Ultra Fast Curing for Advanced Materials

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Introduction

Infrared (IR) curing is one of the fastest growing technologies, mainly in the coating industry [1-3]. As an alternative for convection [4], IR curing can be the right choice for many applications. Since there is a constant need of optimization of the manufacturing time and costs, researchers search for a way to improve the polymerization process. IR curing of carbon fiber-reinforcement epoxy matrix and IR energy has been found by the researchers from University of Toulouse to be an efficient method of curing composites [5]. Curing glass/epoxy systems has also been discussed and there is so far the interest for future works, because of the volumetric distribution of the radiative intensity in the semi transparent mediums.

Adhesives and sealants frequently used in the aircraft maintenance, repair and overhaul (MRO) companies' practices for joining and sealing purposes could be another possible niche and application of IR energy. For some sealants, time to be fully cured is very long and takes up to a few days. This strongly affects delivery time, as aircrafts are grounded and off of service until structural damages are not repaired. Thus, the curing time is a very important technical specification for an adhesive/sealant as it can save the waiting time at the airport for airplanes that need repairing. A new fast method of curing would certainly solve the problem of rapid delivery of repaired parts and thus reduce the operation cost.

The purpose of this work was to investigate different curing techniques- thermal, room temperature and IR, and curing behavior of two certified aviation sealants -DAPCO 18-4F silicone firewall (qualified to Boeing BMS 5-63) and Pro-Seal 870 (qualified to Boeing BMS 5-95) with respective hardeners in order to choose curing method, that enable reducing curing time for these sealants to less than 2 h without its chemical modification. Further evaluation their performance with proposed curing technique had been done as well and benchmarked versus actual existing curing methods, used for the same sealants.

1. Experimental procedure

1.1. Materials used

Both DAPCO 18-4F silicone firewall (qualified to Boeing BMS 5-63) sealant and hardener B4 and Pro-Seal 870 (qualified to Boeing BMS 5-95) were used in this study. Materials were used as received from Jaco Industrials, Inc. Table 1 shows the chemical class of sealants and hardeners used in this study.

Table 1. Chemical class and name of materials used

Materials Name	Chemical class
DAPCO 18-4F (BMS 5-63)	Polysulfide
Hardener B4	Polysiloxane
Pro-Seal 870 (BMS 5-95)	Polysulfide
Hardener	Manganese dioxide

Both sealant resins are based on polysufide, but they differ by their hardener and therefore obey to a different chemistry. Polysulfide polymers, first marketed in 1929, are mature products that are used in specialty adhesive and sealant applications. These important materials seem to not receive much attention today due to their restricted use, especially as adhesives, and to their competitive market displacement as sealants by silicones and urethanes. However, polysulfide polymers provide unique curing and performance properties that are attractive in many applications.

The original polysulfide polymers were solid rubbery materials containing 37-82 percent bound sulfur. However, today the predominant product is the mercaptan-terminated liquid polymer (LP) that contains approximately 37 percent bound sulfur (see Figure 1). It is the high concentration of sulfur linkages that provide these products with their unique chemical properties.

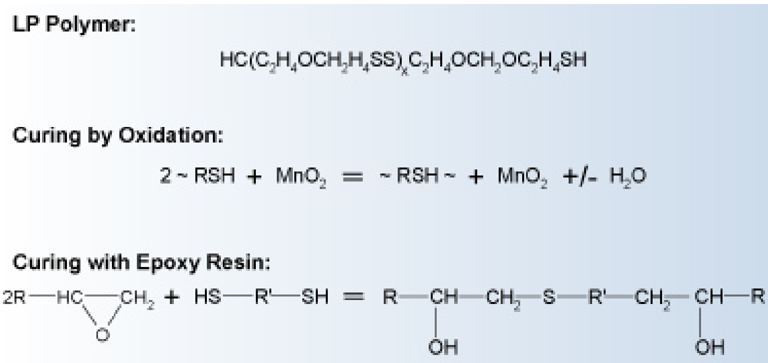


Figure 1 : Conventional polysulfide structure and hardener

The liquid polysulfide polymer can be transformed in-situ from a liquid state into a solid elastomer, even at low temperatures using magnesium oxide, polysiloxane (PDMS) or epoxy resisns. Polysulfide adhesives and sealants have been successful in applications requiring good moisture, solvent and ozone resistance, and good weathering and low temperature properties. However, the chemical linkages that provide these properties also contribute to poor high temperature stability and high compression set because of stress relaxation.

