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RESULTS OF PHYSICAL TESTS ON POLYMERS

AT CRYOGENIC TEMPERATURES

by

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RESULTS OF PHYSICAL TESTS ON POLYMERS AT CRYOGENIC TEMPERATURES

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SUMMARY

This paper describes the results of some physical tests conducted on polymeric materials used in the construction of superconducting magnets. A brief description of the various testing techniques is also given.

I. INTRODUCTION

Polymeric materials play an important role in the construction of superconducting magnets for high energy accelerators and storage rings. The materials used for such applications must possess good mechanical properties which will withstand the stresses introduced during magnet construction and operation. In addition, they should also have suitable thermal and electrical properties at low temperatures even in a radiation field.

II. PROPERTIES OF POLYMERS AT LOW TEMPERATURES

Polymeric materials are used in superconducting magnet technology for conductor insulation, for the impregnation of windings, for structural components as spacers, clamps, supports, etc.

A description of the chemical, mechanical, thermal and electrical properties of these materials as a function of temperature and radiation is given.

There are many variables in the polymer processing that may significantly affect their structure and thus their properties. Therefore, these results are intended for quick reference and comparison of polymers available in Europe.

Various types of thermoplastics, with promising properties at low temperatures, have been investigated. The study of the thermosetting compounds has been limited to epoxy resins of the Bisphenol A type. All materials considered showed a satisfactory resistance to thermal shock (298 - 77 K). In addition, all samples were examined in polarized light after the thermal shock test, and only those free from fissures and internal stresses were further examined. Before physical testing, the specimen were stored for several days in a dessicator to prevent water absorption.

1. Chemical Properties

It is possible to support conductors against electromagnetic forces and reduce their movement to a minimum by casting the windings in suitable resins. To date, epoxy resins have shown the best performance and in particular the Bisphenol A types cured with anhydrides.

These epoxy impregnants possess the following favourable characteristics:

- They have a very low viscosity at the impregnation temperature so that they can penetrate all areas not occupied by conductors, reinforcements, insulating tapes, etc., and a long "pot life", i.e. they are usable during the impregnation period which may extend over several hours (Figure 1);

FIG. 1 EPOXY RESIN
(MY 745 + EPN 1139 + HY 906 + XB 2687)
80 20 95 0.7 %

- They exhibit a low shrinkage and do not form bubbles during the curing process; these effects will minimize the build-up of internal stresses in the cured resin;
- They are not subjected to changes in phase or structure when cooled to the operational temperature of the magnet (Figure 2);
- They are non-toxic and support storing under normal conditions for several weeks.

FIG. 2 SHEAR MODULUS AND DAMPING OF EPOXY RESIN
(MY 745 + EPN 1139 + HY 906 + XB 2687)

2. Mechanical Properties

These tests are carried out using an Instron tensile testing machine on which a LN₂ or LHe cryostat has been fitted. Load versus extension graphs for test specimens are plotted directly by an X-Y recorder. The load signal is taken from an Instron load cell and the strain recorded from the output of a displacement transducer. The sensitivity of the system allows strain in the specimen to be determined to better than 10⁻³ cm. The load may be accurately recorded up to 5000 kg.

The tensile properties of various thermoplastic films and sheet materials at different temperatures are summarized in Table 1. Flexural test results on epoxies (unfilled, filled and glass-reinforced) are given in Tables 2 and 3. These tables show that the tensile and flexural strengths and the modulus of elasticity of all tested polymers at very low temperatures are better than at ambient temperature. At low temperatures, unfilled plastics become very brittle, they all break at the yield point when tested in liquid helium. An example is given in Figure 3.

At cryogenic temperature, the elongation at break of thermoplastics is considerably reduced (often 5 % or less of the value at ambient temperature). It is primarily this reduction which eliminates the use of a large number of polymers in low temperature applications.

