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DYTHERM - A NEW TEMPERATURE RESISTANT REMOVABLE FOAM ENCAPSULANT

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TABLE OF CONTENTS

	PAGE
ABSTRACT	5-6
INTRODUCTION	7
PHYSICAL PROPERTIES	9
PROCESSING AND REMOVAL	12
DYTHERM X214 AGING	14
CONCLUSION AND RECOMMENDATIONS	16
REFERENCES	17
TABLE I	18
TABLE II	18
TABLE III	19
TABLE IV	19
TABLE V	20
FIGURE 1	21
FIGURE 2	22
FIGURE 3	23
FIGURE 4	24
FIGURE 5	25

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ABSTRACT

A new commercially available copolymer produced by ARCO/ Polymers, Inc., under the tradename of DYTHERM X214 has been evaluated for use as a removable foam encapsulant. DYTHERM X214 is a styrene-maleic anhydride copolymer that increases the upper use temperature of previously employed polystyrene bead foam from 80°C to about 115°C.

The processing of DYTHERM X214 is similar to polystyrene foam beads except that higher fusion temperatures (∿125°C) are necessary and polar solvents (e.g., tetrahydrofuran) are needed for foam removal. Mechanical properties (e.g., compressive strength) of DYTHERM X214 are slightly higher than polystyrene foam beads at comparable densities; there is little difference in other physical properties. Preliminary aging studies of DYTHERM indicate that the anhydride portion of the copolymer is hydrolytically stable, consequently, long term corrosion problems appear of little concern. This new material is available for evaluation on prototype hardware.

INTRODUCTION

The principal features of removable encapsulants are their rework capability and associated economic advantages. Continued interest in removable foam encapsulants for electronic packaging has lead to the evaluation and recommendation of a new commercial product manufactured by ARCO/Polymers, Inc., under the tradename DYTHERM. DYTHERM is a random copolymer of styrene and maleic anhydride whose primary advantage is extending the upper use temperature of existing removable foam materials.

In the past, expandable polystyrene beads have been used as a removable foam encapsulant. Polystyrene bead foam has received considerable evaluation both at SNLA (1-3) and BKC (4-7) and as a result has been successfully employed in several WR component programs (e.g., MK-4 radar, a classified electronic component) besides numerous prototype projects. However, polystyrene bead foam has an upper use temperature limitation of about 80°C (175°F). Since an increasing number of advanced designs dictate higher use temperatures, efforts have been made to find new removable encapsulant materials. From our efforts, we have developed and characterized several removable polyurethane casting resins which can withstand temperatures in the neighborhood of 140°C (285°F) without any drastic changes in mechanical properties (8-9). Unfortunately, we have not developed a satisfactory removable foam that functions at these temperatures.

ARCO/Polymers, Inc., has been investigating styrene-maleic anhydride copolymer foams for automobile applications for some time. In the summer of 1980, ARCO went commercial with a series of copolymer bead foams termed DYTHERM's. These materials raise the glass transition temperature of polystyrene from 100°C to about 125°C. This increase results in higher use temperatures and therefore wider applicability. The following report will describe recently developed engineering properties and processing associated with this new product.

PHYSICAL PROPERTIES

ARCO/Polymers, Inc., markets several DYTHERM products. The one we have evaluated and which is currently available for prototype studies is designated DYTHERM X214. The glass transition temperature, T_g, of this material is 120°C (via TMA), therefore, we expect this material to maintain satisfactory mechanical strength to about 115°C (240°F).

DYTHERM is an extruded copolymer, consequently, the particle appears "drum-shaped," about 1 mm in diameter and 1 mm long. This particle size is about 2-3 times larger than our polystyrene bead potting material; thus the filling of very small areas may not be quite as good as with the polystyrene beads. DYTHERM contains pentane as the blowing agent and as such is processed much like the polystyrene beads; processing will be described in the next section. Foam mechanical properties are a function of density; to achieve different densities pre-expansion of the material is necessary. To pre-expand the DYTHERM beads, simply place the unconstrained beads in a 125°C oven for a predetermined time. This process allows the beads to expand to a new volume and resultant density. The following relationship is employed:

$$\frac{V_p}{V_i} = \frac{\rho_i}{\rho_f}$$

where, V_p = bulk volume of pre-expanded beads

V_i = bulk volume of unexpanded beads

ρ_i = bulk density of unexpanded beads

ρ_f = bulk density of pre-expanded beads

For example, suppose a 0.2g/cc ($\sim$12 lb/ft^3) foam was desired; then one would place 100 cc of unexpanded 0.7g/cc beads (as received from vendor) in a 125°C (255°F) oven and expand them to 350 cc (determined by solving for V_p). Once the particles have reached the desired volume, they are immediately removed from the oven which drops the temperature through the T_g so that further expansion cannot occur. Once the required density bead is obtained, the encapsulation and fusion process follows.

