

Simultaneous Polymerization and Molding of Pyrrone Polymers

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Synopsis

Our previously reported one-step method of simultaneously polymerizing and molding pyrrone monomers to produce high-strength, high-modulus, dense, thermally stable moldings has been studied in more detail and improved by using crystalline 1:1 salts of the monomers. Interrelationships between molding powder characteristics and molding conditions required to achieve optimum polymer properties were investigated. Typical properties of the moldings obtained from the salt of pyromellitic anhydride and 3,3'-diaminobenzidine were: density, 1.29 g/cc; diametral tensile strength, 10,700 psi; ultrasonic modulus, 1.3×10^6 psi; hardness, 80 Rockwell B; and thermal stability in air (at 0.5°C/min), 400°C. Quick TGA methods, applied to the salts for estimating the thermal stability of molded polymers, before actual polymerization and molding, have been developed. No problems associated with gas release are observed when molding conditions have been optimized.

INTRODUCTION

A continuing need exists for easier methods of molding intractable high-temperature polymers.

The feasibility of simultaneously polymerizing and molding equimolecular amounts of mechanically mixed powdered monomers to high temperature-stable heterocyclic polymer bodies by reactive hot-pressing has been demonstrated.^{1,2} Products made in this further investigation have high strength, modulus, density, and thermal stability, especially when prepared from 1:1 crystalline salt adducts of the monomers, newly developed for this purpose.

EXPERIMENTAL

Monomers

For a few indicated experiments, the anhydrides were purified by sublimation and the amines by recrystallization as reported earlier.^{3,4} Otherwise, the monomers were used as received: pyromellitic anhydride (PMDA) from Princeton Chemical Co., 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) from Gulf Oil Co., and 3,3'-diaminobenzidine (DAB) from Burdick and Jackson Co. 1,4,5,8-Naphthalenetetracar-

boxylic acid (NTCA), from Aldrich Chemical Co., was dissolved in 25 wt-% KOH in water, treated with activated carbon, filtered, treated with 5 wt-% KMnO_4 in water, heated to 90°C for 30 min, filtered, acidified, and precipitated with concentrated HCl, redissolved in dilute NaOH, treated with activated carbon, filtered, acidified, and precipitated with concentrated HCl, and filtered off and dried in vacuo.

Monomer Mixtures and Salts

Monomers were ballmilled together, or the DAB was ballmilled alone and then suspension-blended in cyclohexane with powdered, as-received PMDA for 15 min in a high-speed blender to yield, after solvent removal, monomer mixtures suitable for molding. Molecular monomer mixing and stoichiometry were optimized, with simultaneous anhydride hydrolysis and monomer purification, by preparing amorphous and crystalline 1:1 salts of the amine and acid monomers as illustrated as follows for the DAB-PMDA system. Crystalline salt was made by adding a solution of 54.5 g crude PMDA in 1200 ml hot distilled water, previously refluxed for 2 hr, to a N_2 -covered, vigorously stirred solution of 54.7 g crude DAB in a mixture of 1200 ml distilled water and 500 ml methanol, previously seeded with crushed orange salt crystals obtained from earlier trials. Resulting fine orange crystals were filtered off, rinsed with water and methanol, and dried in vacuo to give 111 g (95% yield) of 1:1 salt.

ANAL. Calcd for $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_8$: C, 56.41; H, 4.30; N, 11.96. Found: C, 56.18; H, 4.37; N, 11.77 (C, 56.32; H, 4.22; N, 11.84 for tan amorphous 1:1 salt which precipitated when more concentrated unseeded solutions of the amine and acid were added together in a similar manner).

1:1 Salts of the BTDA-DAB and NTCA-DAB monomer systems, also having an almost theoretical elemental content, were prepared by similar methods.

Molding Procedure

A hot-pressing unit with automatic control and recording of temperature and pressure was used as detailed elsewhere.^{1,2,5,6} Indispensable features are the ability to apply a constant pressure regardless of displacement in the sample, to raise the temperature of the sample at a linear or other programmed rate, and, particularly important, to conduct the reactive hot-pressing in a stainless steel die lined with a pure porous graphite which has been shown to be necessary for successful gas escape. All results were obtained on samples heated at various linear rates up to a top temperature of 450°C , held at this temperature for 1 hr, and then the heating and pressure application were removed. Moldings $\frac{3}{4}$ in. in diameter and $\sim\frac{1}{2}$ in. long were produced.

Testing Procedures

Thermogravimetric analyses (TGA) were performed with a du Pont Model 950 analyzer. For TGA of monomer mixtures and salts, useful for

predetermining moldability and molding conditions, the sample cup was covered with an inverted cup to minimize weight loss by monomer sublimation or dusting.

Tensile strength of molded polymers was determined by using the diametral method^{7,8} directly on the cylindrical moldings, loaded across the diameter in a special test rig in an Instron Universal Tester. Values, σ , obtained by using the equation

$$\sigma = 2P/\pi dt$$

where P = applied load, lb, d = diameter, inches, and t = sample thickness, inches, were doubled to correspond more nearly with bend test values.⁸

Longitudinal moduli of elasticity were measured with a Sperry Rand UM715 Ultrasound Reflectoscope, the output of which was read on a Tektronix oscilloscope to improve resolution and attain accuracy to within 1%. The measurements, checked against calibration standards, were made at 10 MHz.

Densities of good nonporous, molded specimens were accurately measured by the Archimedes displacement method in water. Porous specimens (less important) were checked by geometric methods.

Knoop microhardness (100 g load), using a Tukon tester, was used for measuring hardness of samples which were too brittle for measuring Rockwell B macrohardness. Otherwise, the latter was used.

RESULTS AND DISCUSSION

TGA of Starting Powders

In the early work^{1,2} on reactive hot-pressing, monomers were mixed by ballmilling or by blending in cyclohexane. This led to a need to determine how intimate the monomers were mixed and what would be the critical reaction temperature regions. The more intimate the mix, the more nearly the TGA should approach the theoretical. This is shown for PMDA-DAB in Figure 1. The theoretical weight loss ($6\text{H}_2\text{O}$) is indicated; the 1:1 amorphous adduct performs near to expectation, indicating a good cyclized product, whereas the other mixtures behave poorly and will lead to inferior moldings. The weight loss for the orange crystalline (checked by x-ray powder diffraction) 1:1 adduct (Fig. 2) is quite different but more regular. The salt, rather stable in N_2 , decomposes initially and rapidly at 250°C ; the loss is near theoretical, and the choice of top molding temperature at 450°C appears to be good. In air, no difference due to oxidative loss is observed (again significant stability) until 500°C for this heating rate. An immediate evaluation of the thermal stability of the product is achieved ($\sim 500^\circ\text{C}$ for this rate of heating) without separately preparing the cyclized polymer.