Reactor irradiation up to 10⁸ rad in liquid nitrogen showed little change in the mechanical properties of epoxy resins tested at 77 K. A typical example is given in Figure 4. After being warmed up to room temperature, various epoxies irradiated at low temperature release gases. This release of gases, together with the oxidation of the irradiated resin, has a very adverse effect on the mechanical proper-

Table 1 : Tensile strength of various plastics*

Materials	Temperature (K)	Tensile Strength (kg/mm ²)	Elongation at break (%)	Modulus of elasticity (kg/mm ²)
I. Plastic films & paper				
Polyimide (H film)	298	18.2	44	510
	77	32.5	16	640
	4.2	34.0	8	615
Polycarbonate (Makrolon)	298	6.4	112	
	77	13.5	4.5	
	4.2	15.6	3.0	
Polyamide (Nomex)	298	8.3	21	
	77	14.5	3.5	
	4.2	15.8	3.0	
Polyethylene Terephthalate (Mylar)	298	16.5	88	450
	77	26.0	9.5	870
	4.2	26.8	5.5	880
Polyvinylchloride (rigid type)	298	2.3	156	110
	77	9.5	3.6	215
	4.2	11.6	2.9	300
Polyethylene (high density)	298	2.5	525	
	77	10.5	4.3	
	4.2	13.5	3.1	
Polytetrafluoroethylene (Teflon)	298	2.0	480	-
	77	4.3	6.5	145
	4.2	5.6	3.5	217
II. Bulk materials				
Polyimide (Vespel)	77	18.4	3.1	
Polyethylene (high density)	77	13.8	2.3	
Polyvinylchloride (rigid)	77	11.5	1.9	

* Standard deviation : ± 10 %

Number of samples tested : 8 at 298 K

4 at 77 K and 4.2 K

ties. The tensile stress of Araldite D + HY956, irradiated at 10⁸ rad in liquid nitrogen was only 7.2 kg/mm² at 77 K (~50 % of its initial value) after being left for 10 months in atmospheric conditions.

3. Thermal properties

3.1 Thermal contraction

The linear dimensional changes are measured in a quartz dilatometer. It consists essentially of a fused quartz tube into which the sample is inserted. A quartz rod is then placed on top of the sample. The change in length of the sample on cooling was measured with a displacement transducer. Tests were

Table 2 : Flexural strength of cast epoxy resins*

Resin Composition	Flexural strength (kg/mm ²)		Modulus of elasticity (kg/mm ²)	
	298 K	4.2 K	298 K	4.2 K
MY745 (100) HY906 (80) BDMA (0.75)	11	24	373	680
MY745 (80) EPN1139 (20) HY906 (95) XB2687 (0.7)	12	26	379	668
MY745 (100) HY906 (80) BDMA (0.75) Talc (180)	6	11	780	1305

* Standard deviation : $\pm 7\%$ - 6 test samples

Table 3
Flexural strength of glass-reinforced epoxies*

Resin Composition	Flexural strength (kg/mm ²)			Modulus of elasticity (kg/mm ²)
	298 K	77 K	4.2 K	
Araldite F (100) HY972 (27)	27.0	67.5	74.8	2450
Araldite F (100) MY906 (90) BDMA (0.75)	32.5	68.7	76.5	2380
Araldite MY745 Epoxy Novolac 1139 (50) HY905 (95) XB2687(0.7)	26.5	61.4	68.7	2260

* Standard deviation : $\pm 7\%$ - 6 test samples

performed between 298, 77 and 4.2 K, respectively. It was possible to detect relative changes in length of approximately 0.0025 mm.

The dimensional changes produced in unfilled and non-reinforced plastic materials as the temperature falls are more pronounced than in the case of metals (Table 4). As a reference: the thermal contraction of annealed OFHC-copper (grade I) between 298 and 4.2 K is equal to 0.326 %. In addition to embrittlement, this is another main reason for restricting the use of plastic materials in cryogenic applications.