A number of engineering parameters have been determined for molded DYTHERM X214 and are shown in Tables 1-5 and Figures 1-5. This property data has either been generated at SNLA or supplied by the manufacturer. These properties generally change with density, thereby allowing property trade-offs during component design.

Concerning moisture absorption (see Table 1), as the foam density increases, the water absorption decreases to some minimum value. Creep data obtained at 95°C (see Table 2) indicates DYTHERM is structurally quite stable and this parameter will improve at higher densities. Tensile strength and compression set are shown in Tables 3 and 4 and change with density in a direction one would predict.

Compressive strength and modulus of DYTHERM X214 are shown in Figures 1 and 2. Figure 1 shows a compressive strength comparison of DYTHERM X214 with the polystyrene bead foam (Wyandotte STYROPOR BF 414). The copolymer has slightly higher compressive strengths at a given density than the homopolymer. Although not shown, the moduli are comparable. Figures 3 and 4 depict the flexural strength and modulus over a limited density range.

Electrical properties of molded DYTHERM are shown in Table 5. These properties are not only a function of density but how well the copolymer is fused. Poor bead fusion would show marked deterioration in these electrical parameters, in fact, electrical properties measurements could be used as a guide to proper bead fusion. As shown, properly fused DYTHERM is an excellent dielectric.

The shrinkage of DYTHERM X214 is shown in Figure 5. The denser foams exhibit a higher rate of shrinkage because these foams retain proportionally more pentane after fusion. Upon eventual dissipation of pentane, all the densities tested appear to arrive at a constant value. The coefficient of thermal expansion for bulk material was measured to be 4.1×10^{-5} in/in/^{o}C from -40°C to ambient temperature and 6.3×10^{-6} in/in/^{o}C from ambient to 70°C. It should also be noted that DYTHERM materials have poor bonding characteristics similar to the polystyrene bead foam.

PROCESSING AND REMOVAL

Both polystyrene foam beads and DYTHERM function in a similar manner, that is, they use dissolved pentane as a blowing agent to achieve the desired foaming action and final structure. The appropriate density pre-expanded DYTHERM beads are simply poured into a mold or electronic assembly and sealed from the outside environment. Assuming a component is completely filled, expansion and fusion takes place only in the interstices between beads, therefore resultant foam densities are virtually identical with pre-expanded bead densities. Since DYTHERM materials have higher softening temperatures than the polystyrene homopolymer, higher fusion temperatures are required. Consequently, encapsulated components must withstand these same temperatures. Typically, DYTHERM fusion temperatures are about 125°C (255°F); the length of time at this temperature varies depending upon the component geometry and amount of DYTHERM required. The expansion and fusion time will not vary appreciably from that experienced with polystyrene bead foams.

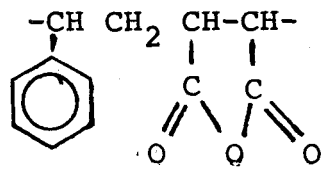
There will be residual pentane after the fusion cycle, perhaps 1-2% by weight. Pentane is considered chemically unreactive, thus long term aging effects due to this blowing agent are believed minimal. Eventually (weeks), the pentane will dissipate from this closed cell encapsulating material. Because of this, purchases material has a refrigerated shelf-life of about 12 months. Once the pentane content depletes to a certain level (<3.5% by weight), the beads will

not fuse properly. If after encapsulating a unit there is still some concern about the residual pentane, it can be removed by conditioning at some elevated temperature (e.g., 80°C).

