthermore, because the rates of these reactions change significantly at or above  $T_g$ , aging these specimens below  $T_g$  the reaction rates should approximate those that would be experienced in actual use environments. It is anticipated that, by keeping the rates and mechanisms approximately the same as those that likely to be experienced by a part in actual use, accurate scaling of the lifetime of such parts may be achieved by accelerating via the use of elevated pressures.

## 2. Experimental methods

Two materials were selected in the present study: AS4/3501-6 and IM7/8552 carbon/epoxy both from

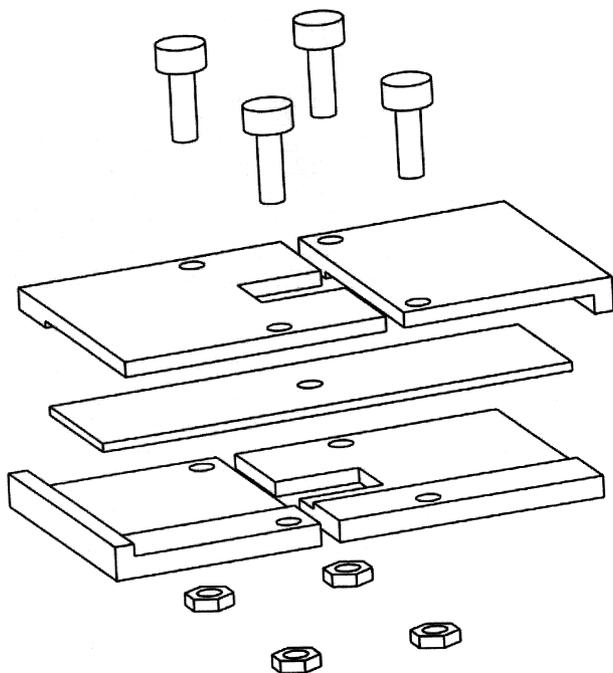


Fig. 1. Exploded view of open hole compression test fixture.

Hexcel Composites, Magna, UT. The AS4/3501-6 was used to make the  $[\pm 45^\circ]_{2s}$  shear specimens and the IM7/8552 used to make the  $[+45^\circ/0/-45^\circ/90^\circ]_{2s}$  quasi-isotropic open hole compression specimens. All panels were cured according to the manufacturer's recommended cure cycles: UCLA processed the AS4/3501-6 panels and the IM7/8552 panels were processed at Boeing–Long Beach. Shear tests were performed according to ASTM D3039.

The open hole compression fixture was based on the specimen and fixture in Boeing BSS 7260—the specimen and fixture are shown in Figs. 1 and 2. This specification requires a specimen larger than required to provide a uniform far-field stress state. For this reason, the specimen used in BSS 7260 was scaled to reduce its overall length while still providing adequate grip areas. The specimen used was 38.1 mm (1.5 in) wide and contained a 6.35 mm (0.25 in) diameter hole. Initial testing at UCSB confirmed that the specimen failed properly and that the strengths recorded were consistent with past data for the full-size open hole compression specimens.

Pressure chambers manufactured at UCLA were made from steel with one welded and one bolted end. The bolted end was fitted such that it allowed a slight bleed of air so that the chambers had a continuous refreshing of air from pressure cylinders. Calibrated pressure regulators and rupture disks were used to maintain pressure and to prevent over-pressurization from occurring. Specimens were placed on racks inside the chambers such that air flow was allowed freely around each specimen. The chambers were closed and placed in an oven with the ambient-pressure specimens inside the same oven. After 1000 h of aging time, 5 specimens from each pressure were removed from the chambers for testing.

Compression and shear tests were selected as they are highly reliant on resin properties. By contrast, tensile tests containing  $0^\circ$  fibers are almost completely reliant on the fiber strength. This difference may be seen in examining the results of Kerr and Haskins [3] in which tensile coupons which visibly exhibited severe resin degradation saw only small decreases in strength even for a  $[0^\circ/\pm 45^\circ]_s$  lay-up. Additionally, the results of Tsotsis [2] give direct comparisons of compressive and tensile test results for the same materials at identical exposure times. In these data large drops were observed in compressive properties well before such changes were

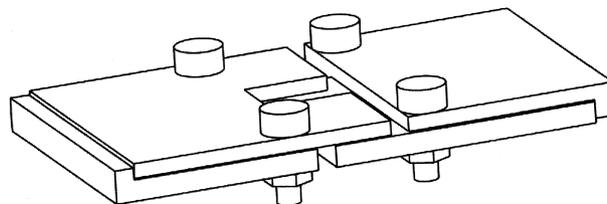


Fig. 2. Assembled open hole compression test fixture with specimen.

observed in tensile ones. Similarly,  $[\pm 45^\circ]_{2s}$  tensile shear coupons also demonstrated decreases well before  $[0^\circ]_8$  ones.