1.2. Mixing procedure and sample preparation

1.2.1. Mixing procedure

Formulations were prepared according to recommended by CYTEC Engineered Materials Technical Data Sheets mix ratio for DAPCO18-4F (BMS 5-63) and Pro-Seal 870 (BMS 5-95) (Table 2).The formulations were mixed just prior to the application.

Table 2. Recommended mix ratio for DAPCO18-4F (BMS 5-63) and Pro-Seal 870 (BMS 5-95)

Sealant DAPCO18-4F (BMS 5-63)	weight, (parts)	volume, (parts)
Part A	100	11.7
Part B (hardener)	7	1
Sealant Pro-Seal 870 (BMS 5-95)		
Part A (Hardener)	17	-
Part B	100	-

1.2.2. Moulding of Thermal and Room Temperature Cure Specimens

Steel wires of 2 mm diameter were placed at either sides of the mixed sealant and a glass slide was lowered over the setup to create flat moulding surface. Small ceramic weights were placed on top of the set-up and the specimens where then left to cure at room temperature or placed in the oven for thermal cure. The moulding surfaces on the steel plate and glass slides were acetone wiped prior to moulding to remove surface grease and contaminants. Only the glass and steel surfaces used for moulding of the Pro-Seal 870 sealant was coated with release agent to achieve easier specimen release after cure.

1.2.3. Moulding of IR Specimens

The moulding of the sealant specimens for IR cure was achieved by placing a ring spacer of 2 mm thickness around the sealant samples that has been apportioned on the steel plate. A spatula was then used to scrape off the excess sealant protruding above the ring spacer to create uniform thickness samples.

1.3. Room temperature, thermal and IR curing of sealants

1.3.1. DAPCO 18-4F firewall sealant

For the DAPCO 18-4F firewall sealant, room temperature curing at 25 °C was conducted for 1, 3, 7 and 14 days respectively.

The thermal cure for this system was conducted in a circulating air convection oven set to 65 °C for 1, 2, 3, 4, 10, 12, 14 and 24 hours.

IR curing, which generated the fastest cure, was performed for 15, 30, 45, 60, 90, 120, 150, 180, 210 and 240 minutes. The 800W shortwave IR lamp source was fixed at a distance of 10mm from the surface of the cured sealant plates. This was the minimum distance required to avoid material degradation.

1.3.2. Pro-Seal 870 sealant

The sealant Pro-Seal 870 was cured at room temperature (25 °C) for the following durations: 24, 30, 48 and 72 hours, 7 day and 14 day.

The IR curing of this sealant could not be accomplished as the irradiation was too intense for the material which resulted in severe degradation.

1.3.3. Shore hardness measurements

At the end of the stipulated cure times for each sealant, the cured specimen plates were carefully demoulded and Shore A hardness test was then conducted immediately on the surfaces. A total of 10 hardness readings were made on each surface with a spacing of at least 2 mm apart in between each measurement.

2. Results and discussion

Aircraft certified sealants, which are usually used for repairing fuel leaks, installing windshields and windows, sealing out moisture, etc often take over 12 h and more (depending on temperature used for curing) to be fully cured. So, it's obvious that curing method enabling reducing cure time of some sealants, using different than convection techniques would solve problem of faster delivery of repaired parts and thus reduce the operation cost of aircraft`s maintenance.

