# PTFE Resin Selection for High Performance Wire and Cable

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## SUMMARY

Polytetrafluoroethylene (PTFE) resins have been used for over 30 years in high performance wire and cable applications because of their unique electrical, thermal and chemical properties. Wire insulated with PTFE is used successfully in aircraft, computers, military and industrial electronics, and other demanding applications. In some instances, however, PTFE insulation has cracked during service. The following discussion deals with this problem by comparing the stress crack resistance of six different commercial grades of PTFE resin using insulated wire samples in an accelerated stress cracking test. Results are related to important resin properties including standard specific gravity (SSG) and thermal stability (TII). A theory describing the cracking mechanism is discussed and a new test for stress crack susceptibility is developed based on that theory.

## IMPORTANCE OF RESIN SELECTION

Investigators have attributed the cracking of PTFE insulated wire to one or more of the following:

- Improper sintering.
- Improper maufacturing conditions (wrong tooling).
- Resin selection.

Military specifications such as MIL-W-22759 are designed to identify insulations which have been improperly processed. Dr. Kuettner's paper, "A Contribution Toward Quality Consistency of PTFE Insulated Wire", discusses the effects of sintering and manufacturing conditions in detail (Ref.1).

The remainder of this paper will focus on the importance of resin selection. Resin selection should be influenced primarily by two factors, conductor diameter and insulation wall thickness. Normalized stresses are much greater in large diameter conductors and thin wall constructions. Therefore, resins with superior crack resistance are especially important for these applications.

### *Resin Differentiation*

Many PTFE resins are available today. A number of physical and electrical properties of PTFE resins are generally similar. These properties include outstanding chemical resistance, high temperature resistance, low flame and smoke properties, excellent dielectric properties, outstanding resistance to weather, anti-stick characteristics and high purity.

However, there are significant differences between resin grades which will affect their end use performance as wire insulations. Resin properties already identified as being important to end use characteristics such as resistance to cracking include molecular weight, crystallinity and thermal stability. Crystallinity and thermal stability can be measured using test methods specified in ASTM D 1457 (Ref. 2).

Standard Specific Gravity (SSG) is an accepted measure of crystallinity. Crystallinity is a function of molecular weight, thermal history and composition. As the molecular weight is increased, the crystallinity (and the SSG) decreases. The SSG measurement uses a specially prepared test disk of molded resin. Sample preparation is described in ASTM D 1457. SSG determination is made in accordance with procedures described in ASTM D 792. Specific gravity is defined as the ratio of the weight in air of a unit volume of impermeable material at 23°C to the weight in air of equal density of an equal volume of gas free distilled water at the same temperature (Ref. 3). Crystallinity can also be measured by X-ray, infrared or differential scanning calorimetry analysis. However, these methods require significantly more expensive equipment than SSG determination. SSG has the added benefits of simplicity and convenience.

The results of MIT flex testing illustrate the dramatic relationship of SSG to mechanical properties. This test measures the folding endurance of a 5 mil film sample (Ref. 4). The commercial resins available for wire and cable cover a wide range in crystallinity (SSG 2.14 to 2.23). The low end of this range would have a flex life two orders of magnitude greater than the high end.

Thermal Instability Index (TII) is a measure of molecular weight stability at elevated temperatures. This test is also described in ASTM D 1457. SSG and extended specific gravity (ESG) must be determined. ESG specimens are sintered like SSG specimens except that the hold time at 380°C is 360 minutes. The thermal instability index is calculated as follows:

$$TII = (ESG - SSG) \times 1000$$

TII measures the change in resin density due to thermal stress. As the thermal stability is reduced (increased TII), molecular weight degradation will increase at elevated temperatures. The decrease in molecular weight is reflected by an increase in crystallinity (higher ESG). Higher TII has also been found to correlate with a higher rate of weight loss in thermogravimetric analysis (TGA) measurements.

