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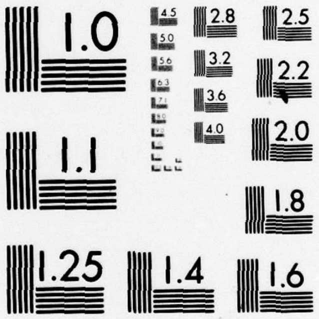

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The processing conditions expected to optimize interactions at a molecular level between poly(bisbenzimidazobenzophenanthroline) (BBB) and polybenzimidazole (PBI) have been investigated and the reaction products evolved under these conditions examined. Studies of the mechanical properties and the morphology indicate that binary interactions between BBB-BBB, PBI-PBI and BBB-PBI may all be occurring. The BBB-BBB interactions occur at temperatures greater than 500°C but PBI-PBI and BBB-PBI interactions arise at temperatures more than 100°C lower. Mass spectroscopic studies indicate that the principal reaction products in the presence of PBI are water and phenol whereas with BBB alone only water is evolved. Moreover in the mixture of BBB-PBI, phenol is evolved at lower temperatures than is the case with PBI alone. Possible end group reactions and reactions with partially cyclized rings, consistent with the observed evolution of water and phenol, are proposed for the improved processability of BBB in the presence of PBI. Further work to confirm the proposed reactions and the use of other additives to enhance these reactions is recommended.

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SUMMARY

An earlier study on processing BBB polymers(2) indicated that the incorporation of PBI as an additive in BBB was effective in yielding well consolidated specimens at temperatures some 100°C lower than for the pure BBB alone. The study reported here was undertaken to characterize the mechanisms which led to this improvement in processing and the properties which could be achieved.

A range of BBB-PBI compositions were hot pressed at temperatures between 300°C and 550°C at pressures of up to 20,000 psi. The mechanical properties of the samples were characterized using the three point bending test; the morphology of the samples was examined by optical and electron microscopy, x-ray diffraction and thermal analysis; and chemical changes were looked for using infra-red spectroscopy and mass spectroscopy.

The results obtained confirm the earlier observations on the improved processability of a BBB/PBI blend over that of the pure BBB. Furthermore, they show that the increase in properties is due to the development of interparticle bonds as opposed, for example, to the PBI flowing and acting as a binder. The possibility that all three binary interactions occur; namely, BBB-BBB, PBI-PBI and BBB-PBI, is suggested by the results.

The BBB-BBB reaction arises at temperatures greater than 500°C but the PBI-PBI, BBB-PBI interactions are generated at temperatures more than 100°C lower. The reaction products observed by mass spectroscopy, water and phenol in the case of PBI and water in the case of BBB, indicate that the most probable chemical processes are further end-group reactions in the polymers and/or reactions with partially cyclized rings. Of particular interest was the evolution of phenol at much lower temperatures in BBB/PBI blends than in the PBI alone.

Three principal areas are recommended for further study:

1. Modification of the end groups to ehnance processability of the pure BBB;

2. The possibility that the phenol released by the PBI is acting as a plasticizing agent;

3. The feasibility of suppressing reactions, such as decarboxylation, which could lead to a reduction in final properties.

SECTION I

INTRODUCTION

A. Historical

Continuing advances in aerospace missile and weapons technology have created a growing demand for high-temperature lightweight materials. In meeting such a demand, research chemists have synthesized a substantial number of new polymer systems, many of which indeed possess a remarkable degree of thermal stability. Among these are several highly condensed, heterocyclic polymers, including polyimidazopyrrolones (pyrrones) and poly (bisbenzimidazobenzophenanthrolines) (BBB and BBL), the so-called "ladder" polymers.

Regrettably, some of the most stable systems have proved to be difficult to process into useful forms by currently available fabricating techniques, even at prepolymer stages. Thus, although BBB polymers, for example, can be converted into continuous fibers(1), they defy shaping by conventional molding and extrusion processes.

In recognition of the problem, the Air Force Materials Laboratory (AFML) mounted an exploratory development effort directed toward finding new methods to process high Tg polymers of the BBB type. Celanese was selected in a competitive solicitation by AFML to carry out the project.