One of the challenges of this study - impossibility neither exploring of suitable catalysts to promote cure reaction or using ultra violet (UV) radiation curing for reducing cure time of sealants – has been the main reason for IR to be chosen as a heating technique for sealants in order to reduce their curing time. Any sealant admixture and addition of photoinitiators or catalysts were not feasible in this case as that could entail changing in chemical structure, which is not acceptable in case of certified sealants. Thus another, different from chemical and UV radiation curing methods needed to be explored. In this study, IR energy as a source of heating has been proposed to study curing behaviour of aviation sealants in order to reduce their curing time. As a form of electromagnetic energy, IR energy stays between visible light and microwaves in the electromagnetic spectrum and travels in waves like other forms of electromagnetic energy. That is why the known relationship between the wavelength, frequency and energy level where the energy (temperature) increases as the wavelength decreases is applied as well to IR energy. Since IR rays are electromagnetic radiations they do not require a medium for transmission. Unlike convection, which first heats air to transmit energy to the part, IR energy applies infrared rays to the part surface by direct transmission from an emitter, so may directly be absorbed by the surface or substrate, although it may partly be reflected by substrate. Hence, the need for air recirculation is eliminated. The direct transfer of energy causes an immediate reaction in the substrate and cross-linking begins rapidly. Moreover the IR units can be powered to full power in less than one second, which results in fast curing.

2.1. Curing of the DAPCO 18-4F Firewall Sealant System

It should be noted that all above mentioned contingencies, and limitations of any actions, including chemical structure changing restrictions of certified sealants could strongly affect performance (in term of mechanical properties) of cured materials by any than convection or room temperature curing methods. It was evident that performance of materials cured by proposed method must be comparable to performance of those, thermally curable with long curing time sealants. Thus, evaluating their performance with proposed IR curing technique and benchmarking against actual existing curing methods had therefore been done.

Three curing approaches were investigated on the DAPCO 18-4F sealant system, namely, the (i) room temperature cure at 25 °C (as control), (ii) elevated temperature cure at 65 °C, and (iii) infra-red (IR) cure at 800 W, 10 mm displacement from IR source. Their corresponding Shore A Hardness values as a function of the cure time elapsed are shown in Figures 2, 3 and 4.

The Shore A hardness value of the DAPCO 18-4F sealant system cured according to the manufacturers' recommended cycle of 7days at 22°C, 50% R.H. is reported to be 50 [6].

The results in Figure 2 show that the sealant attained full cure and hence maximum hardness at around 7 days, which is in agreement with the product specifications. However, after 7 days room temperature cure in our laboratory environment (25 °C, 60-80 % R.H.), the cured sealant attained a hardness of 64.4 ± 1.1 (Shore A), which is about 25 % higher than that of the reported value. Noting that property of this sealant is known to be enhanced by moisture, the higher room temperature and humidity of the cure environment in our laboratory is likely to have contributed to this discrepancy.

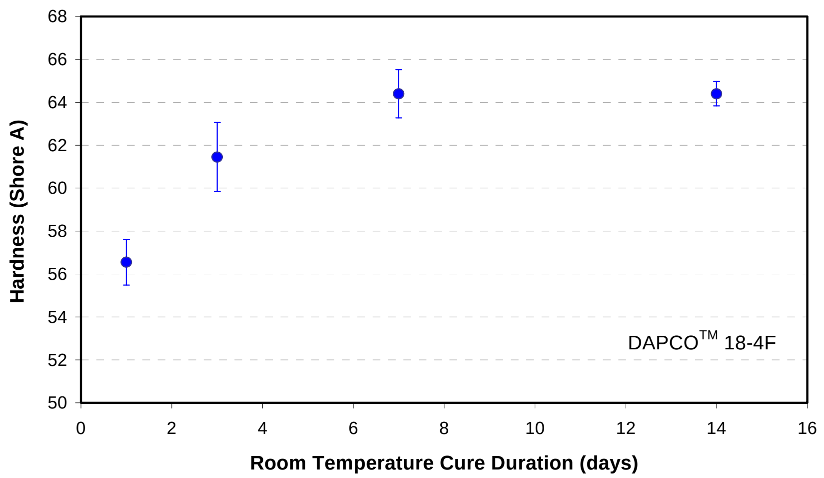


Figure 2. Hardness against cure time results for DAPCO 18-4F sealant cured at room temperature.