Thermal contraction is not as marked in filled plastic materials and is dependent to a large extent

FIG. 3 TENSILE PROPERTIES OF POLYAMIDE (NYLON PA6) at 77K and 4.2 K

FIG. 4 TENSILE PROPERTIES OF EPOXY RESIN (ARALDITE D + HY 956) at 77K under radiation

on the type and quantity of the filler and reinforcement. The desired coefficients of expansion can be obtained by the judicious choice of a filler and its quantity (Table 4).

However, it must be remembered that during contraction, glass-reinforced plastic materials may exhibit considerable anisotropy, depending on the type and direction of the incorporated reinforcement material. Contraction parallel to the glass fibres (warp direction) is less marked than perpendicular

to them (weft direction) and much more marked in the direction perpendicular to both. All contraction is essentially finished by the time the material reaches 20 K and most of the contraction has occurred by 77 K (Table 4).

Table 4
Thermal contraction of selected organic materials

Chemical Name	Commercial Designation	$\Delta L/L$ (%)	
		77 K	4.2 K
Polyethylene	RCH 1000	1.82	2.05
Polyphenylene oxide	PPO	1.30	1.35
Polycarbonate	Makrolon	1.04	1.16
Fluoro-silicone	X201/1	2.20	2.40
Unfilled Epoxies	Araldite, Epon	--	1.4 ± 0.4
Filled Polyimide	Vespel SP1 or SP21	--	0.50
Filled Epoxies	Araldite, Epon	--	0.5 ± 0.2
	Stycast 2850 GT + Catalyst 9	0.374	0.413
	Stycast 2850 FT + Catalyst 11	0.405	0.442
Filled Polyphenylene sulfone	Ryton PPS	0.296	0.326
E-Glass reinforced Epoxy resins	Vetronite EPG: - warp direction - weft direction - perpendicular	0.168	0.185
		0.191	0.210
		0.555	0.630

A radiation dose of 10^8 rad does not alter the thermal contraction (298 and 4.2 K) of various Bisphenol A type epoxy resins cured with anhydrides (unfilled, filled or glass-reinforced).

3.2 Thermal conductivity

The samples are rods of 10 mm diameter by 30 mm length and are mounted into the measuring cell at room temperature. The heat conduction is measured in the temperature range from 6 K to about 100 K in a vacuum of 10^{-5} mmHg. The thermocouple junctions were in contact with thin copper rods which were pushed through the cross-section of the sample. The temperature measured was, therefore, the average cross-sectional sample temperature. The distance between the junction of the two thermocouples used for determining the temperature gradient was 10 mm (the middle 10 mm of the sample length). This temperature difference was determined with an accuracy of $\sim 0.04^\circ\text{C}$

by means of Au-Fe-chromel thermocouples. The absolute temperature of the sample was measured with a precision of ~ 0.1 K by means of a germanium resistor between 6 and 40 K and with a platinum resistor between 40 and 100 K. The applied power of the furnace was in the range 1 - 10 mW with a precision of 10^{-3} . The precision of the thermal conductivity values for these polymers is $\sim 5\%$.

Organic materials are poor heat conductors and as the temperature drops their thermal conductivity diminishes (Figure 5). The organic materials which exhibit the greatest ductility at low temperature are also the best conductors of heat.

FIG. 5 THERMAL CONDUCTIVITY VS TEMPERATURE FOR POLYPHENYLENE OXIDE (PPO)

The thermal conductivity of many epoxy resins tested measures between 0.3 and 2 mW.cm⁻¹.K⁻¹ at ~ 4.6 K depending on their chemical composition, cure conditions and presence of diluents. The thermal conductivity parallel to the direction of lamination of glass epoxy materials is higher than the value transverse thereto in the temperature range tested (Figure 6).

FIG. 6 THERMAL CONDUCTIVITY VS TEMPERATURE FOR EPOXY GLASS LAMINATE (VETRONITE EPG11)

Reactor radiation up to a dose of 1×10^8 rad does not influence the conductivity at low temperatures of various polymers tested. Figure 7 gives an example for polyurethane.