In the course of working on contract F33615-72-C-1642, Celanese investigators studied(2) the processability of different molecular weight BBB polymers by hot pressing the material, as-received or modified in various ways, under different conditions and characterizing the formed specimens by suitable analytical techniques. The BBB polymer can be densified without additives to over 94% of true density by hot pressing at about 500°C and 51,000 psi pressure, but the strength of the molded piece is low. Addition of BBB precursor monomers as binders and chopped BBB fibers as reinforcement yielded molded pieces with a slightly higher flexural strength, but the temperature and pressure conditions remained beyond those in industrial practice.

It was found toward the end of the contract period that the addition of polybenzimidazole (PBI) polymer was most effective in yielding a well-consolidated specimen at lower temperatures and pressures, but the contract ended before this observation could be fully explored. Among other accomplishments made under the contract, the Celanese researchers showed that the thermo-mechanical analysis (TMA) thermograms correlate with the processing temperature and state of purity of the BBB polymer and these are useful in identifying potential plasticizing additives. A procedure for fabricating fiber reinforced BBB matrix prepreg plies was partially developed but well-consolidated laminates were not achieved.

Subsequent to the completion of the AFML contract, Celanese, with its own corporate funds, supported additional experimental work to confirm and verify the observation that mixtures of BBB and PBI polymers are more tractable and processable than is BBB by itself. On the basis of these results and observations, Celanese Research Company submitted an unsolicited proposal to AFOSR to study the mechanism of the improved processability of BBB/PBI polymer alloys and related systems(3). This proposal was funded by AFOSR, Starting February 1, 1977 under Contract F49620-77-C-0046 and finishing January 31, 1979.

B. Technical

The hot pressing or pressure sintering of powdered metals, oxides or other nonpolymeric materials has been studied extensively.(4,5) The objective of such processes is to cause densification of the material at lower temperatures such that the grain growth, which occurs in standard low-pressure high-temperature sintering, is suppressed. The processes which occur in hot pressing, to a greater or lesser extent dependent on the system, can be categorized by:

1. Improvements in packing of the particles to give a close packed density - generally on the order of 60% of theoretical density.
2. Deformation of the particles.
3. Sintering in order to give a melding or blending together of individual particles by diffusive processes.

The densities (>90% of theoretical) that are achieved upon hot pressing pure BBB imply that, even in this case particle deformation occurs. However, the unsatisfactory property levels suggest that sintering effects are minimal.

Three molecular mechanisms can be suggested for the BBB plus additive system, all of which may be involved in promoting intra-particle deformation and/or interparticle consolidation. The first of these is a simple plasticization effect. Plasticization of commodity polymers is a well-known effect; for example, the processing of PVC with diethylphthalate plasticizer.(6) In this case, van der Waal's forces between chains of BBB would be reduced in the presence of the additive at the processing temperature, allowing one chain to slide with respect to the other. On returning to atmospheric conditions, no permanent change in the character of the bonding would be expected. The second mechanism again involves interchain effects. In this case, however, bonds may be broken on the side or end groups of the chains giving rise to crosslinking within or between chains on returning to normal temperatures, or further polymerization may occur. Thirdly, bonds in the backbone of the chains may be broken, leading to a greater flexibility of the chains. A similar mechanism was proposed by Bagley(7) to explain the processability of pyrrones at elevated temperatures. Again, the broken bonds will reform at room temperature, either within the BBB or between the BBB and the additive.

Evidently the latter two cases, in which bonds are broken and reformed, may occur in the BBB or additive separately. The earlier results(2) suggest a synergistic effect when the BBB and additive are processed together, lowering the temperature and pressure requirements for processing to occur.

C. Program

In a program proposed by Celanese(3), the work on this project was considered to fall into two broad categories: firstly, to confirm and expand the earlier results obtained at Celanese, with regard to the effect of processing conditions on properties, in order to define the conditions under which a maximum response can be obtained; and, secondly, to acquire a basic understanding of the microscopic changes which give rise to the improved processability. To this end, the work in the first year was directed at exploring a range of processing variables using the change in mechanical properties as a principal means of characterization. Changes in morphology were also followed using a variety of microscopical techniques. An interim report covering this aspect of the work was submitted to AFOSR in April 1978(8).

The second year of the project was directed toward studying the effects that occur at a molecular level, utilizing Fourier-Transform infrared spectroscopy (FTIR) and mass spectral analysis as a function of temperature.