## PREPARATION OF WIRE SAMPLES - STANDARD TESTING

Six different resin types were compared using insulated wire samples (Type E-10, 37/26 Unilay Silver plated copper). These samples were made at the commercial production facilities of a large wire and cable maufacturer using standard production techniques. All resins were subjected to identical processing steps during fabrication to eliminate processing as a variable affecting wire performance. The lubricant levels were adjusted based on anticipated extrusion pressures. Pigmentation, preform preparation, extrusion, lubricant removal and sintering conditions were held constant for all resin types. Process conditions for each resin are summarized in Table 1.

| Resin Type | % Lube | Barrel Pressure (psi) |
|---|---|---|
| A | 18 | 2200 |
| B | 17 | 2400 |
| C | 17.5 | 2200 |
| D | 17 | 2600 |
| E | 18 | 4400 |
| F | 18 | 5000 |

Reduction Ratio: 690:1
Oven Profile, °F: 260 360 370 520 690 810

*Table 1. Process Conditions*

A reduction ratio of 690:1 was used. Each resin was extruded using an approximate blow-up of 5% to avoid introducing longitudinal or circumferential stresses into the PTFE coatings. In all cases, the PTFE extrudate was very smooth. All wire was tested for dielectric integrity at 3.4 kV with a high frequency spark tester. Very low fault counts were observed with all samples. There were no problems with splitting after cooling.

All wire samples were tested in accordance with MIL-W-22759. Tests included wrap back, shrinkage, thermal shock, cold bend and life cycle. All samples were found to be acceptable. Results are listed in Table 2.

## ACCELERATED STRESS CRACKING

An accelerated stress crack test was run to differentiate the end use performance of the six resins under severe conditions. This test compares accelerated stress crack resistance of wire insulations through the use of mechanical stress and temperature cycling. Silicone oil is used as an environmental stress crack agent to accelerate cracking. Since crack initiation is a random phenomenon, use of a statistically valid number of test specimens is important. Therefore, 20 specimens per resin sample were used.

Du Pont has used this test for a number of years to compare the stress crack resistance of different fluoropolymer resins. Apparatus, reagents and procedures are listed in the Appendix.

Results of the accelerated stress crack test are illustrated graphically in Figure 1.

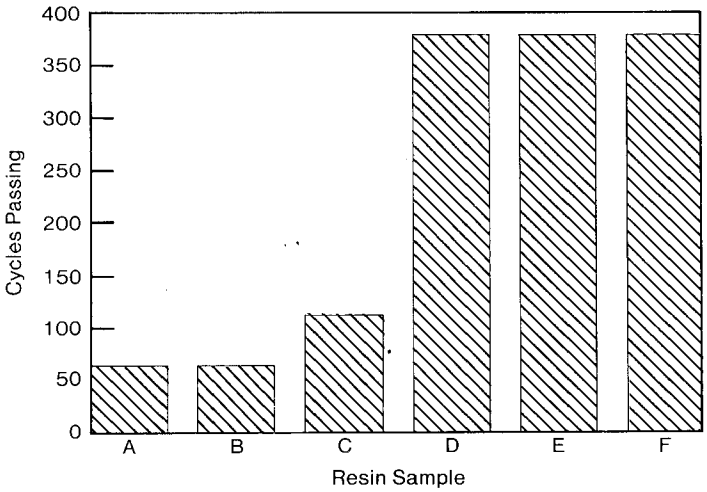


*Figure 1. Accelerated Stress Crack Performance*

| Resin Type | Tensile (psi)/ Elong. (%) (std. dev.) | Wrap Back (2 Hrs @ 313°C) | Shrinkage, in. 6 Hrs @ 290°C) | Thermal Shock, in. MIL-W-22759 | Low Temp Test MIL-W-22759 | Life Cycle MIL-W-22759 |
|---|---|---|---|---|---|---|
| A | 4779/208 (913/62) | 3 of 3 Pass | +0.030 | +0.01 | 2 of 2 Pass | 2 of 2 Pass |
| B | 7040/261 (708/40) | 3 of 3 Pass | +0.050 | +0.03 | 2 of 2 Pass | 2 of 2 Pass |
| C | 6897/156 (774/42) | 3 of 3 Pass | +0.025 | +0.04 | 2 of 2 Pass | 2 of 2 Pass |
| D | 6191/326 (658/33) | 3 of 3 Pass | +0.025 | +0.05 | 2 of 2 Pass | 2 of 2 Pass |
| E | 7883/199 (297/16) | 3 of 3 Pass | -0.015 | +0.04 | 2 of 2 Pass | 2 of 2 Pass |
| F | 7512/195 (320/21) | 3 of 3 Pass | +0.005 | +0.03 | 2 of 2 Pass | 2 of 2 Pass |

*Table 2. MIL-W-22759 Test Results*

When specimens were first examined after 54 cycles, it was found that all specimens from resins A and B failed. Failure may have occured at much fewer than 54 cycles. Visual examination showed that sample A was more severely cracked than sample B (Photo 1).