FIG. 7 THERMAL CONDUCTIVITY VS TEMPERATURE FOR POLYURETHANE (ADIPRENE)

3.3 Specific heat

A differential adiabatic calorimeter equipped with two sample holders, one for the reference, the other for the sample proper is used. Absolute powers of 0.1 to 300 mW applied continuously to each sample and regulated in order to maintain a linear heating rate (1 K/min), strictly identical on both sides, are recorded. The difference of the applied powers allows the determination of the specific heat of the test sample. The accuracy of the measurement is about 5 % depending on the thermal diffusivity of the samples. The samples have a diameter of 9.9 mm and a length of 10 mm for tests between 4.2 and 300 K.

The specific heat of organic materials decreases markedly at low temperatures (Figure 8) and the specific heat of mineral-filled epoxies is lower than for unfilled ones in the temperature range tested.

No changes in specific heat were observed for epoxy resins irradiated to 10^8 rad, post-irradiation heat treated and tested between 4.2 K and 300 K. A typical example is given in Figure 8.

3.4 Heat transfer

i) Resin to copper thermal interface resistance:

This resistance was measured on test samples consisting of 2 copper rods glued together with either unfilled or mineral-filled epoxy resins. The epoxy layer was between 0.03 and 0.07 mm thick with an interlayer contact surface of 1.22 cm^2 . Measurements were made under vacuum between 4.8 and 10 K.

The method used to measure the interface resistance was to inject a heat power P through the sample and measure the temperature difference in the copper rods across the epoxy interface. From these results, the thermal resistances were derived:

$$\Delta T/P = R_{\text{Tot}} = R_{\text{Epoxy}} + 2R_{\text{Interface}}$$

The results of a typical epoxy resin are summarized in Table 5 from which it can be seen that the interface resistance has a tendency to decrease with temperature and to be independent of resin compositions studied, filled or unfilled.

FIG. 8 SPECIFIC HEAT VS TEMPERATURE FOR EPOXY RESIN (MY 745 + HY 905 + DY 065 + XB 2687)

Table 5
Resin to copper thermal interface resistance

Epoxy resin	Thermal conductivity ($\text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$)	Thermal resistance epoxy layer ($\text{K} \cdot \text{W}^{-1}$)	Interface resistance epoxy/Cu ($\text{K} \cdot \text{W}^{-1}$)
MY745+HY905+DY065+XB2687	9×10^{-4} between 4.5 and 10 K		
0.04 mm	at 6 K	3.5	3
0.07 mm	at 4.8 K	6.2	4.5
0.07 mm	at 10 K	6.2	3.5
Mineral-filled MY745	1.2×10^{-3}		
0.03 mm	at 6 K	2	3

ii) Between varnished copper surface and liquid helium:

The heat transfer from a polyvinyl-acetal varnished copper cooling surface placed perpendicularly in liquid helium, to liquid helium has been measured (Figure 9). The heat flux per unit surface area, to liquid helium (q), is given as:

$$q = h \times \Delta T$$

where ΔT is the temperature difference between the varnished copper surface and the liquid helium, and h the coefficient of heat transfer.

Transition from the nucleate boiling region to film boiling occurs in liquid helium when ΔT is about 3 K and q about 1 W/cm^2 . At the end of the transition boiling region, the temperature of the varnished copper cooling surface was about 20 K.

For reference, the heat transfer from a flat polished copper surface to liquid helium is also shown in Figure 9.

4. Electrical Properties

The dielectric properties of some insulating materials have been measured according to VDE 0303 but modified for our cryogenic equipment and conditions. The dielectric constant and loss factor were measured over the temperature range 4.2 - 300 K while the dielectric strength and resistivity were only measured at 4.2, 77 and 300 K. The spread in the results is within 25 %.

4.1 Dielectric strength

The dielectric strength of the polymers studied is slightly higher in both liquid helium and liquid nitrogen than in air at room temperature (Figure 10). The dielectric strength exceeds 5 kV/0.1 mm in helium gas as well as in liquid nitrogen and liquid helium. Their behaviour seems better in liquid nitrogen than in liquid helium and there is a tendency that the dielectric strength of these polymers is better in liquid helium than in its corresponding gas.