D. Statement of Work

The work, as set forth in this report, was guided by the Statement of Work which is part of Contract F49620-77-C-0046:

1. The contractor will study the processability of intractable polymers, such as, but not limited to BBB, when alloyed with compatible polymers and monomers, such as, but not limited to PBI polymer and BBB monomers.

2. The contractor will utilize his capabilities and experience in the chemistry and physics of polymers to investigate the particulate form and character of polymer mixtures before hot pressing and correlate these with physical and mechanical properties after consolidation. To the extent that it is desirable, statistically designed experiments will be used to define critical variables. To examine physical changes which occur before and after consolidation, appropriate microscopic techniques will be employed.

3. The contractor will consider several approaches to establish the presence or absence of changes in chemical bonding occurring during processing. Fourier-Transform infrared spectroscopy, thermal-spectrometric analysis and electron-proton resonance analysis are representative of techniques expected to yield information relating to the chemical nature of the polymer alloys.

4. Interim reports detailing the progress of the work will be submitted on an annual basis. At the completion of the project a final scientific report will be delivered.

SECTION II

EXPERIMENTAL

A. Materials

Samples of BBB and PBI polymers were furnished by Celanese Research Company at no direct cost to the project. The BBB used had the identification 22323-30 and was in the form of coarse flakes. Two PBI samples were used with different inherent viscosities (I.V.). The lower I.V. sample (#21684-12) was in the form of a fine powder, while the other (#P915A) had a larger particle size in which agglomeration had occurred to form large lumps.

The coarse nature of both the BBB and the higher I.V. PBI made them unsuitable for blending as is and the particle size was reduced by cryogenic grinding using a Mikro-Pulverizer hammer mill. The grinding procedure used was to pre-cool both the polymer and the mill with liquid nitrogen and then to feed a mixture of polymer and liquid nitrogen slowly into the grinder. Two passes were made. The first pass used a 20-mil herring bone screen, the second, a 10-mil screen. After grinding, the polymer was vacuum dried at 150°C for 12 hours.

The polymers were characterized for I.V. and surface area before and after grinding (Table I). The I.V. was measured in 97% H_2SO_4 using a concentration of 0.2% for the BBB and 0.4% for the PBI. Specific surface areas were measured by the BET method using a Quantisorb Surface Area Analyzer. Particle size analysis was carried out on a Quantimet Image Analyzer using the longest dimension of each particle for characterization. Apparent and tap densities were also measured using methods similar to the ASTM standard Methods B417 and B527. These results are also listed in Table I.

The high surface area, large particle size and low apparent density value, taken together, suggest that the BBB powder particles are highly porous and hence, the change in surface areas during grinding, could be due to compaction of the particles. Scanning and transmission electron microscopy (SEM and TEM) of the untreated BBB also indicate that this sample is very porous (Figures 1a and 1b). This may be deduced, for example, in Figure 1b, where the white areas are voids, the dark areas BBB.

TABLE I

CHARACTERIZATION OF POLYMER POWDERS USED FOR BBB/PBI BLENDS

Polymer	Lot #	Inherent Viscosity (dl/g) As Rec'd	Inherent Viscosity (dl/g) Powdered	Surface Area m^2/g As Rec'd	Surface Area m^2/g Powdered	Particle Size mm	Powder Density g/cc Apprt	Powder Density g/cc Tap
BBB	22323-30	2.32	2.26	15.2	8.3	0.06*	0.20	0.27
PBI	P915A	0.90	0.93	0.22	0.24	0.02	0.59	0.84
PBI	21684-12	0.59	-	8.5	-	0.01	0.48	0.71
BBB/PBI Coppt.	26085-12	-	-	-	-	0.047*		

*Very broad range of sizes.