Results observed for the DAPCO 18-4F sealant system that undergo 65 °C curing, presented in Figure 3 shows that temperature has a non-trivial influence on material hardness of the cured sealant. The Shore A hardness ranged from 65-70 for the cured sealant, which is marginally higher than the room temperature cure system. The curing time required was also significantly shorter, in the order of hours rather than days. As can be seen from figure 2 after 10 h of curing DAPCO 18-4F sealant system, the value of shore hardness reaches plateaux, where it remains quite stable (68-70) starting from 10 h until 24 h of curing. The measurements therefore were stopped after 24 hours, although some trend of small further increase in hardness was possible if the duration was extended, especially as if compared to sealant, cured at room temperature, the value of Shore hardness of the sealant cured at 65 °C has already exceeded its room temperature cured value after 1 hour of curing.

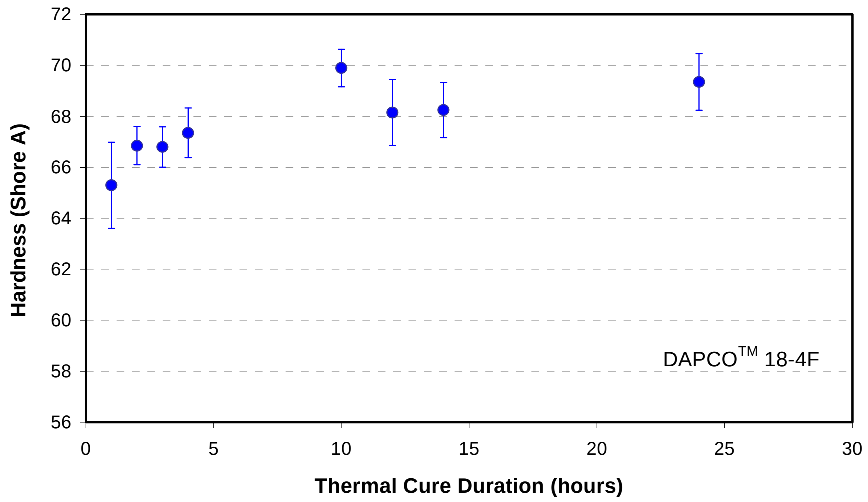


Figure 3. Hardness versus cure time results for DAPCO 18-4F sealant cured at 65°C.

Figure 4 shows the hardness results of DAPCO 18-4F sealant cured under IR energy. The hardness increased and attained a plateau value of 74-76 (Shore A hardness) after just 90 minutes of treatment. The IR curing gave an improvement of +16.9 % over the cured hardness of the conventional room temperature cured system and utilized only 0.89% of the original cure time. When measured against the 65 °C thermally cured sealant results, the improvement in hardness was +9.2 % and the time used was 37.5 % of the 4 hours (minimum) recommended in the product datasheet.