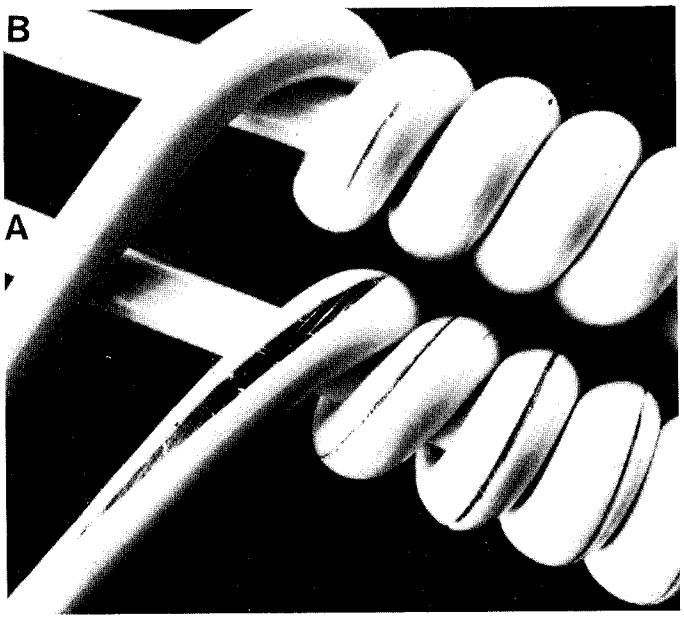


*Photo 1. Cracked Wire Samples*

Fifty percent of the specimens from resin C cracked after 106 cycles and the test was stopped. One specimen from sample E cracked after 106 cycles. The remaining 19 specimens from resin E and all specimens from resins D and F passed 376 cycles and are still undergoing temperature cycling. Results are summarized in Table 3.

| Resin | Cycles | # Passing (20 Specimens Tested) |
|---|---|---|
| A | 54 | 0 |
| B | 54 | 0 |
| C | 106 | 9 |
| D | 376 | 20 |
| E | 376 | 19 |
| F | 376 | 20 |

*Table 3. Accelerated Stress Crack Results*

SSG and TII for each resin type are listed in Table 4. The three resin types with TII of 15 and below exhibited accelerated stress crack resistance superior to that of resin types with TII greater than 30. SSG correlated with accelerated stress crack results (Figure 2). A better correlation can be seen when accelerated stress crack results (cycles passing) are plotted versus specific gravity after the TII cycle (Figure 3). This indicates that both thermal stability and crystallinity are important factors in determining a resin's crack resistance.

| Resin Type | SSG | TII |
|---|---|---|
| A | 2.2229 | 33 |
| B | 2.1769 | 56 |
| C | 2.1768 | 42 |
| D | 2.1675 | 9 |
| E | 2.1449 | 15 |
| F | 2.1538 | 5 |