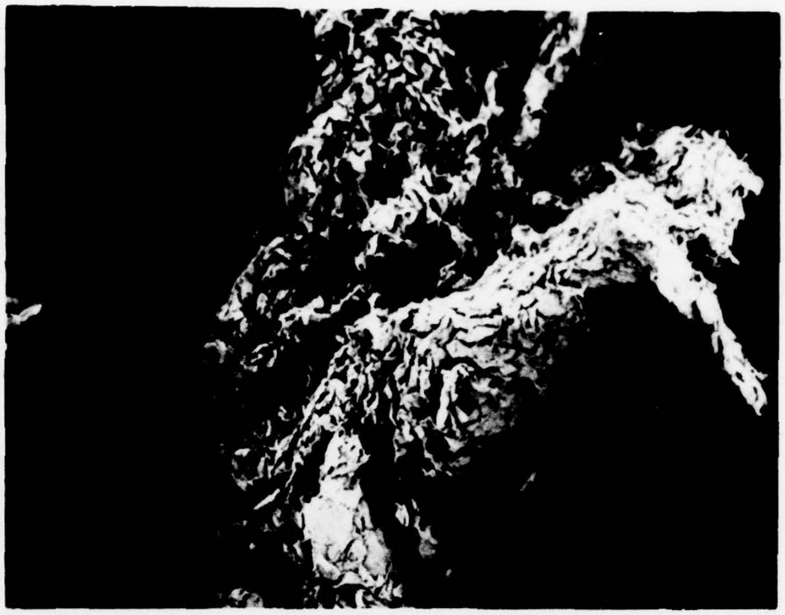


Fig. 1a. (200X) SEM: BBB Polymer Particle

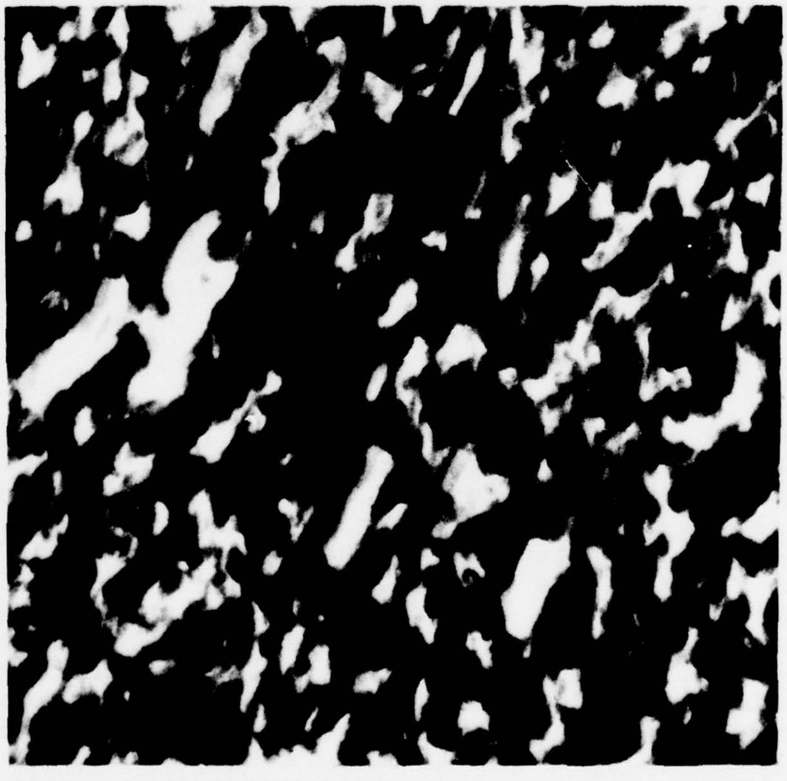


Fig. 1b. (18,400X) TEM: Thin Section BBB Polymer Particle

The low surface area of the 0.90 I.V. PBI and the scanning electron micrograph (Figure 2a) show that the particles of this polymer are much more compact. The small change in I.V. on grinding is not considered to be significant. The 0.59 I.V. material, however, again has a somewhat higher surface area indicating a porous sample. This too is indicated by the SEM (Figure 3a). Transmission electron micrographs of these two powders (Figures 2b and 3b) show the 0.90 I.V. material to be featureless, whereas the 0.59 I.V. polymer has a highly nodular appearance. This probably arises from the fact that, by x-ray diffraction, the lower I.V. material appears to be quite crystalline.

Only particle size was measured for the co-precipitated materials and this was in the same range as that of the other materials. Optical microscopic examination of the co-precipitate (Figure 4) showed that the particles were quite dense.

B. Mixing

Dry blends of the powders were prepared by tumbling a mixture of the component polymers for several hours. The co-precipitated material was prepared by dissolving 8 gms of BBB and 2 gms of PBI in 1000 mls. of 100% H_2SO_4 under nitrogen at room temperature for 5 hours with constant stirring. After solution of the polymers, 3,000 ml. of methanol was then added slowly with constant agitation to the mixture surrounded by a cold water bath. The precipitated BBB/PBI blend was filtered and washed successively with dilute ammonium hydroxide, water and methanol. The fine particles were dried in air for 72 hours and then under vacuum for 5 hours at 100°C. A yield of 9.5 gms of the blend was obtained.