### 3. Theoretical considerations

The degradation reaction (simplistically) may be considered to be of the following form



where A is the reactive group(s) on the polymer chain which react with oxygen to produce the product(s), C. The coefficients,  $r$ ,  $s$ , and  $t$  are the stoichiometric ratios for this reaction. If the reaction is considered to be diffusion controlled, then the oxygen concentration will dictate the rate of reaction because the reactant(s), A, are in excess. An increase in the oxygen pressure will correspondingly increase the amount of oxygen present and will thereby accelerate the reaction postulated above.

In this simplistic model, in the absence of other changes, increased oxygen pressure increases the concentration of oxygen available for reaction. As has been noted by several researchers [1,5,7] the degradation of polymeric composites is a diffusion-controlled phenomenon: oxygen must reach the active sites on the polymer chains before degradation will take place. This behavior accounts for the differently shaded regions and transverse microcracks observed by both Tsotsis and Lee [8] as well as Bowles, et al. [6]. These differently shaded regions represent material which has oxidized. The transverse microcracks are a result of stress differences between the unaffected or core material and the reduced strength of the degraded region. The formation of these microcracks has the additional effect of providing an enhanced diffusion path for oxygen. Once such microcracks form, oxidative degradation will continue to promote crack extension because the microcracks are preferential sites for oxygen penetration.

The present work does not attempt to characterize the subtleties of diffusion behavior and correspondent microcrack formation, though several points should be made. The degree of microcrack formation is directly related to the toughness of the resin system considered [8]. Thus, even resins with the same basic structural backbone may have widely different thermo-oxidative stabilities simply because one resin system is toughened and thus resists microcracking. Microcrack formation, as noted above and by previous studies [6,8] does lead to enhanced paths for oxygen diffusion and thus increased rates of degradation.

Other factors to be considered are the effects of the reaction mechanism of cross-linking or chain extension. Cross-linking tends to stiffen the resin by creating additional bonds between polymer chains. The relative rate

of chain scission due to the oxidation reaction to the rate of chain extension due to cross-linking dictates whether properties increase or decrease. Furthermore, as exposure times increase, the number of potential reactive sites for cross-linking decreases as they are consumed so that chain scission will eventually be a much greater effect relative to cross-linking. Indeed, it was noted by Tsotsis [1] that for the Hexcel carbon/epoxy system G30-500/R922-1 some mechanical properties were initially observed to increase after aging before showing significant reductions with longer aging times.

It is important to note that cross-linking and chain extension are thermally activated processes. This distinction is necessary because, if an accelerated test program is conducted solely relying on temperature to accelerate the degradation process, the rates of thermally activated processes will likely not be scalable to different temperatures to predict useful lifetimes.

Accelerating using the desired aging temperature with elevated pressure avoids these pitfalls. In this case, all thermally activated processes occur at the same rate they would at the desired temperature irrespective of the pressure. However, diffusion-related phenomena such as oxidative degradation are accelerated by increased pressure without affecting the purely thermally activated mechanisms. Because the chief cause of degradation is oxidation which is diffusion-controlled in the present case, it is anticipated that the use of elevated pressure will be scalable to different pressures so that useful lifetimes may be estimated.

Furthermore, in a diffusion-controlled process, the rate-limiting step in the thermo-oxidative aging process is the diffusion of oxygen to reactive sites—as the results presented herein strongly suggest—then the rate of degradation will be completely controlled by it. As shown in the simple reaction equation above, increasing the oxygen concentration should drive the reaction forward as would the increasing of the surface area of the polymer exposed to oxygen.