*Table 4. SSG and TII for Resins Tested.*

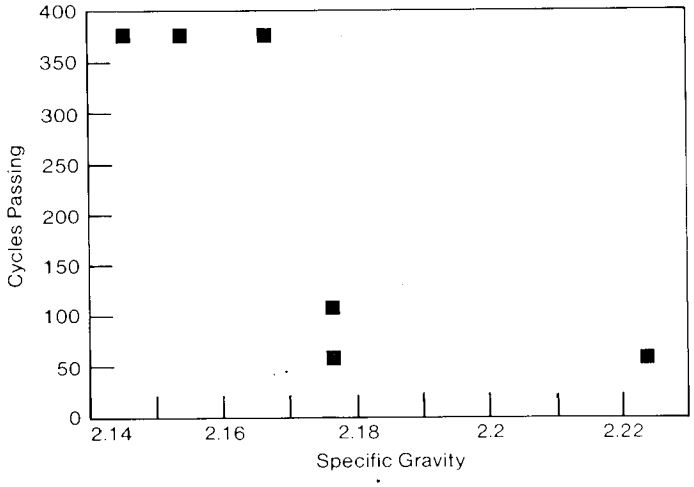


*Figure 2. Accelerated Stress Crack Performance versus Specific Gravity.*

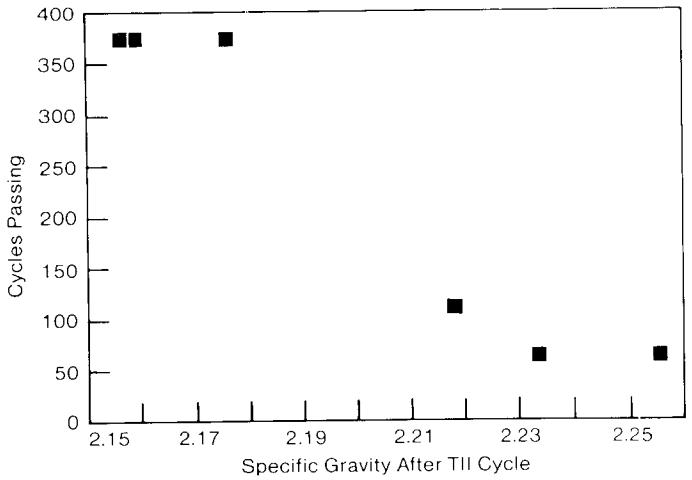


*Figure 3. Accelerated Stress Crack Performance versus Specific Gravity After TII Cycle.*

## CRACKING MECHANISMS

An excellent correlation between accelerated stress crack results and SSG and TII can be seen. However, the correlation is limited because of its empirical basis. Because of this limitation, there is a need to understand the fundamental causes responsible for cracking.

A scanning electron microscope was used to investigate the cracked surfaces of the wire specimens from the accelerated stress crack test. When micrographs of crack surfaces were examined, the presence of microvoids were observed at the leading edge of cracks (Photos 2A, B, C). Void formation appeared to be the pre-cursor of crack formation. Polymer fracture mechanics can be used to explain this phenomenon.

To understand the effect of resin properties on stress cracking, it is useful to study the mechanism of cracking. Stress cracking can be caused by mechanical (fatigue), thermal and/or environmental stresses. Localized stresses can be caused by surface defects or impurities which act as stress concentrators. Deformation in polymers generally occurs by two competing mechanisms, shear yielding and crazing (Ref. 5). Shear yielding leads to a ductile response while crazing leads to brittle cracks. The mechanism of failure depends on which of the mechanisms dominates under the loading conditions. Thus under different loading conditions, the same material may fail by shear yielding or by crazing.

Failure by shear yield is accompanied by a high level of elongation characteristic of ductile failure. Crazing is characterized by the concentration of bands of microvoids. Crazes can be visualized as microcracks bridged by fibrils or alternatively as a region of interconnecting microvoids and fibrils. Crazes usually form at areas of stress concentration such as surface defects, air bubbles or dust particles (Refs. 6, 7, 8, 9, 10). Cracks initiate and grow by the growth and breakdown of the fibrillar structure in crazes. Crazes are oriented perpendicular to the stress direction and the subsequent growth and breakdown of the craze leads to crack formation.