C. Pressing and Testing

The samples were prepared as 1 inch discs, about 0.05 inch thick, by vacuum hot pressing in the Astropress. With either the blended powder or the co-precipitate, 0.875 gms of the mixture were loaded into a one-inch diameter single acting die. To avoid problems of the discs sticking to the die, the die surfaces were sprayed with Freekote - a mold release agent. The mold was then placed in the press and a load of 6,000 lbs. applied while the sample heated up to the desired temperature. When this temperature was reached, the load was increased to the predetermined value and held for the desired time. The sample was then cooled, under pressure, to about 275°C before being removed from the press.

Fig. 2a. (1000X) SEM: 0.9 I.V. PBI

Fig. 2b. (7000X) TEM: 0.9 I.V. PBI

Fig. 3a. (1000X) SEM: 0.59 I.V. PBI

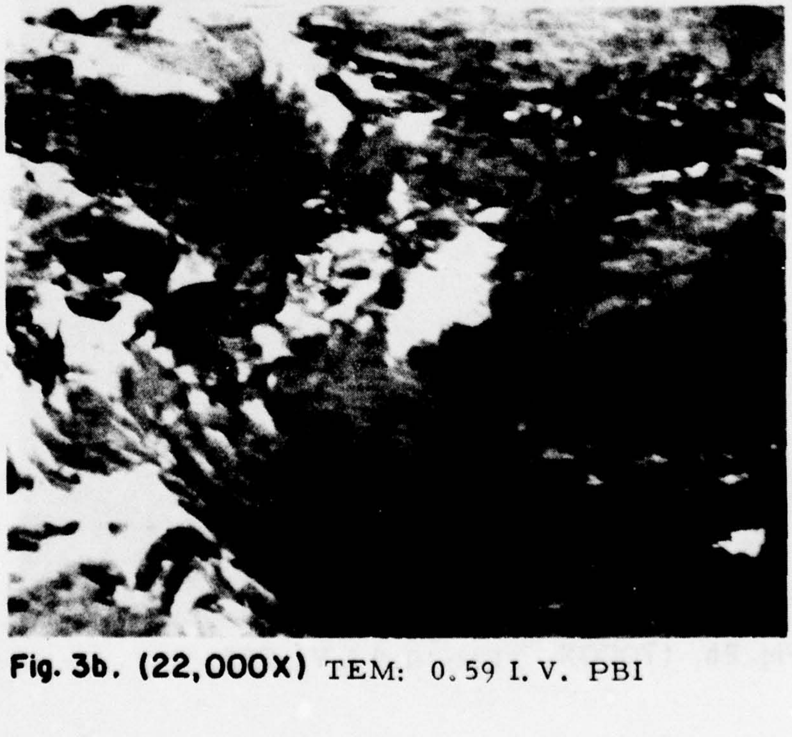


Fig. 3b. (22,000X) TEM: 0.59 I.V. PBI

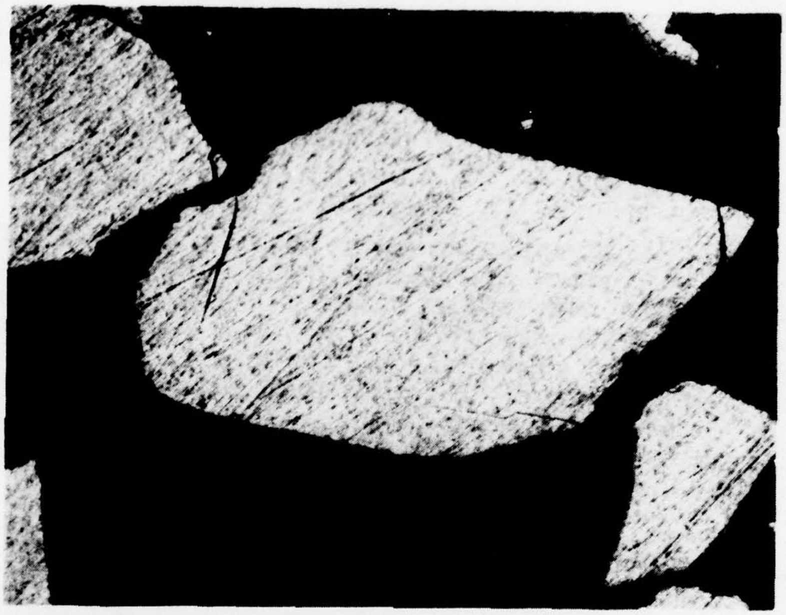


Fig. 4. (200X) Optical Micrograph: Co-precipitated BBB/PBI

To obtain pieces suitable for testing, the discs were cut on an Imanco Micro-Slice using diamond loaded saw blades. Two 1/4" wide bars were cut from each disc. With this width, the maximum length of the bars was about 0.8". In general, good unchipped bars were obtained. However,with the pure BBB and with the co-precipipated material, difficulties were experienced in cutting satisfactory specimens. Smaller pieces were also cut for the TMA and x-ray study.

Testing was carried out using the ASTM 70 standard test for flexural modulus and strength. The 0.05" thickness was chosen to give a 16:1 or greater aspect ratio for the maximum bar length of 0.8".

D. X-ray Diffraction

Wide and low angle x-ray studies were carried out photographically on several of the molded discs. The wide angle studies were made on standard flat plate cameras. The low angle studies used pinhole collimated cameras mounted on a high intensity rotating anode generator. Intensities of some of the wide angle patterns were measured on a Joyce Loebel microdensitometer for comparisons of orientation to be made. The scans were made parallel and perpendicular to the thickness of the disc and the ratio of peak intensities calculated.

E. Microscopy