Figure 3 illustrates the different TGA behavior of BTDA-DAB as a milled mixture and as the 1:1 salt. Polymerization of the salt is com-

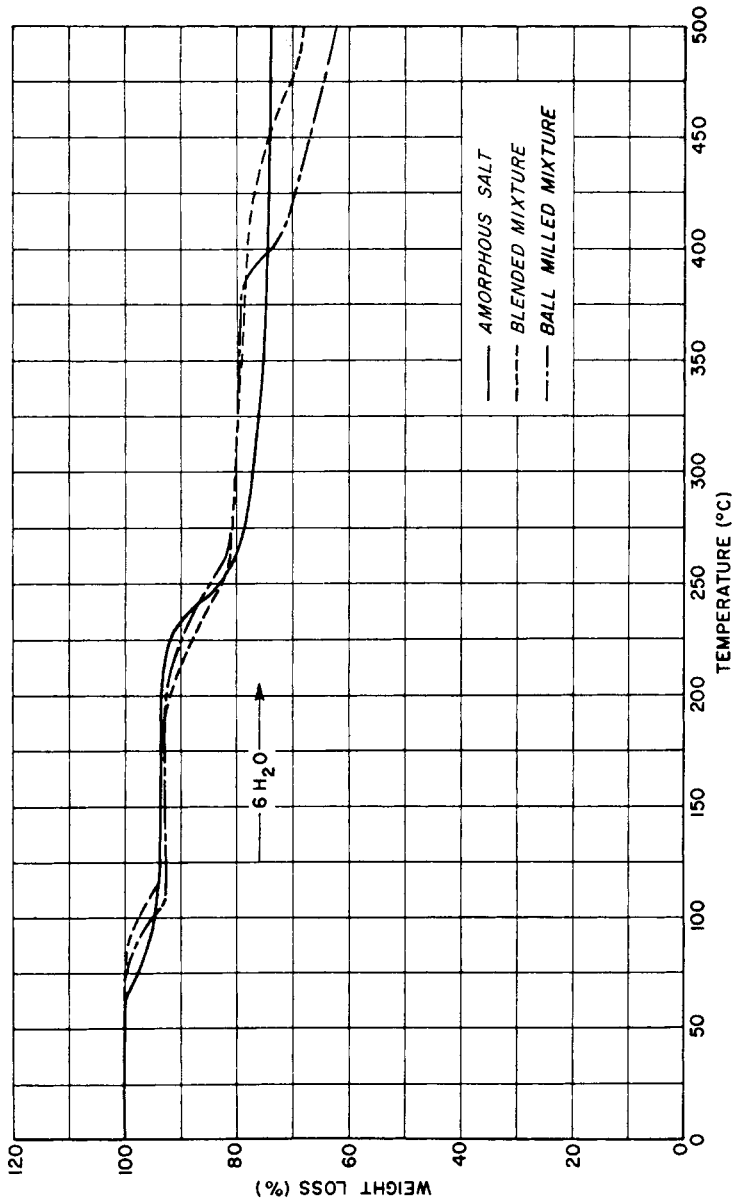


Fig. 1. Thermogravimetric (5°C/min, N₂) analysis of three 1:1 PMDA-DAB compositions.

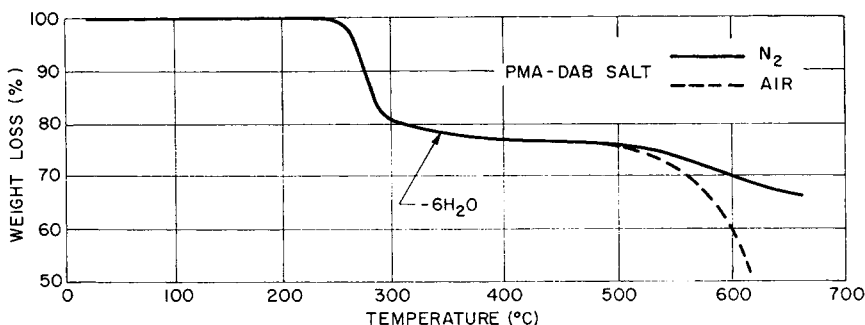


Fig. 2. TGA (5°C/min, N₂, air) of orange, crystalline PMA-DAB salt.

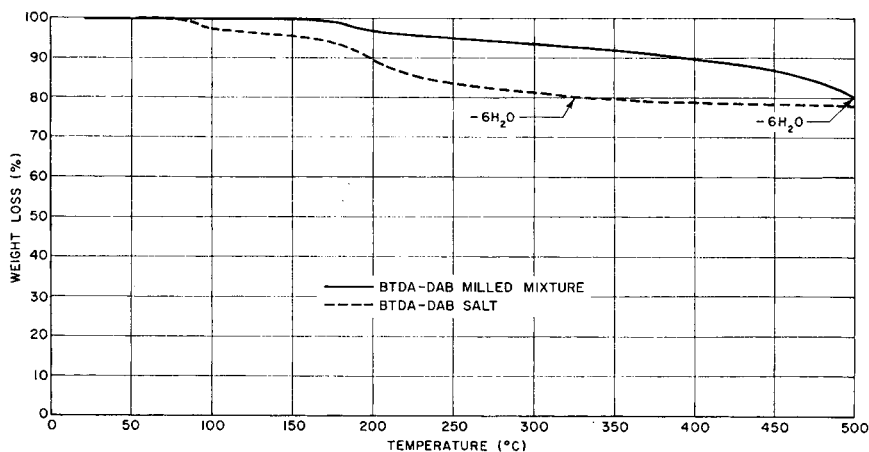


Fig. 3. TGA (5°C/min, N₂) of BTDA-DAB molding compositions.

pleted at lower temperatures, around 400°C, due to the molecular scale of mixing. The flat region between 400° and 500°C indicates that good thermally stable moldings would be obtained at 450°C. The milled mixture still shows mass loss at this temperature and should produce moldings with poorer properties.

Figure 4 illustrates the good TGA behavior of the purple crystalline (checked by x-ray powder diffraction) NTCA-DAB salt. The theoretical weight loss occurs at 450°C with a stable flat region between 450° and 550°C.

The TGA behavior of a molecule containing all the functional groups necessary for a high-temperature polymer, namely, 4,5-diaminonaphthalic anhydride,^{9,10} appears in Figure 5. A short decomposition region is seen between 300° and 425°C with theoretical weight loss at 450°C. However, no flat region seems to be present for this particular monomer. A few samples were, however, molded around 450°C with this material.