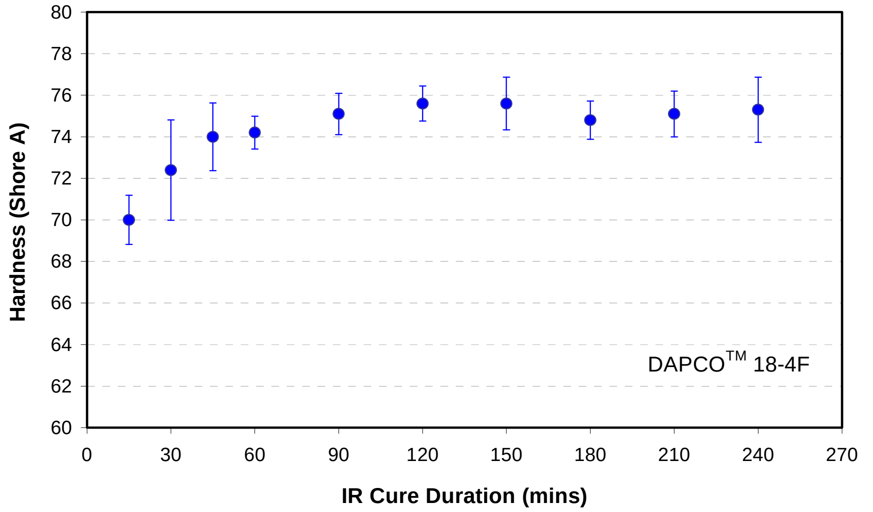


Figure 4. Hardness versus cure time results for DAPCO 18-4F sealant cured via IR.

These results indicate that it is feasible use of an 800 W IR lamp at 10 mm distance to achieve cure acceleration for this particular sealant.

1.2. Curing of the Pro-Seal 870 (BMS 5-95) Sealant System

The cured hardness results of the Pro-Seal 870 sealant cured at room temperature is shown in Figure 5. The average maximum cured hardness of this system was found to be 47.3 ± 0.3, as could be seen from the plateaux on Figure 5, attained after approximately 3 hours of cure.

IR curing could not be done due to severe material degradation even with increased distance from IR source.

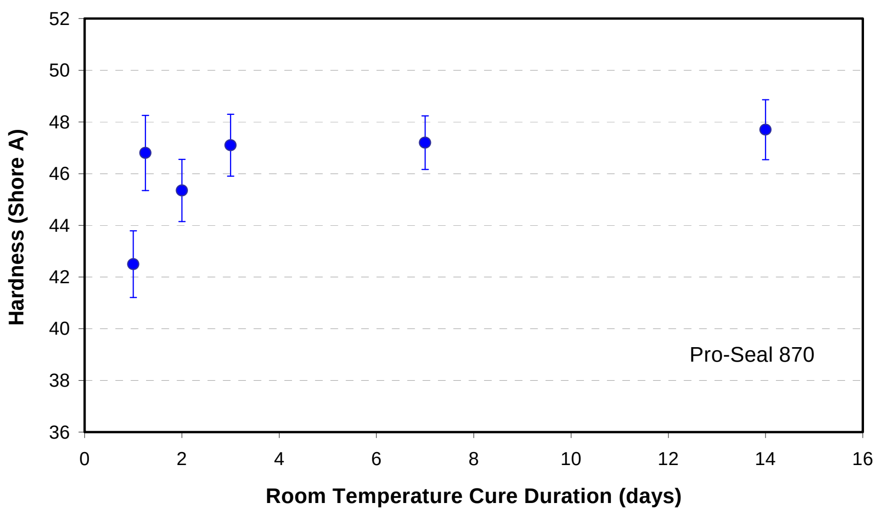
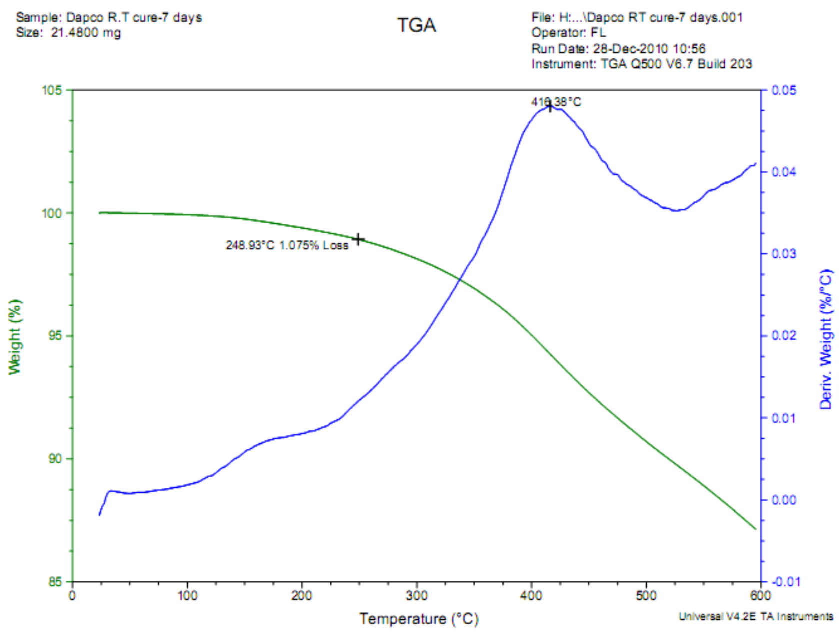
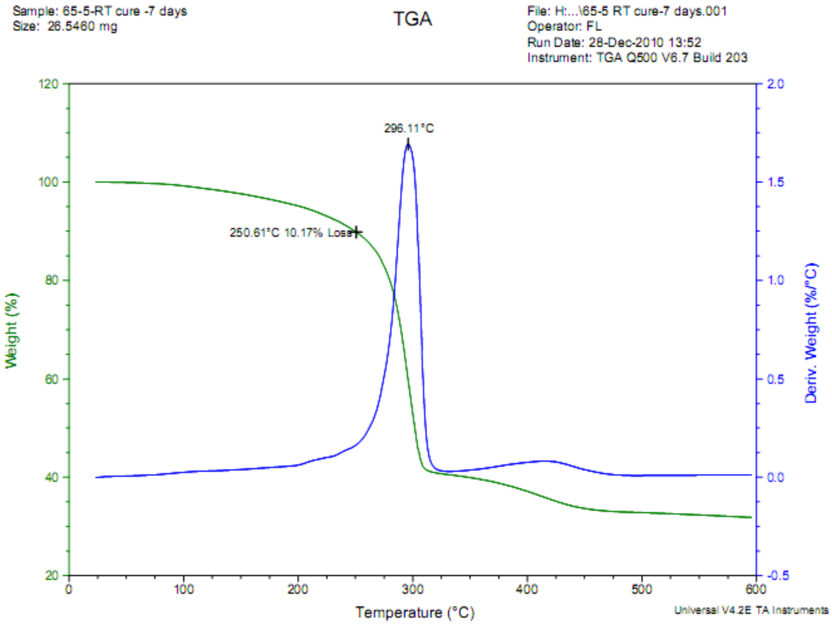