Polar solvents such as tetrahydrofuran (THF) and methylene dichloride are recommended for foam removal prior to rework. Toluene was used for polystyrene beads, but this is not effective in the removal of DYTHERM materials. The above polar solvents may be more damaging than toluene towards other polymeric materials, thus care must be taken in evaluating the compatibility of these solvents with other materials. In general, rubbers are swelled, some thermoplastics are attacked whereas crosslinked materials (e.g., epoxies, phenolics) survive quite well. The time it takes to dissolve DYTHERM materials depends on the surface area exposed, the amount and density of the polymer and the degree of agitation; the more vigorous the agitation the quicker the dissolution. Large material volumes and dense foams may require fresh solvent because of polymer saturation. After depotting, units are thoroughly washed with acetone and baked-out at 71°C for a minimum of 6 hours to overnight. If any "wicking" is suspected in components, it would be advantageous to bake-out the entire unit under reduced pressure.

DYTHERM X214 AGING

As previously mentioned, DYTHERM X214 is a random copolymer of styrene and maleic anhydride shown as follows:



Infrared spectra of this material indicates not only anhydride absorption bands at 1860 and 1780^{-1} cm but a carboxyl band at 1715^{-1}cm (see Figure 6). Apparently some hydrolysis of the anhydride occurs in polymer production (aqueous emulsion polymerization process) to account for the presence of organic acid. More importantly, the possibility exists of further anhydride hydrolysis during material aging to yield carboxylic acid groups. This aging phenomenon could result in an encapsulant with corrosive properties. To ascertain whether hydrolysis can take place to any appreciable extent, an accelerated aging study was performed. The study consisted of isothermally aging DYTHERM films (prepared by solvent casting) at 23°C, 60°C and 77°C and 50% RH. These films were analyzed via infrared to determine whether there were any increases in the acid absorption or decreases in the anhydride content. Two bands were followed, the acid carboxyl peak at 1715^{-1}cm and the anhydride absorption at 1780^{-1}cm. This study lasted 14 months with no appreciable changes in functional group intensities (see Figures 7-8). There were a couple abnormal deviations (e.g.,

2 and 12 months) which could not be explained, yet upon continued aging, the data returned to relatively constant values. Because there may be some change in spectral background, the two principal absorption bands were ratioed each month; again no dramatic changes were observed using this ratioing technique.

From this study we concluded that the copolymer is relatively hydrolytically stable and would not pose a serious corrosion problem. However, an added aging study will be conducted to insure our conclusion. DYTHERM films will be cast on highly polished aluminum, steel and copper and these coupons will be aged under the above stated conditions. Periodically, analysis will be made to detect evidence of corrosion. We are not anticipating any serious corrosion problems since organic acid of this nature are generally weak. Compatibility with other potentially harmful materials (e.g., polyamides) would have to be evaluated on an individual basis.

CONCLUSION AND RECOMMENDATIONS

A new commercially available removable foam encapsulant, DYTHERM X214, is being recommended for prototype evaluation. The primary advantage of this product is in extending the upper use temperature range to about 115°C compared to 80°C for polystyrene bead foam. The physical property data accumulated to date indicates this new material is comparable to polystyrene bead foam. However, DYTHERM does possess the following differences: 1) a larger initial particle size, 2) a 125°C expansion and fusion temperature 3) slightly higher mechanical strength and 4) the foam must be removed with polar solvents such as tetrahydrofuran or methylene dichloride.

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TABLE I

WATER ABSORPTION, MOLDED DYTHERM

FOAM DENSITY, lbs/ft^3	WATER ABSORPTION* % BY VOLUME
5.8 (.06g/cc)	0.20
11.0 (.12g/cc)	0.23
15.8 (.17g/cc)	0.11

*ASTM C-272

TABLE II

CREEP STUDY* MOLDED DYTHERM

FOAM DENSITY, lbs/ft^3	EXPOSURE TIME, HRS	CREEP MEASURED AT UNSUPPORTED LEVEL, IN
4.5 (0.05g/cc)	4	.0156 (.04 cm)
4.5	8	.0156 (.04 cm)
4.5	24	.0469 (.12 cm)
8.0 (.08g/cc)	4	.0156 (.04 cm)
8.0	8	.0156 (.04 cm)
8.0	24	.0313 (.08 cm)
9.0 (.095g/cc)	4	0 0
9.0	8	.0313 (.08 cm)
9.0	24	.0313 (.08 cm)

*Conditions: 205°F Oven Temperature, 14" x 6" x 1" Specimen Size, 12" Unsupported Length