Figure 6 illustrates an imide system. The TGA in both air and nitrogen at 5°C/min is shown. Even the finely divided polymer material, as

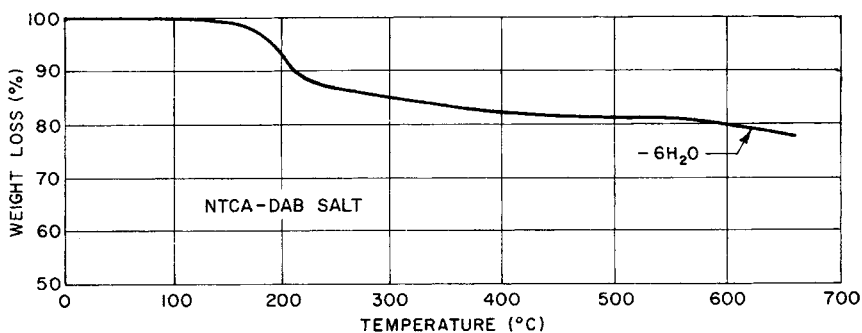


Fig. 4. TGA (5°C/min, N₂) of purple, crystalline salt of NTCA-DAB.

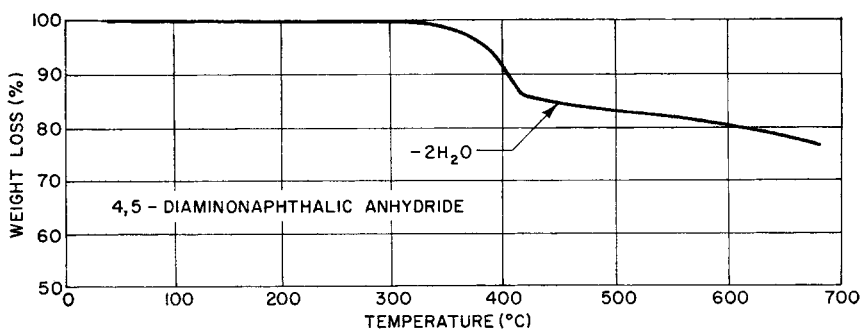


Fig. 5. TGA (5°C/min, N₂) of olive-green, crystalline DANA.

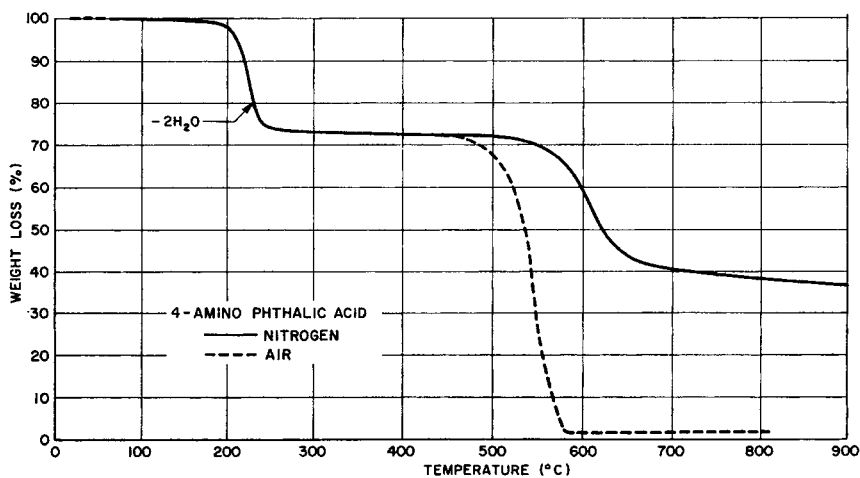


Fig. 6. TGA (5°C/min, N₂ and air) of 4-aminophthalic acid.

produced in the TGA apparatus, appears stable in air to 450°C with this rate of rise of temperature.

Molding Performance

Figure 7 illustrates a typical shrinkage-temperature-time sequence of PMDA-DAB ballmilled and heated at 3.8°C/min at 4000 psi. Several regions of rapid shrinkage can be observed. The shrinkage regions around 100° and 250°C correspond to weight losses indicated by TGA. The intermediate rapid region at 150°C may coincide with the lowered melting point of DAB, normally 175°C. The region at about 250°C could also correspond with the lowered melting point of PMDA, normally 275°C.

In order to optimize the molding process, a data chart, illustrated in Figure 8, was constructed. Both rates of rise of temperature and applied constant pressure were varied within the bounds indicated as final densities were plotted to detect an optimum between rate of temperature rise and applied pressure, for the highest density, assuming that the highest density was desirable. A complex interaction between the two parameters was observed. Because polymerization and molding are occurring simultaneously, the control of both pressure (primarily affecting densification) and rate of temperature rise (primarily affecting the rate of polymerization) is very important. Too high a pressure or too rapid a heating rate causes the material to squeeze out of the die cavity, whereas the opposite conditions cause insufficient densification. The optimum conditions appear to allow the polymerization to proceed fairly rapidly, possibly with incipient melting of monomers or low oligomers plasticizing the mixture for densification.

Under the best molding conditions, Figure 8, densities as high as 1.27 g/cc were obtained in samples from ballmilled mixtures. In addition, as indicated by the filled circles, high strength and modulus values were obtained from most of the dense specimens; lower-density specimens were variously cracked or delaminated, had open porosity or other internal defects, and had poor, if any, strength. However, the best molding region was somewhat indistinct; and the samples, mottled in appearance, with varying hardness in the different colored areas, indicated that much more intimate mixing was desirable.

Using blended mixtures, it was immediately apparent that polymerization was occurring more rapidly and uniformly. The optimum molding conditions are illustrated in Figure 9. The range of temperature required was as before; but, as expected, the pressure required was somewhat higher. The more intimate mixture polymerizes more rapidly, therefore, more pressure must be applied to densify the intractable polymer as it forms. A larger good molding region is observed. However, cracked specimens occurred within the best molding region. As before, the highest density specimens, up to 1.28 g/cc, usually manifested the best strength and modulus.