Figure 5. Hardness versus cure time results for Pro-Seal 870 sealant cured at room temperature.

Figure 6 (a and b) presents TGA analysis of both sealants, where can be clearly seen that Pro-Seal 870 (BMS 5-95) sealant (Fig.6b) degrade faster and under lower temperature (~300°C with 60% weight loss) than its polysulfide homologue cured with polysiloxane (~420 °C with about 5% of weight loss) (Fig.6a



a)



b)

Figure 6. TGA analysis of a) DAPCO 18-4F (BMS 5-63) and b) Pro-Seal 870 (BMS 5-95) sealants with respective hardeners

Conclusions

In conclusion one can say that proposed IR heating method for sealants curing has significantly decrease its curing time as compare to thermal and room temperature curing of the same sealants.The hardness increased and attained a plateau value of 74-76 (Shore A hardness) after just 1.5 h of treatment.

The IR curing gives an improvement of +16.9 % over the cured hardness of the room temperature cured system and utilized only 0.89 % of the original cure time. When measured against the 65 °C thermally cured sealant results, the improvement in hardness seen to be +9.2 % and the time used was 37.5 % of the 4 hours (minimum) recommended in the product data sheet. These results indicate that it is feasible use of an 800 W IR lamp at 10 mm distance to achieve cure acceleration for these two particular aviation sealants- 18-4F (BMS 5-63) and b) Pro-Seal 870 (BMS 5-95).

Future work

We believe that more work has to be done on mechanical properties (tensile strength and modulus) of the sealants cured at room temperature, thermally in oven and by IR heating. Different thicknesses of applied sealants have to be considered to establish the IR heat penetration limit.

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