In order to fully characterize diffusion-related degradation, considerations to lay-up such as given by Nam and Seferis [5] must be made. Nam and Seferis considered the effects of lay-up on the diffusion, but the lay-up also affects mechanical property degradation due to diffusion-related oxidation because decreases in mechanical strength are directly related to which plies have degraded (e.g. load-bearing or non-load-bearing). Thus any diffusion model must be coupled to a mechanical model to accurately characterize thermo-oxidative degradation.

Ciutacu et al. [4], in an approach similar to the present work, accelerated the aging of glass/epoxy composites with varying oxygen pressures. In their work, a relationship between mechanical property (flexural strength) degradation and degradation kinetics was

developed. This relationship showed the flexural failure strain ( $\epsilon$ ) degradation to depend on the oxygen pressure in the following manner

$$\epsilon \propto Ae^{-BP^n}, \quad (2)$$

where  $A$  is a constant related to the initial strain-to-failure value and  $B$  is a function of exposure time and temperature.

Although good agreement was obtained by Ciutacu et al. in their experiments, the dependence on material anisotropy as noted by Nam and Seferis [5] does not allow for generalization of their results without further verification.

As noted above, previous results [2] have shown that resin toughness plays a role in thermo-oxidative stability. Thus, the results presented below not only compare two different tests, but also consider the effect of matrix toughness.

#### 4. Results and conclusions

Measurements of the strength changes in AS4/3501-6  $[\pm 45^\circ]_{2s}$  specimens showed significant differences between the different aging conditions. Strength losses were significantly higher for the elevated-pressure samples than for the ambient-pressure ones as shown in Fig. 3. In this figure, an offset is used for the exposure time between the various pressure exposures to improve the readability of the graph.

The trend in degree-of-strength loss monotonically increased from ambient pressure to 1.03 MPa (150 psi), but the 1.72 MPa (250 psi) specimens showed less of a strength loss than the 1.03 MPa specimens, though still greater than for the 0.345 MPa (50 psi) ones.

In Fig. 4, the weight changes at each pressure are shown and show increasing pressure above 0.345 MPa increases weight loss. A slight weight gain at 0.345 MPa

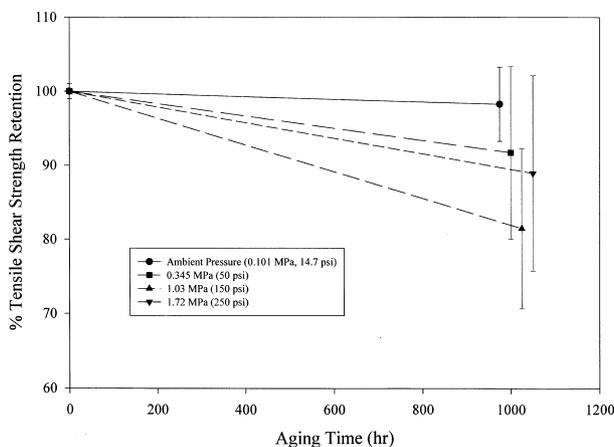


Fig. 3. Percent relative strength retention of  $[\pm 45^\circ]_{2s}$  AS4/3501-6 tensile shear specimens tested after aging at  $121^\circ\text{C}$  ( $250^\circ\text{F}$ ) for up to 1000 h at various aging pressures.

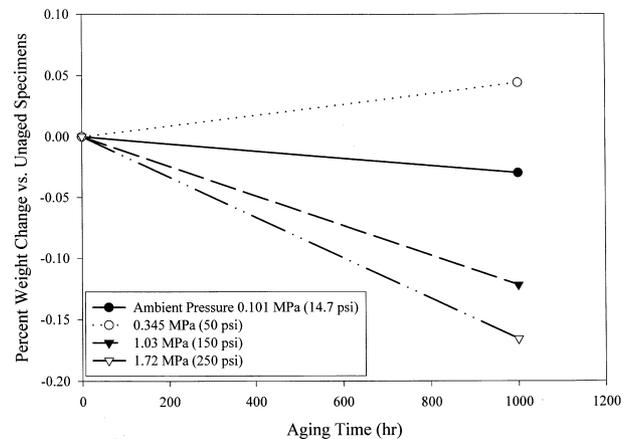


Fig. 4. Percent weight change of  $[\pm 45^\circ]_{2s}$  AS4/3501-6 tensile shear specimens tested after aging at  $121^\circ\text{C}$  ( $250^\circ\text{F}$ ) for up to 1000 h at various aging pressures.

is likely due to oxygen uptake being greater than weight loss due to chain scission over this time period as has been previously observed [1]. Because of the paucity of data after only one aging time, it is unclear as to whether this is a real trend or an artifact of limited data. Visible discoloration was observed on all aged specimens.