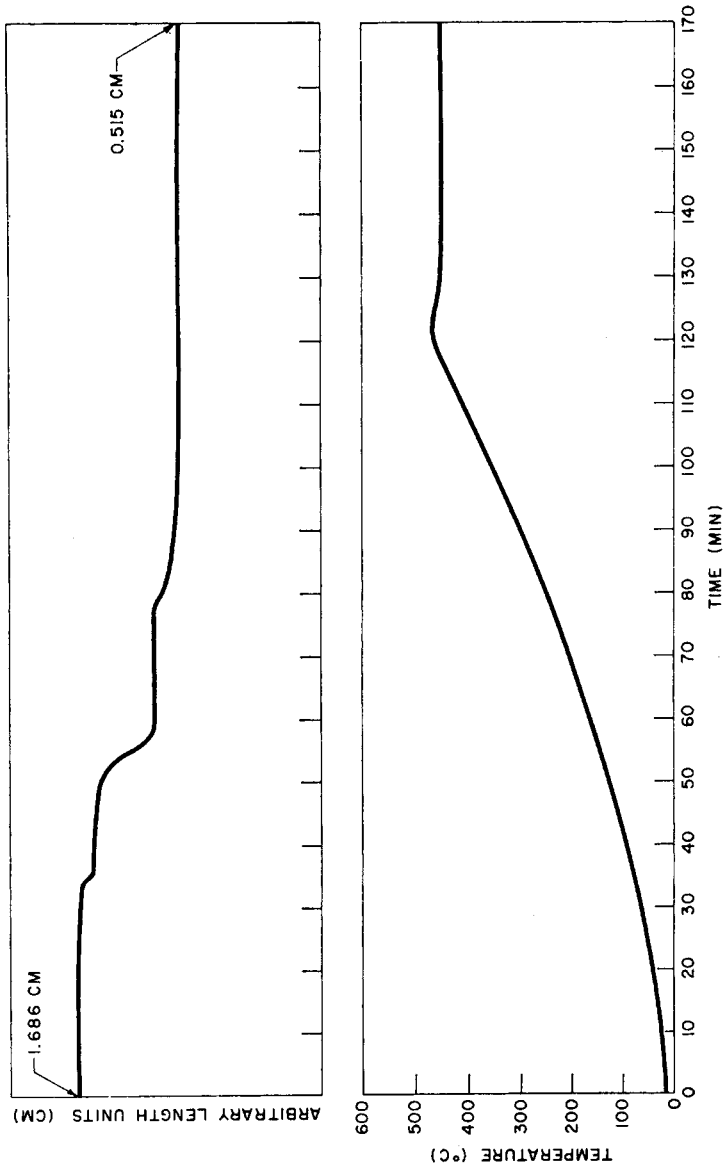


Fig. 7. Typical shrinkage behavior of milled PMDA-DAB at constant pressure.

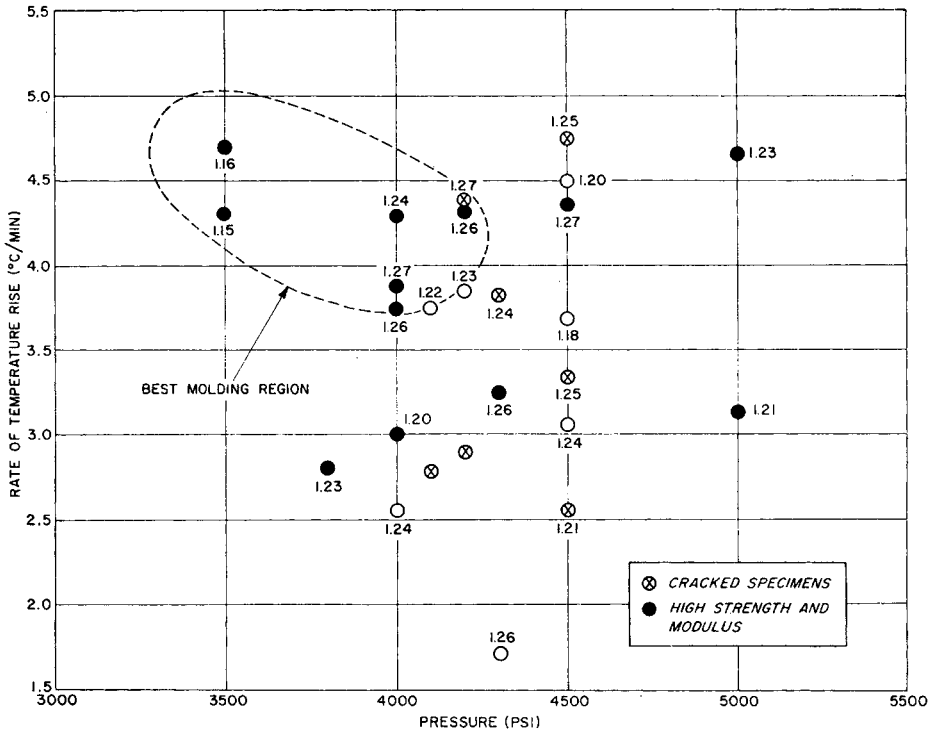


Fig. 8. Densities achieved in samples from milled PMDA-DAB as a function of applied constant pressure and heating rate (up to 450°C held for 1 hr).

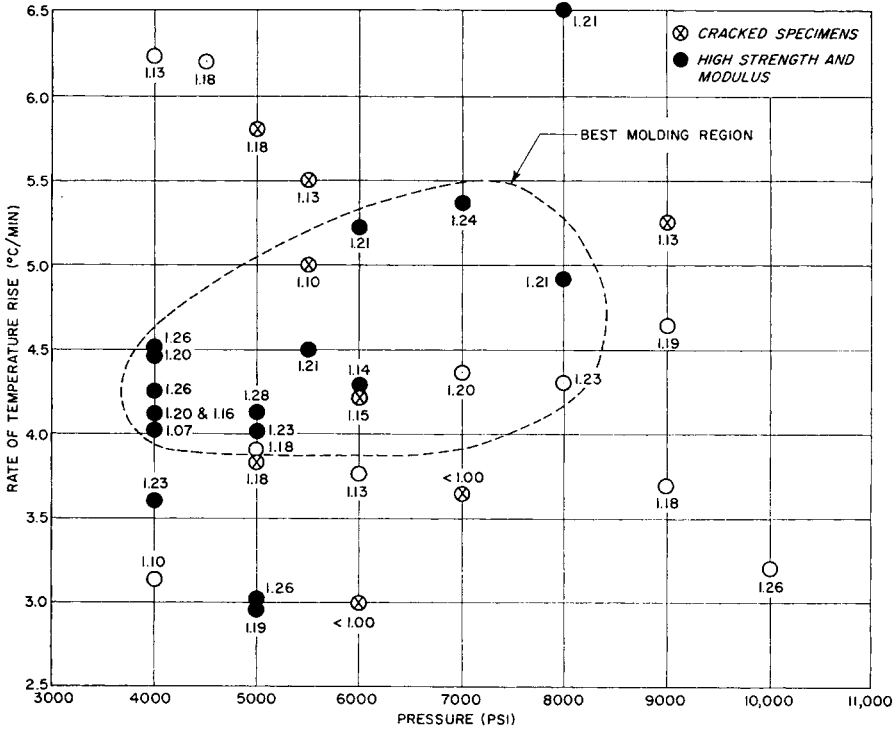


Fig. 9. Densities achieved in samples from blended PMDA-DAB as a function of applied constant pressure and heating rate (up to 450°C, held for 1 hr).