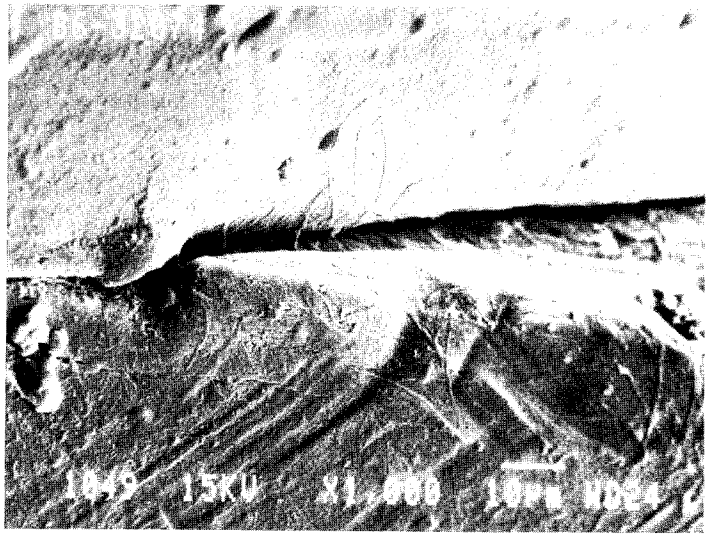

*Photo 2A.*

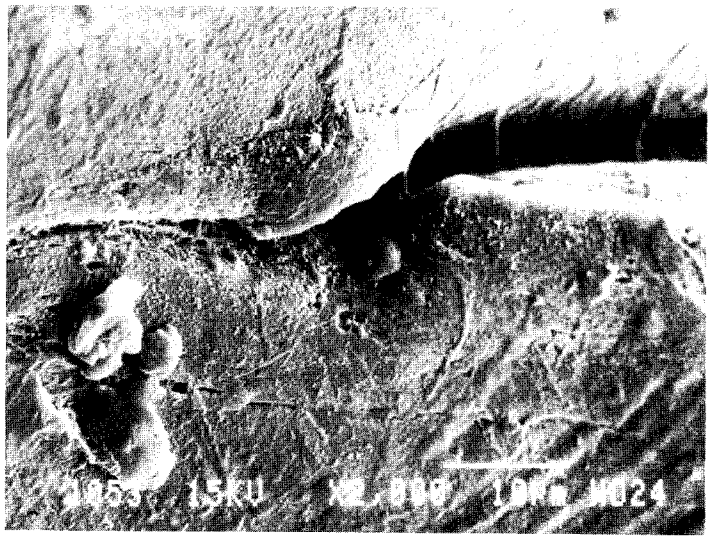

*Photo 2B.*

*Photo 2C.*

Craze nucleation appears to be controlled by the nucleation of microvoids in localized regions under stress. The polymer forms microviods which nucleate and expand. Groups of these microvoids coalesce to form a craze structure (Ref. 11). These voids can be observed in electron micrographs of fracture surface (Photo 2C). At sufficiently high stresses, these voids may grow slowly to a critical size. Beyond this critical size, propagation (the breaking of craze fibrils) is very rapid (Ref. 12).

Based on this mechanism, there are two stages to crack formation: initiation and propagation. Once a critical crack size has formed, propagation is very rapid. Therefore, the crack formation time is controlled by crack initiation. One of the factors affecting crack initiation is the tendency of a resin for void formation. In properly sintered PTFE, the resin is essentially void free. Under mechanical stresses over a long period of time, voids may develop in some resin types which eventually coalesce and lead to a crack.

## MEASUREMENT OF CRACKING PERFORMANCE

Measuring the tendency of a resin to form microvoids is suggested as a simple method to indirectly measure cracking performance. By stretching test specimens at high strain rates, microvoids are nucleated throughout the resin. Specimens of compression molded resin were stretched to break on a tensile testing machine. Microvoid formation is indicated by the whitening of the stretched resin (Photo 3). The change in specific gravity between the unstrained and the strained specimen is a measure of the void formation in the resin. Percent voidage is calculated as follows:

$$\text{Percent Voidage} = \frac{(\text{unstrained SG} - \text{strained SG})}{\text{unstrained SG}} \times 100$$

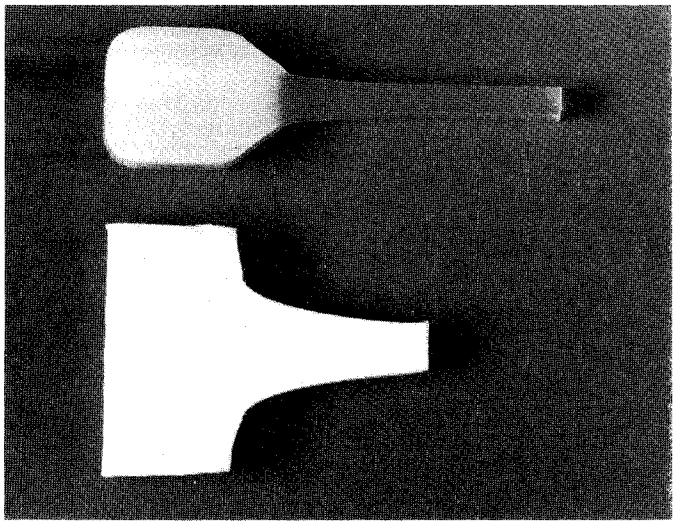

*Photo 3.*

The difference between unstrained and strained specific gravity is scaled by a factor of 1000 as in the TII to yield a measure we term the Crack Susceptibility Index (CSI). The equation is as follows:

$$\text{CSI} = (\text{unstrained SG} - \text{strained SG}) \times 1000$$

Increasing CSI denotes increased tendency for void formation. This translates into an increased susceptibility for stress cracking. We determined that changes in SG upon stretching were not caused by changes in crystallinity through the use of differential scanning calorimetry.

The same resin types which were used in accelerated stress crack testing were tested with this technique. CSI results and percent voidage are given in Table 5. These results indicate the following order for stress crack resistance: A < B < C< D < E < F.

| Resin | SSG | SSG (at break) | CSI | % Voidage |
|---|---|---|---|---|
| A | 2.200 | 1.808 | 393 | 17.8 |
| B | 2.177 | 1.921 | 256 | 11.8 |
| C | 2.178 | 2.072 | 106 | 4.9 |
| D | 2.169 | 2.071 | 97 | 4.5 |
| E | 2.148 | 2.079 | 69 | 3.2 |
| F | 2.151 | 2.140 | 11 | 0.5 |

*Table 5. CSI and Percent Voidage.*

### *Discussion*

This data confirms that Standard Specific Gravity (SSG) is an important variable with respect to crack susceptibility. However, lower SSG does not always translate to lower crack susceptibility, because the TII and the CSI should also be considered. A good correlation is seen when accelerated stress crack results (cycles passing) are plotted versus CSI for each resin type (Fig. 4). These results are consistent with the proposed cracking mechanism.

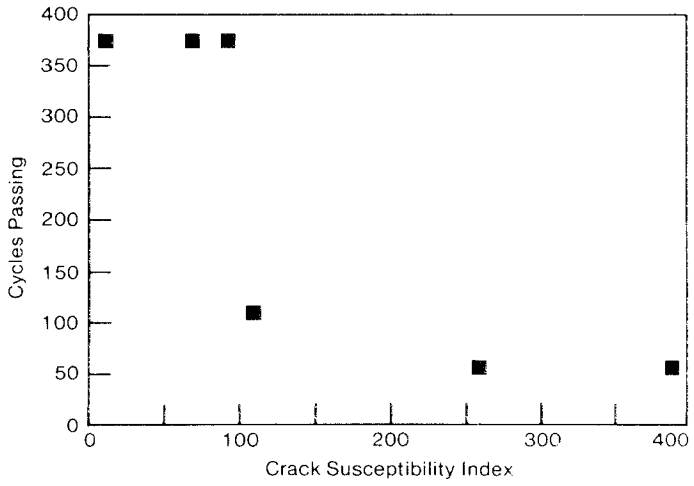


*Figure 4. Accelerated Stress Crack Performance versus Crack Susceptibility Index.*

Based on these results, two new specifications have been proposd for ASTM D 1457. These specifications have reduced maximums for TII and SSG. We expect these new specifications to be issued by 1987. Type III, Grade 6, Class C is the specification intended for wire sizes of AWG 14 and smaller. This specification has a maximum SSG of 2.190 and a maximum TII of 15. Type III, Grade 7, Class B is the specification intended for wire sizes AWG 8 to 12. This specification has a maximum SSG of 2.160 and a maximum TII of 15.

## CONCLUSIONS

A cracking mechanism has been proposed. The key points are:

- Cracking is divided into two steps, initiation and propagation.
- Initiation is the critical step.
- Microvoids are formed during the initiation step.

The following measurements correlate with relative stress crack performance:

- SSG: Measure of crystallinity.
- TII: Measure of change in density due to thermal stress.
- CSI: Measure of change in density due to mechanical stress.

New specifications have been proposed for ASTM D 1457 based on these findings.