TABLE III

TENSILE STRENGTH*, MOLDED DYTHERM

FOAM DENSITY, lbs/ft^3	TENSILE STRENGTH, psi
5 (.053 g/cc)	120 (0.83 MPa)
11 (.12 g/cc)	215 (1.48 MPa)
17 (.18 g/cc)	290 (2.0 MPa)

*ASTM D-1623

TABLE IV

COMPRESSIVE SET*, MOLDED DYTHERM

FOAM DENSITY, lbs/ft^3	% COMPRESSIVE SET AFTER DEFORMATION OF		
	10%	20%	30%
6.1 (.066g/cc)	4.4	-	-
6.4	-	11.4	-
6.4	-	-	20.5
11.5 (.12g/cc)	2.7	-	-
11.1	-	11.1	-
11.3	-	-	19.5
15.7 (.16g/cc)	2.2	-	-
15.2	-	10.1	-
15.9	-	-	18.0

*ASTM D-1621

TABLE V

ELECTRICAL PROPERTIES, MOLDED DYTHERM

Dielectric Constant, K	10.0 (.11 g/cc)	15.3 (.16g/cc)	24.3 (.26g/cc)
Freq. 10^3	1.186	1.296	1.487
10^4	1.186	1.295	1.484
10^5	1.185	1.294	1.481
10^6	1.184	1.292	1.478
Dissipation Factor, D			
Freq. 10^3	-	-	-
10^4	.0006	.0008	.0021
10^5	.0008	.0010	.0015
10^6	.0008	.0014	.0018
Volume Resistivity, ρ ohm-cm			
500 volts	-	5.02×10^{17}	9.33×10^{16}
1000 volts	1.26×10^{18}	1.17×10^{18}	9.60×10^{16}