The unnotched compression data also show a marked increase in the amount of scatter in the ultimate strength values especially at the higher pressures. The causes for this are multiple. The posture of the resin increases the modulus and correspondingly the brittleness of the resin, however this is not the principal reason for the observed behavior. Likewise, the scatter increased in the Open Hole Compression specimens, as shown in Fig. 5, but by a far smaller degree.

Thermo-oxidative aging does degrade an outer layer of the material as well as causing transverse microcracks as noted above. Although the outer-layer degradation may be somewhat uniform (because the medium through which the air (oxygen) diffuses is largely uniform along the length of the specimens), the formation

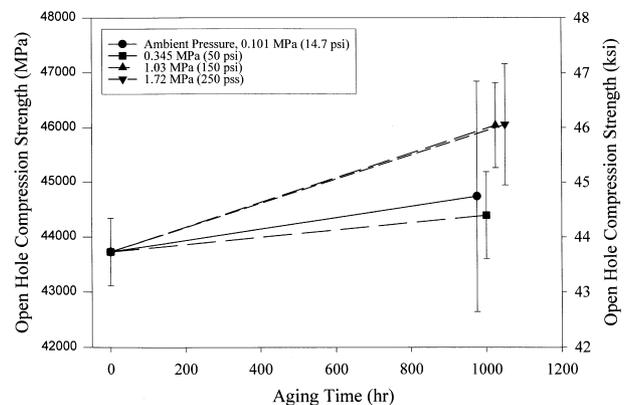


Fig. 5. Open hole compression strength changes for  $[\pm 45^\circ/0^\circ/-45^\circ/90^\circ]_{2s}$  IM7/8552 quasi-isotropic specimens tested after aging at  $121^\circ\text{C}$  ( $250^\circ\text{F}$ ) for up to 1000 h at various aging pressures.

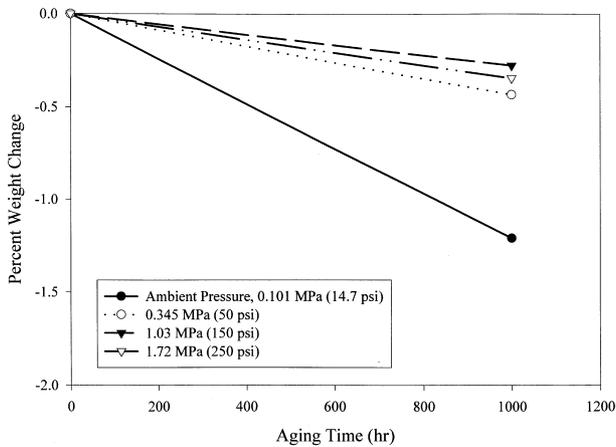


Fig. 6. Percent weight change of for  $[\pm 45^\circ/0^\circ/-45^\circ/90^\circ]_{2s}$  IM7/8552 quasi-isotropic open hole compression specimens tested after aging at  $121^\circ\text{C}$  ( $250^\circ\text{F}$ ) for up to 1000 h at various aging pressures.

of the transverse microcracks is likely dependent on local defects and stochastic processes. As such, the amount and location of these microcracks will necessarily vary from specimen to specimen. Notwithstanding this effect, it is clear from the results presented herein that the potential for large strength degradation increases significantly with increasing thermo-oxidative aging and that the effect increases as the air pressure increases.

Results from open hole compression tests of the aged IM7/8552 specimens shown in Fig. 5 showed no significant changes in strength from the unaged specimens; in fact, a slight increase was noted with the higher pressures showing greater increases in strength. This change is due to a post-curing effect from the long exposure to elevated temperature which increases the resin modulus. It is well known that, in general, increased resin moduli result in improved open hole compression strengths for polymeric composites.

The open hole compression specimens, unlike the tensile shear coupons, have 25%  $0^\circ$  fibres. Thus, the

shear coupons are more sensitive to reductions in resin properties than the open hole specimens because the  $0^\circ$  fibers in the open hole compression specimens tend to mask reductions in the properties of other plies. In the lay-up used in the present work, the  $0^\circ$  fibers are one layer in from the outside so that degradation must reach at least this ply before significant strength changes will be observed.