4.2 Volume resistivity

The volume resistivity of the insulating materials tested increases with decreasing temperatures. For all polymers, except Teflon, this value is higher than $10^{17} \Omega \cdot \text{cm}$ both at liquid nitrogen and helium temperatures (Table 6).

FIG. 10 DIELECTRIC STRENGTH OF POLYMERS

Table 6
Volume resistivity (in $\Omega \cdot \text{cm}$) of
solid polymer materials vs. temperature

Materials	300 K	~80 K	~5 K	Remarks
Polyimide (Kapton)	2×10^{15}	$> 2 \times 10^{17}$	$> 2 \times 10^{17}$	Vacuum treated
Polycarbonate (Lexan)	3×10^{15}	$> 2 \times 10^{17}$	$> 2 \times 10^{17}$	Vacuum treated
Polyethylene-Terephthalate (Mylar)	2×10^{17}	$> 2 \times 10^{17}$	$> 2 \times 10^{17}$	Vacuum treated
Polytetrafluoroethylene (Teflon)	3×10^{13}	4×10^{12}	--	Aged for two weeks at 300K and 90% relat. humidity

4.3 Dielectric constant and loss factor (Figures 11 and 12)

Non-polar materials, e.g. polyethylene, contain no permanent dipole moments and show very low dielectric losses at room temperature whereas the polar materials, e.g. polyimide, aromatic polyamide, etc., exhibit a high dielectric loss.

Loss angles fall with temperature, the values at 4.2 K being generally lower than at room temperature by a factor of at least 10 for polar materials. This factor is somewhat lower for non-polar materials. The essentially non-polar materials give the lowest loss at 4.2 K, being about 2 to 4×10^{-5} compared to about 10^{-4} for polar materials.

Many polymers show one or more loss regions with a maximum in loss factor between 100 and 300 K. These peaks are related to relaxation phenomena in the amorphous regions in the polymer.

FIG. 11 DIELECTRIC CONSTANT VS TEMPERATURE FOR POLYMERS (1kHz)

The dielectric constant measured at 1 kHz of the non-polar materials, e.g. polyethylene, teflon, etc., was substantially temperature independent but that of the polar materials fell with decreasing temperature.

III. CONCLUSIONS

1. Low temperature effects on the properties of the polymers studied can be summarized as follows:

Increase in: - Tensile strength
- Flexural strength
- Modulus of elasticity
- Dielectric strength
- Volume resistivity;

Decrease in: - Elongation
- Ductility
- Specific heat
- Coefficient of thermal expansion
- Thermal conductivity
- Dielectric constant
- Dielectric loss factor.

Consequently, it can be broadly stated that, in general, as the temperature falls, the strength increases whereas ductility decreases.

FIG. 12 DISSIPATION FACTOR VS TEMPERATURE FOR POLYMERS (1kHz)

2. Polymers commonly used for high temperature applications ($>200^{\circ}\text{C}$) also seem to have the most suitable physical properties at very low temperature. Typical examples are polyimide, polyphenylene oxide, epoxy resins, polyamide-imide and ester components, polycarbonates, polytetrafluoroethylene.
3. The thermal properties of all polymers studied fall with decreasing temperature. The specific heat is particularly temperature sensitive: it falls by more than 2 orders of magnitude between 300 and 4.2 K.
4. Polymer coatings on copper surfaces change the heat transfer coefficient between the surface and the liquid helium quite considerably. This applies in particular to the nucleate boiling region.
5. The dielectric properties of polymers tend to improve as the temperature drops. The data measured at room temperature can be used as a basis for determining whether or not a material satisfies the dielectric requirements.

6. The electrical and thermal properties of insulating materials are not influenced by ionizing radiation at low temperature as long as the mechanical strength of the material is good.

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