TABLE I
Summary of the Molding Conditions and Properties of Better Samples of PMDA + DAB

Method of mixing	Rate of rise of temp. up to 450°C, °C/min	Applied pressure, psi	Density, g/cc	Strength equivalent tensile ^a	Hardness Knoop (100-g load)	Modulus, ^b psi × 10 ⁶	TGA ^c (0.5°C/min in air), °C
Milled	4.35	4,000	1.24	10,200	55		300
Milled	4.3	3,500	1.15	21,000	34		
Milled	4.7	5,000	1.23	19,000	58		300
Milled	3.1	5,000	1.21		26	2.6	300
Milled	3.9	4,000	1.27	11,000	39		300
Milled	3.75	4,000	1.26		23	1.7	300
Blended	4.15	4,000	1.20	14,500			350
Blended	2.9	5,000	1.19	11,800	38		350
Blended	3.9	5,000	1.18		35	2.8	350
Blended	6.85	4,000	1.21	12,500	37		350
Blended	6.5	8,000	1.21	10,700	32	0.25 ^c	350
Blended	4.9	8,000	1.21	12,600	15	0.29 ^c	350
Blended	2.9	5,000	1.19	12,100			350
Blended	3.0	5,000	1.26	13,000			350

Amorphous 1:1 salt	5.8	5,000	1.25	19,800	40	1.6	350
Amorphous 1:1 salt	7.0	4,000	1.26	16,300	50	1.12	350
Amorphous 1:1 salt	6.2	4,500	1.27	17,300	43	1.16	390
Amorphous 1:1 salt	3.5	6,300	1.29	14,300		1.13	375
Amorphous 1:1 salt	3.1	6,500	1.30	15,600	45	1.12	375
Amorphous 1:1 salt	2.7	6,750	1.30	15,200	43	1.01	375
Amorphous 1:1 salt	4.25	7,300	1.29	14,600	48	2.00	375
Orange crystal, 1:1 salt	5.0	7,500	1.28	11,500	88 ^d	1.1	410
Orange crystal, 1:1 salt	5.0	7,500	1.28	5,100	17		410
Orange crystal, 1:1 salt	5.0	7,500	1.32	11,500	52 80 ^d	1.1	410

^a By the diametral method.

^b Sonic method.

^c Temperature at which weight loss starts.

^d Macrohardness Rockwell B.

^e Anomalously low values (no explanation).

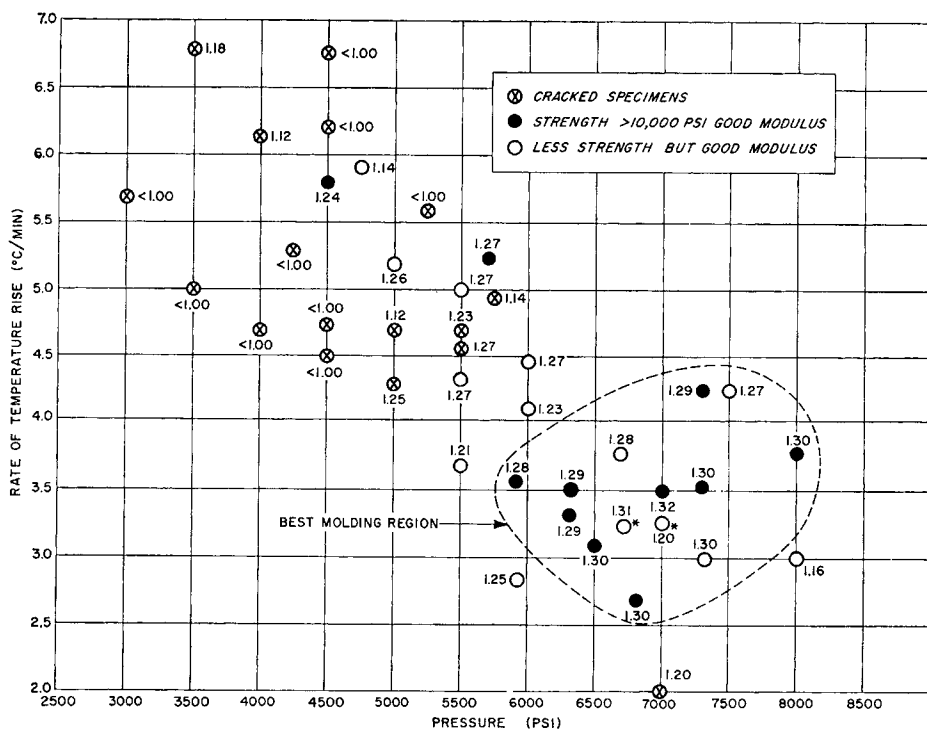


Fig. 10. Densities achieved in samples from second batch of amorphous PMA-DAB "salt" as a function of applied constant pressure and heating rate (up to 450°C, held for 1 hr).

The molding of amorphous 1:1 PMDA-DAB adduret is shown in Figure 10. The molded specimens appeared very uniform; and, most importantly, the TGA, detailed later, showed a superior thermal stability in air. Microhardness results, randomly taken over the specimen, also were much more uniform than from moldings derived from either the milled or blended mixtures.

The effect upon the shape of the shrinkage curve of going from milled to blended to salt mixtures was to smooth out the shape of the shrinkage curve so that the sharp periods of shrinkage were greatly reduced. Moreover, densities achieved in this case were much higher, as can be seen, and other good properties as given in Table I were obtained. This may be related to the lesser chance that gas may be entrapped because of the slower, more uniform shrinkage, and also to the more intimate mixing and, therefore, more complete and linear polymer formation. The crystalline 1:1 salt showed an improved behavior again, as was expected from the TGA. Total shrinkage is greatly reduced; monomers in the salt are already tightly packed with a density of 1.38 g/cc. This system was not completely optimized but, nevertheless (Table I), good reproducible properties were obtained.