Despite the lack of significant change in strength, a discoloration of the specimens was observed. The specimens have taken on a brownish tinge which was not present in the unaged coupons. The weight losses (shown in Fig. 6) at 0.345 MPa and above are nearly equal, but the ambient pressure weight loss is much greater. This was due to a temperature control problem with UCSB's oven which reached  $400^\circ\text{F}$  thereby artificially increasing the weight loss—these specimens will need to be remade to obtain data at the same temperature exposure as the other specimens.

The enhanced strength reductions observed in the  $[\pm 45^\circ]_{2s}$  shear coupons due to increased pressure support the hypothesis of this work that elevated pressure may be used to accelerate thermo-oxidative aging. Weight gain data for both the shear and open hole compression specimens also support this hypothesis.

In contrast to the shear tests, the results of the open hole compression tests indicate that aging for 1000 h is insufficient for the observation of any degradation of this mechanical property in IM7/8552 composites (see Table 1). This result is consistent with previously observed behavior [1] for aging at  $177^\circ\text{C}$  of a similar material (Hexcel G30-500/6376 carbon/epoxy) in which a significant reduction in open hole compression strength was not observed until 5000 h exposure.

It is believed that the phenomena observed in the open hole compression strength data are a result of the competing post-cure and oxidation reactions as described above. Because weight losses are slightly less for the

Table 1  
Test results after 1000 h aging time for shear and open hole compression coupons

| Aging time (h)  | Aging pressure |        | Strength |         | % Retention |
|---|----------------|--------|----------|---------|-------------|
|   | MPa            | (psi)  | (ksi)    | (kPa)   |             |
| Tensile testing of $[\pm 45^\circ]_{2s}$ AS4/3501-6 coupons |                |        |          |         |             |
| 0   | N/A            |        | 21.5     | (0.148) | N/A         |
| 1000  | 0.101          | (14.7) | 21.2     | (0.146) | 98.3        |
| 1000  | 0.345          | (50)   | 19.8     | (0.136) | 91.8        |
| 1000  | 1.03           | (150)  | 17.5     | (0.121) | 81.5        |
| 1000  | 1.72           | (250)  | 19.2     | (0.132) | 89.0        |
| Open hole compression testing of IM7/8552 coupons           |                |        |          |         |             |
| 0   | N/A            |        | 43.7     | (0.301) | N/A         |
| 1000  | 0.101          | (14.7) | 44.7     | (0.308) | 102.3       |
| 1000  | 0.345          | (50)   | 44.4     | (0.306) | 101.5       |
| 1000  | 1.03           | (150)  | 46.0     | (0.317) | 105.3       |
| 1000  | 1.72           | (250)  | 46.1     | (0.317) | 105.3       |

specimens aged at 1.03 and 1.72 MPa than for those aged at 0.345 MPa, it is likely that the oxidation reaction (which initially causes a weight gain) is more advanced than at the higher pressures and may additionally enhance the post-cure reaction. Only by obtaining results at longer exposure times may this hypothesis be tested.

Because the initial aging time of 1000 h showed significant mechanical strength degradation in the  $[\pm 45^\circ]_2$ , a continuation of these experiments should give a clearer understanding of the mechanisms behind the observed phenomena. Though the open hole compression specimens did not show a strength degradation—reflecting both the different test geometry of the open hole compression test as well as the difference between the two matrix resins studied herein—the specimens displayed visible signs of degradation of the surface due to discoloration suggesting that degradation had begun at the surface. Therefore, further aging of the open hole specimens will allow examination of how a specimen with interior  $0^\circ$  plies behaves with respect to the elevated pressures and thus give a clearer understanding of the effects of diffusion and lay-up on degradation rate.

Further aging will additionally allow for more conclusive indications as to the merits of the use of elevated pressure as an accelerating methodology. Based on the promising results gathered so far, it may be of interest to examine the effect of even higher pressures (e.g.  $\geq 2.42$  MPa (350 psi)) on the accelerating behavior of elevated pressure. Moreover, a better understanding of this methodology might then lead to examining the use of higher-temperature materials potentially suitable for HSCT usage such as K3B (E.I. duPont de Nemours,

Wilmington, DE) and PETI-5 (NASA-Langley, Langley, VA).

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