Figure 1

Compressive Strength of

ARCO Polystyrene - Maleic Anhydride Molded Foam

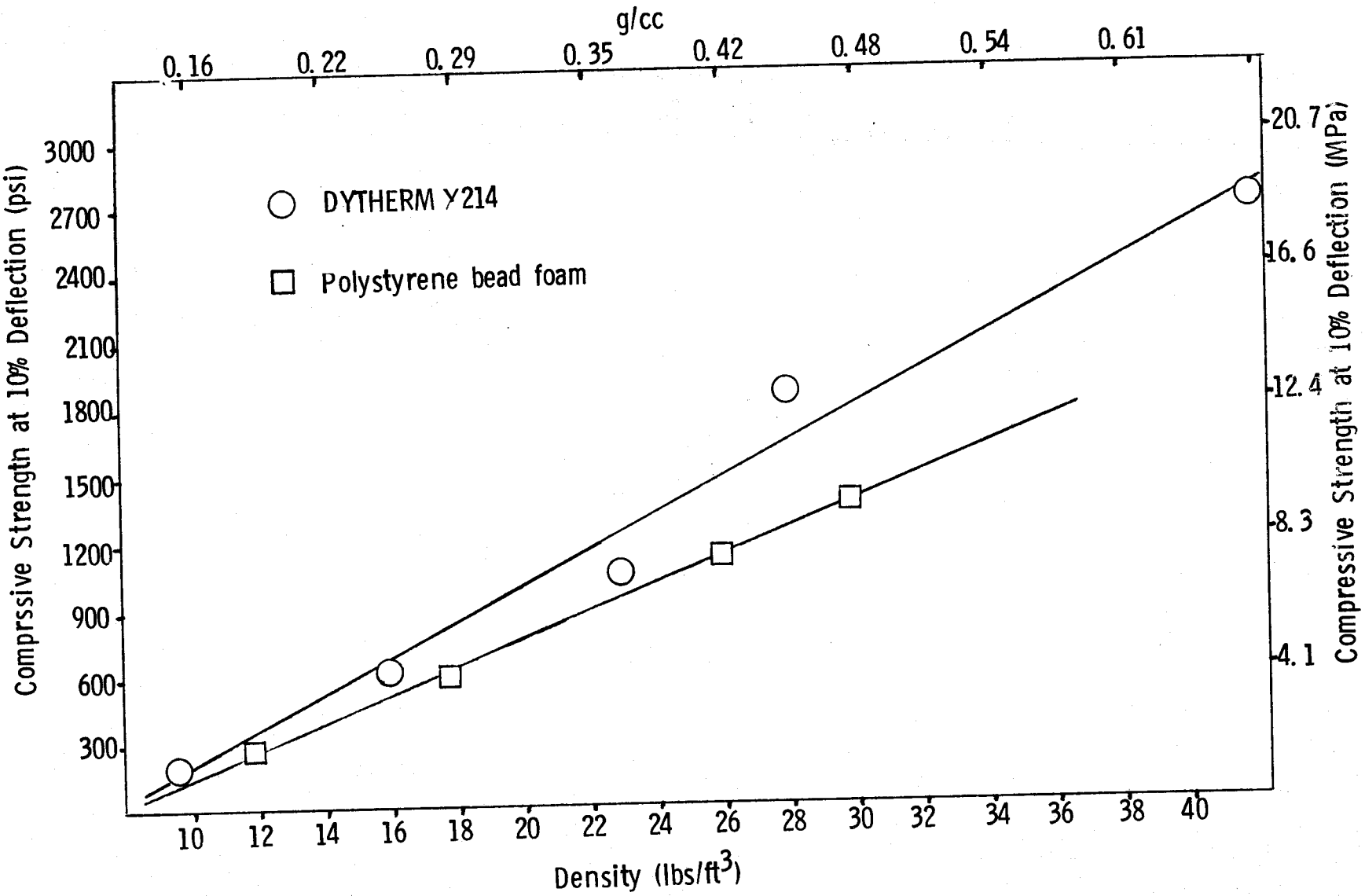