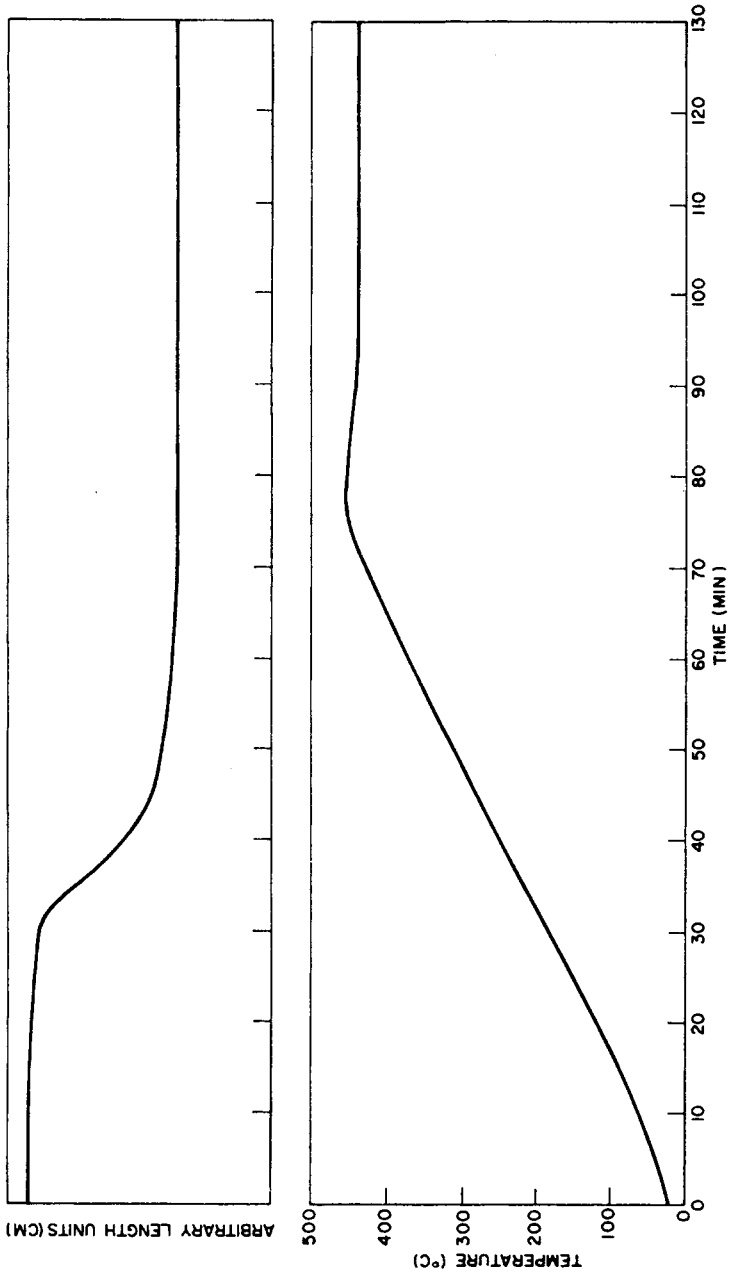


Fig. 11. Typical shrinkage behavior of orange, crystalline 1:1 salt of PMA-DAB at constant pressure.

As might be expected from the tightly bonded structure of the orange salt (high green density, etc.) and the rapid polymerization rate at 250–300°C (Fig. 2), higher pressure is necessary (7,500 psi) and faster rates of rise of temperature (4.5°C/min). Densities of the same order as attained with the amorphous salt were achieved. All samples molded from this salt showed as desirable slow, uniform shrinkage as depicted in Figure 11. The period of maximum shrinkage occurred around 250°C, which agrees with the onset of rapid polymerization as depicted in Figure 2.

The properties of samples molded by this method from this kind of salt of various monomer combinations were in every way superior to specimens made from milled, blended, or amorphous salt material. Elemental content of the pyrrone polymer produced on molding the crystalline 1:1 PMDA–DAB by reactive hot-pressing is much closer to theory than that of the same polymer made by conventional prepolymer methods:

ANAL. Calcd for $C_{32}H_8N_4O_2$ (%): C, 73.33; H, 2.22; N, 15.56. Found: C, 73.50, 73.01; H, 4.05, 3.83; N, 15.46, 15.70 (Galbraith Laboratories).

The pressure ranges used here are comparable to those used in other molding studies where prepolymers or oligomers are utilized.¹¹

Although good results were obtained with commercial monomers, it was, nevertheless, of some interest to see if purified materials would give better results. For a blended pure PMDA–pure DAB mix, it was readily apparent that polymerization was much slower than for the impure grade, resulting in the need for lower pressure or slower rates of rise of temperature to prevent squeezing the much more fluid mix from the die. These conditions are less desirable.

To follow up, we briefly examined product densities as a function of monomer purity with the following blended mixes molded arbitrarily at 4000 psi and about 4.0°C/min:

Pure PMDA and pure DAB	1.26 g/cc
Pure PMDA and impure DAB	1.23 g/cc
Impure PMDA and pure DAB	1.16 g/cc
Impure PMDA and impure DAB	1.07 g/cc

Since a lower density reflects faster viscosity buildup and thus faster polymerization, these results indicate that impurities catalyze polymerization. The conditions were not optimal for each mix, but the mixes were prepared to minimize the interference of purely physical effects such as particle size, etc. It is clear that both the commercial grades of DAB and PMDA have contaminants which promote polymerization. In case of PMDA, this is almost certainly the free acid form, and this is consistent with previous reports of acid catalysis of polymerization and cyclization in the formation of polyheterocyclics^{12,13,14} such as using polyphosphoric acid as a solvent and catalyst or organosulfonic acids as catalytic additives.¹⁵

The need to study effects of purity was greatly reduced when the 1:1 salts were discovered. Purification was achieved during the preparation,

TABLE II
Significant Molding Conditions and Properties of the BTDA-DAB and NTCA-DAB^a Systems

Composition	Method of mixing	Rate of rise of temp. up to 450°C, °C/min	Applied pressure, psi	Density, g/cc	Strength equivalent tensile, ^b psi	Hardness Knoop (100-g load)	Modulus ^c psi × 10 ⁶	TGA ^d (0.5°C/min in air), °C
BTDA + DAB	blended in cyclohexane	4.4	4,000	1.3e			0.9	360
BTDA + DAB	blended in cyclohexane	3.3	4,000	1.14			0.9	400
BTDA + DAB	blended in cyclohexane	2.4	Varied	1.20	14,600			400
BTDA + DAB ^e	cyclohexane	5.9	Varied	1.17	4,800	19		390
Pure NTCA + DAB	amorphous salt	4.0	4,500	1.37	1,400	28	1.2	460
Pure NTCA + DAB	amorphous salt	6.0	4,500	1.37	3,600	26		460
Pure NTCA + DAB	amorphous salt	4.0	5,500	1.35	3,100	31		460
Pure NTCA + DAB	amorphous salt	6.4	5,500	1.33	3,000	30		460
Pure NTCA + DAB	crystalline salt	3.0	5,800	1.35	2,700			460
Pure NTCA + DAB	crystalline salt	3.2	5,800	1.33	1,400		0.64	460

^a NTCA = 1,4,5,8-naphthalenetetracarboxylic acid.

^b By the diametral method.

^c Ultrasonic method.

^d Temperature at which degradation starts.

^e Strongest BTDA + DAB specimen; allowed mix to stand in air picking up water vapor to catalyze polymerization.

as indicated by good analyses. Moreover, PMDA is present as the free acid, obviating the need for acidic impurities or added catalysts.

A range of other variously prepared materials were molded without optimization of conditions; some results on these are given in Table II.

TGA of Moldings

Of most interest is the thermal stability of moldings in air, although some data in nitrogen have also been obtained. Thermal stability of materials in air are commonly measured at up to $10^{\circ}\text{C}/\text{min}$, for example, as reported in the literature. However, *such results bear no absolute relation to useful applications where materials are going to be held at elevated temperatures for long periods of time.*

Figure 12, for example, shows a representative TGA curve for a PMDA-DAB molding from a milled mixture with the highest tensile strength found, 21,000 psi. The upper curve at $10^{\circ}\text{C}/\text{min}$ suggests a thermal stability (i.e., no weight loss) to about 500°C for this material. A more realistic value, however, is obtained by measuring the TGA at $0.5^{\circ}\text{C}/\text{min}$ as shown in the lower curve with weight loss commencing at a little more than 300°C . With slow rates of rise of temperature, we were able to discriminate fairly easily between small differences in molded samples, whereas, with the fast rate of heating, most products appeared stable to near 500°C .