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### APPENDIX

Test procedures for accelerated stress cracking of wire samples and CSI determination are given below.

**Test: Determination of Stress Crack Resistance Via Accelerated Procedures.**

***Apparatus:***

1. Heat aging oven capable of operating up to 230°C ± 5°C.
2. Tenny Environmental Chamber.
3. Cold box capable of holding −20°C ± 5°C.

***Reagents:***

Dow Corning 550 silicone oil, Dow Corning Corp., Midland, Mich.

***Procedure:***

1. Cut 20 specimens of sufficient length so that 1X wraps can be made.
2. Soak specimens before wrapping in DC-550 oil at ambient temperature for 6 hours.
3. Anneal straight in air circulating oven at 230°C for 16 hours. Inspect for cracks.
4. 1X wrap specimens.
5. Place 1X wraps in air circulating oven at 230°C for 4 hours. Inspect for cracks.
6. Place in cold box at −20°C in air for 16 hours. Inspect for cracks.
7. Reverse the 1X wrap of each sample.
8. Place in environmental chamber and cycle −20°C to +150°C, 6.5 hours per cycle. Inspect for cracks once per week until 50% of test specimens have developed cracks.
9. Report number of failures each time specimens are inspected.

**Test: Determination of Crack Susceptibility Index (CSI).**

***Apparatus:***

1. Hydraulic Press.
2. Temperature Programmed Oven.
3. Tensile Testing Machine.

***Procedure:***

1. Weight out 29 grams of resin into a 3 in. diameter circular mould.
2. Load hydraulic press to 7.0E03 lbs (corresponding to 1.0E03 psi) for 2 minutes.
3. Raise the load to 35.0E03 lbs (corresponding to 5.0E03 psi) and hold for 2 minutes.
4. Sinter the compression molded disk in a temperature programmed oven according to the SSG temperature cycle stated in ASTM D1457. The oven is normally maintained at 290°C.
5. After introducing the disks, the temperature is held at 290°C for at least 15 minutes.
6. The temperature is then raised at 2°C/min. to 380°C.
7. Hold at 380°C for 30 minutes.
8. The temperature is then cooled to 294°C at 1°C/min.
9. Hold at 290°C for 24 minutes.
10. Reduce oven temperature to 290°C.
11. Remove disks from oven any time after the temperature stabilizes at 290°C.
12. Cut tensile specimens of 0.2 in. width from the sintered disk using a die. The specimen shape is similar to the microtensile bar shape in ASTM D1708.
13. Place tensile specimen in tensile testing machine. Position specimen to ensure the portion between the jaws is of constant width.
14. Strain the specimen at a constant rate of 40%/min. until it fractures.
15. Cut off a portion of the stretched part of the specimen.
16. Determine specific gravity as per ASTM D792. Care should be exercised to avoid air bubbles on the surface when measuring the weight in water.
17. Determine specific gravity before stretching by measuring a piece from the sintered disk.
18. Determine percent voids and CSI by using equations given earlier.

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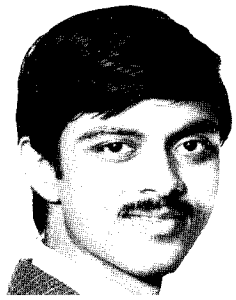

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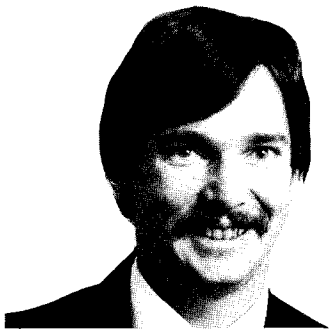
John Bednarczyk received his B.S. in Chemical Engineering from Rutgers University in 1981. He joined Du Pont in 1981 and worked in the Photographic and Electronic Products Department. In1984 he joined the Polymer Products Department, specialty Polymers Division where he is responsible for technical support for fluoropolymers used in the wire and cable industry.



Richard Baillie received his B.S. in Chemical Engineering from the University of Washington in 1980. He joined Du Pont's Polymer Products Department in 1980 and worked in fluoropolymer research and product development. His present responsibilities include development of wire and cable applications for high performance resins in the military electronics and aerospace industries.



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