Figure 2 Compressive Modulus of ARCO Polystyrene - Maleic Anhydride Molded Foam

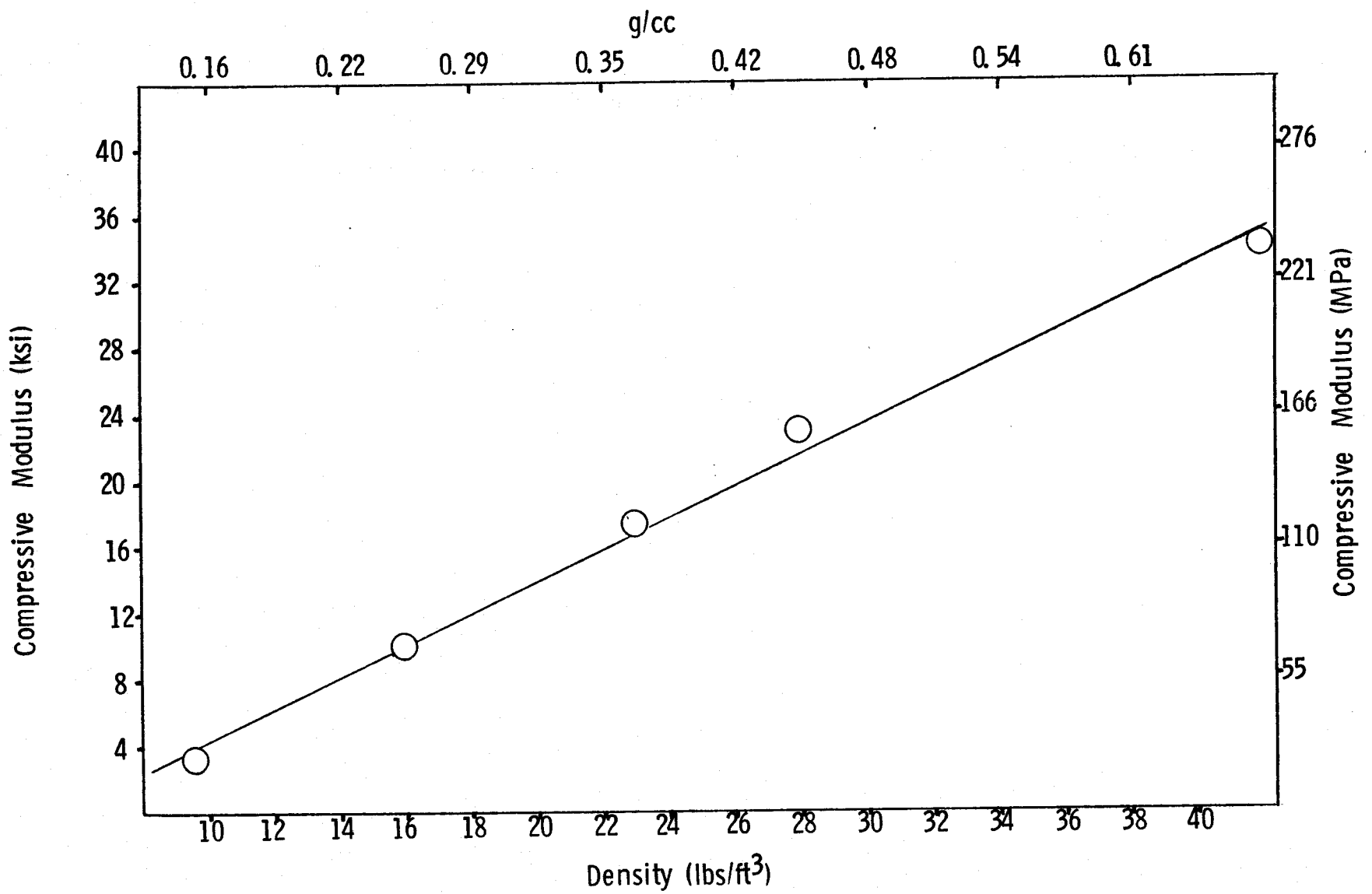


Figure 3 Flexural Strength of