The progressive improvement in thermal stability, as the molding techniques improved and methods of mixing became more intimate, is

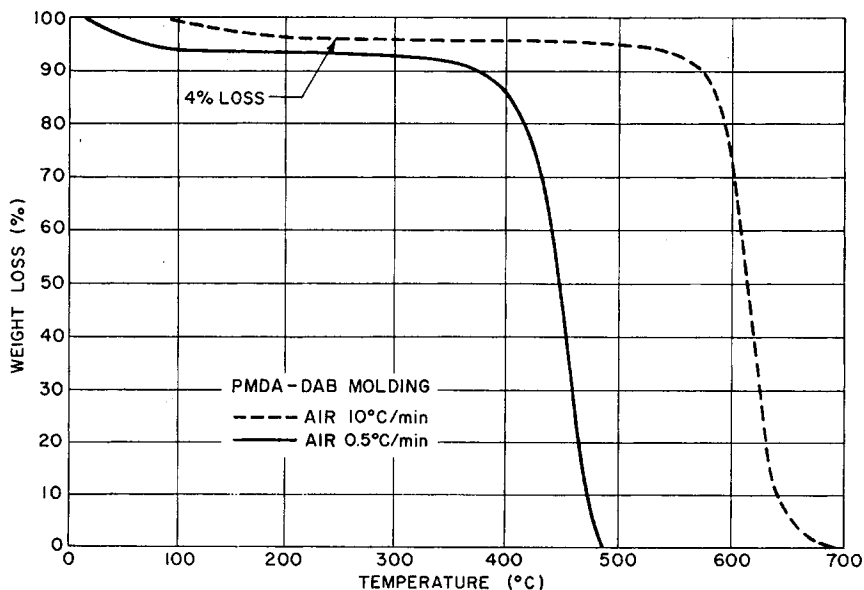


Fig. 12. TGA of a molding from milled PMDA-DAB done in air at $10^{\circ}\text{C}/\text{min}$ and $0.5^{\circ}\text{C}/\text{min}$, showing need for slower rate for meaningful interpretation.

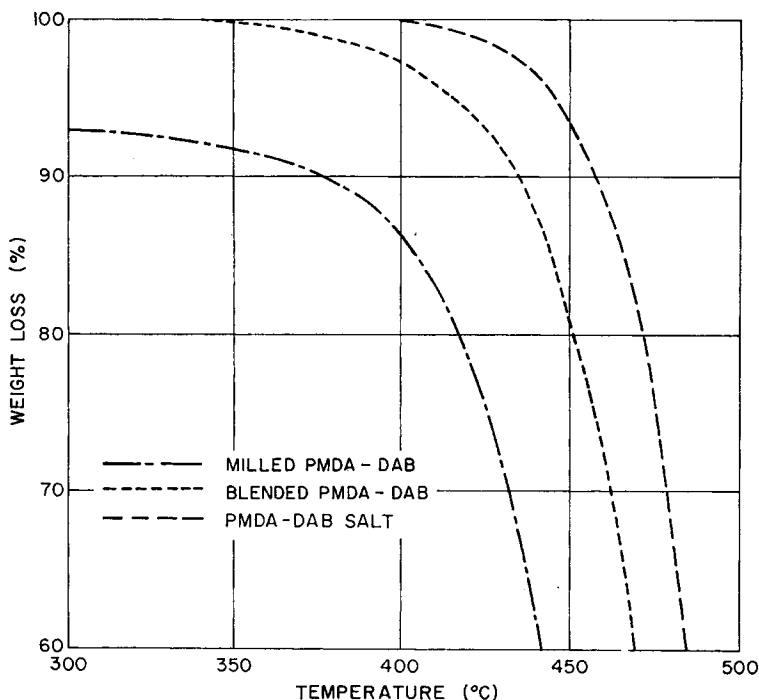


Fig. 13. TGA (air, 0.5°C/min) of variously prepared PMDA-DAB moldings.

shown enlarged in Figure 13. For a given method of mixing, thermal stability generally improved as the density increased, and Figure 13 shows results that were typical of the best for each particular method. The best stability is shown by moldings made from the 1:1 crystalline PMDA-DAB salt with stabilities to 400°C. The improvement doubtless is related to more perfect polymerization due to better monomer alignment and stoichiometry, as indicated by exceptionally good agreement of elemental analysis results with theory.

With milled and blended materials, the thermal stability was very irreproducible; but with the salt materials made under the optimum conditions, the TGA analysis was extremely reproducible.

A brief investigation was made of the effect of the top molding temperature on the thermal stability of moldings made with the crystalline salt. For three samples, molded identically, except that the samples were held for 1 hr at 450°, 500°, and 540°C, the air stability was 400°, 380°, and 360°C, indicating that 450°C was the best top temperature. Others¹¹ have used the 400-425°C region for oligomer starting materials. Table III shows similarly obtained air stability temperatures for other systems. At the low end of the thermal stability range were moldings made from aminophthalic acid, at 330°C. PMDA-TABP (tetraminobenzophenone) was stable to 350°C. This system should be superior to the PMDA-DAB

TABLE III
Thermal Stability in Air (0.5°C/min) of Moldings of Monomer Mixtures

Monomer mixture		Mixing method	Thermal stability, °C
Commercial PMDA	commercial DAB	milled	320
Pure aminophthalic acid		monomer	330
Commercial PMDA	commercial DAB	blended	350
Commercial PMDA ^a	pure TABP	salt	350
Commercial PMDA	commercial DAB	freeze-dried	350
Commercial PMDA	commercial DAB	blended	350
Commercial BTDA	commercial DAB	milled	360
Commercial BTDA	commercial DAB	blended	370
Pure PMDA	pure DAB	salt	380
Pure PMDA	pure DAB	blended	390
Pure BTDA	pure DAB	salt	390
Pure NTCDA	pure DAB	blended	400
Pure PMDA	pure DAB	freeze-dried	400
DANA ^b		single	400
		monomer	
Pure NTCDA	commercial DAB	blended	410
Commercial PMDA	commercial DAB	salt	410
Pure NTCDA	pure DAB	salt	460

^a TABP = 3,3',4,4'-tetraaminobenzophenone.

^b DANA = 4,5-diaminonaphthalic anhydride.

mixture with more work. Similar was the PMDA-TAB (tetraminobenzene), but here only the HCl salt of TAB was used. Milled commercial BTDA-commercial DAB was thermally more stable at 360°C than the equivalent PMDA-DAB, 320°C, as expected. Similarly, the stability at 370°C of commercial BTDA-commercial DAB, blended, was 20°C higher than the equivalent PMDA-DAB mix. For the pure amorphous BTDA-DAB salt, a 10°C increase was found over the equivalent PMDA-DAB salt. For milled and blended mixtures the thermal stability definitely increases with purity; salts gave the most thermally stable products. Particularly encouraging were the results for the pure NTCA-pure DAB blended mix giving molding stable to 400°C; for the equivalent crystalline salt, stability to as high as 460°C was seen, the highest of any molded high-temperature plastic made in this work.

Ultrasonic Modulus Results

Increasingly reproducibly high ultrasonic modulus values were achieved as work progressed. In many early specimens, it was not possible to measure modulus at all because of internal flaws. The range of modulus measured with each type of mixing is as follows:

Milled	1.7-2.8 × 10 ⁶ psi
Blended	1.0-2.8 × 10 ⁶ psi
Amorphous salt	0.9-4.2 × 10 ⁶ psi
Crystalline salt	1.0-1.2 × 10 ⁶ psi

It can be seen that the higher values measured increased as the method of mixing improved, reflecting much better internal bonding, while higher density reflected more perfect specimens. The values are generally higher than for pyrrones made by the oligomer route.¹¹

Results of the order of magnitude expected, with the limited amount of work possible, were obtained in other systems. For the BTDA-DAB system, a modulus of 0.9×10^6 psi was achieved; for the NTCA-DAB, 1.2×10^6 psi.

Hardness Results

Progressively more uniform hardness was achieved. Early samples made by milling showed great variations particularly from dark brown colored regions, where hardness was high and perhaps attributable to more crosslinking, to lighter orange colored areas where the hardness was lower. The milled samples showed a large variation in hardness both within single specimens and as a function of density. The Knoop hardness (100-g load) rose in good specimens from about 35 kg/mm² at a density of 1.15 g/cc to the highest values around 60 kg/mm² at a density of about 1.23 g/cc; hardness then dropped again to about 30 kg/mm² at a density of about 1.27 g/cc. A maximum in hardness versus density has been seen in all compositions. The better blended samples showed much less variation in hardness, both within single specimens and as a function of the density. The highest hardness values were, in this case, about 50 kg/mm² at a density of about 1.23 g/cc. At low and high densities, hardness values around 35 kg/mm² were observed.

With specimens made from the amorphous salt, a very large variation in hardness ranging between 20 and 50 kg/mm² was seen with much less apparent density dependence. It was found that hardness was roughly proportional to strength for samples that were strength tested. However, no close relationship between hardness and density or strength was unearthed, and hardness cannot, as far as we can see at present, be used as a "quality control" parameter. This may be partly because microhardness tests too small a region of nonuniform pyrrone moldings. In the crystalline salt-derived specimens, hardness was much more reproducible, and in these cases, macrohardness tests (Rockwell B) could be carried out on the less brittle samples; it may be possible to use this for NDT.

It is interesting to note that these plastics appear to be the hardest unfilled plastics ever made. A value of 100 on the Rockwell E scale, commonly used for plastic materials, corresponds to 70 on the Rockwell B. The range of 70-100 Rockwell B is typical of high-temperature stainless steels and hardened titanium alloys. Special applications, i.e., for bearings, etc., may arise using this particular property of pyrrones.

For the BTDA-DAB system, a range of Knoop hardness between 14 and 36 kg/mm² (100 g load) was seen. For the NTCA-DAB mixture, rather reproducible hardness, between 21 and 39 kg/mm², were achieved.

Diametral Strength

Diametral tensile strengths followed a similar pattern to the other physical properties measured. Increasing reproducibility was achieved, but sometimes at the expense of less high values. For example, the highest tensile strength found during the whole work period was 21,000 psi on a sample of milled PMDA-DAB; but this molding composition often gave other samples of very low density and strength. Blended materials gave more reproducibility in strength, but samples generally reached strengths of only about 15,000 psi. Improvements were obtained with the amorphous salt starting material; the highest value achieved was 19,800 psi.

For the crystalline salt, the highest value was 11,500 psi; but offsetting this is much higher thermostability, which is of paramount importance. Strength results are summarized in Tables I and II. The increasing uniformity and reproducibility of strength results again reflect a more uniform, more linear polymer formation. Better reproducibility, even at the expense of slightly lower upper tensile strengths, is clearly more desirable in any engineering application. For the later specimens, it was apparent that tensile strength was related to the measured modulus, i.e., as the modulus increased so also did the tensile strength. Again, a nondestructive test may be available.

For each composition, again an optimum strength-density relationship was confirmed. The general quality of specimens of anomalously high density was poor, believed due to polymer degradation.

A high-strength molding, 14,600 psi, was obtained from BTDA-DAB. This was a particularly interesting result because generally during the molding of the BTDA-DAB composition, polymerization of the purified starting materials appeared very slow so that squeezing out of the die occurred at quite low pressures. With the discovery that polymerization in the PMDA-DAB system was influenced by the presence of acid, the BTDA-DAB composition was allowed to stand in the open air for several days, to pick up water. The molding behavior was found to be completely different, producing specimens that were much superior. Acid catalysis of polymerization must be occurring. Work was very limited with the very thermostable NTCA-DAB system^{12,13} because of an inadequate supply of high-quality NTCA. The best strength, 4800 psi, was obtained with an amorphous 1:1 salt of these monomers.

Coefficient of Thermal Expansion

A single molding from the PMDA-DAB crystalline 1:1 salt gave the following values for the coefficient of thermal expansion: 0-150°C, $2.1 \times 10^{-5}/^{\circ}\text{C}$; 150°-400°C, $3.8 \times 10^{-5}/^{\circ}\text{C}$.

Infrared Absorption

The infrared absorption spectrum of a pyrrone molded product, made under optimum conditions from the PMDA-DAB crystalline salt, dispersed

in KBr, was essentially identical to that reported¹⁶ for a film cured from a conventionally cast prepolymer.

CONCLUSIONS

Aromatic tetraamine and tetraacid (or anhydride) monomers can be milled, blended, or converted to 1:1 salt adducts and reactively hot-pressed to pyrrone moldings. This result is potentially applicable to other high-temperature systems including new, cheaper polyfunctional monomer types.

Estimates of necessary molding conditions, especially the top molding temperature, can be obtained by thermogravimetric analysis on the starting powders. But, nevertheless, very close investigation of pressure/temperature parameters is needed to optimize the physical properties of the finished moldings.

Water loss arising from condensation reactions has not been observed to cause any problems in molding when porous linings are used in the pressing dies. Water appears to diffuse readily through pyrrone polymers.¹⁷ The physical properties (strength, modulus, hardness, etc.) generally improve with density as long as no polymer degradation has occurred. Modulus and hardness may be usable as N.D.T. Acidic monomers or impurities appear to enhance the rate of polymerization.

The most intimate molecular mixing, as afforded through the use of amorphous or crystalline salts of the monomers, increases the rate of polymerization and improves the thermal stability and reproducibility of the properties of the resulting moldings.

Typical physical properties attainable for the PMDA-DAB pyrrone were: density, 1.29 g/cc; diametral tensile strength, 10,700 psi; ultrasonic modulus, 1.3×10^6 psi; hardness, 80 Rockwell B; and thermal stability in air (at 0.5°C/min), 400°C. However, further work will almost certainly improve these values.

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