MOLDED DYTHERM X214

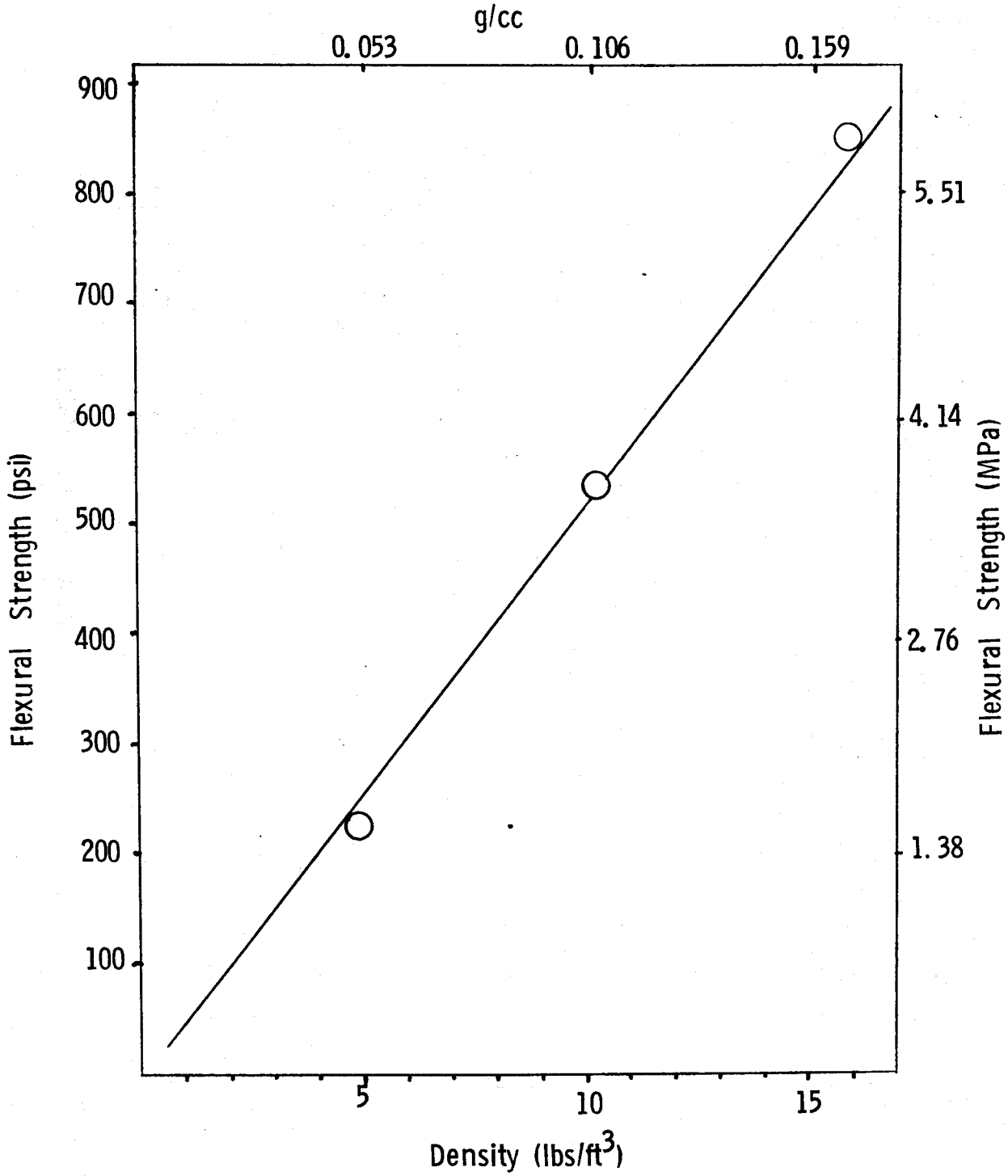


Figure 4 Flexural Modulus of MOLDED DYTHERM X214

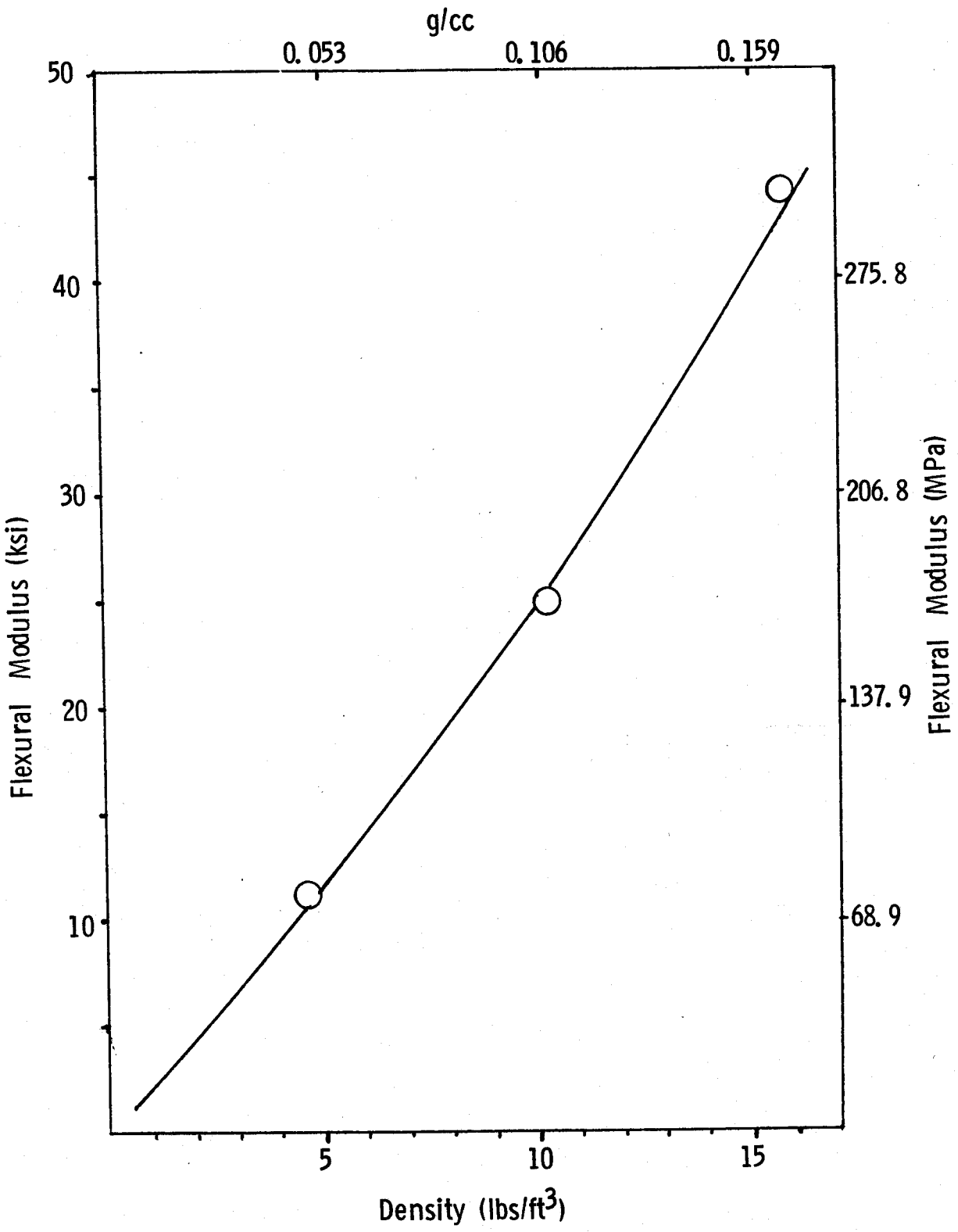
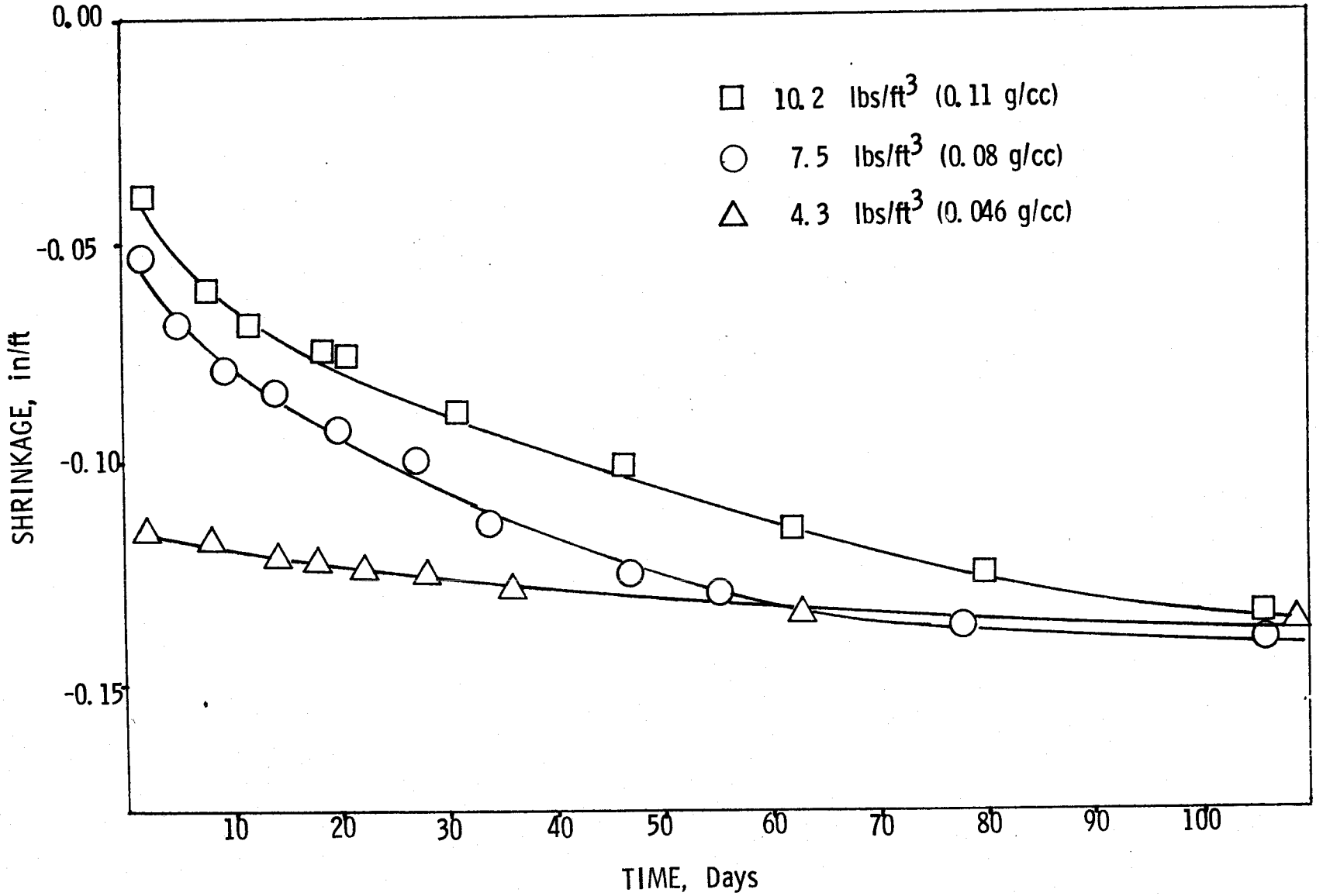


Figure 5 DYTHERM FOAM SHRINKAGE



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