For optical microscopy, pieces of the disc were embedded in Buehler Epoxide Resin (20-8130-032) with Buehler Epoxide Hardener (20-8132-009), using a 5:1 mixture ratio for room temperature hardening, and then polished to reveal a cross-section through the thickness of the disc. Standard polishing procedures were used, i.e. grits 240, 320, 400 and 600 successively followed by final polishing with 1μ and 0.3μ alumina powder. The polished samples were examined in a Leitz microscope using bright field vertical illumination.

For transmission electron microscopy, pieces of the samples were embedded in Maraglas resin and cured overnight at 60°C. Sections were cut at room temperature on an LKB III ultra-microtome using a diamond knife. The sections were examined using either a Siemens Elemiskop I transmission electron microscope or a JEOL-100CX.

The scanning electron microscopy studies were made on fractured samples, which had been coated with gold to minimize charging effects, in an AMR 100A scanning electron microscope.

F. Thermal Studies

Thermal expansion was measured on a duPont Thermo-mechanical analyzer set for measuring change in thickness. The samples used were cut with the micro-slicer so that changes parallel and perpendicular to the thickness could be monitored. Calorimetric studies were made using a duPont differential scanning calorimeter.

G. Spectroscopic Studies

The samples used for the spectroscopic studies are listed in Table II. They include pure BBB, both 0.59 and 0.93 I.V. PBI and several mixtures of the two polymers. The form in which the sample was used is also given.

The mass spectrometer was an AEI M5-9. This apparatus permits the examination of products evolved as a function of temperature up to 440°C. Samples were mounted in a glass capillary and evacuated to 10^{-6} torr before heating.

The infra red unit was a Nicolet 7199 Fourier Transform infrared spectrometer (FTIR). Samples were examined in KBr.

TABLE II

SAMPLES USED FOR SPECTROSCOPIC STUDIES

Sample	Composition	Sample Pre-Treatment
26050-49	100% BBB	Powder
P-915A	100% PBI 0.93 I.V.	Powder
25975-18-4	50% BBB, 50% PBI (0.93 I.V.)	Powder (Dry Blend)
25975-19-11A,B	60% BBB, 40% PBI (0.59 I.V)	Pressed at 10,000 psi at 475°C, for 20 min.
25975-11-H	80% BBB, 20% PBI (0.93 I.V.)	Pressed at 10,000 psi at 475°C for 20 min.
25975-11-D	100% BBB	Pressed at 10,000 psi at 475°C for 20 min.
25975-22-A 1,2	80% BBB, 20% PBI (0.59 I.V.)	Pressed at 10,000 psi at 350°C for 20 min.

SECTION III

RESULTS AND DISCUSSION

A. Results

1. Mechanical Properties

Strength and modulus values obtained for various processing conditions are plotted in Figures 5 to 8 and in Tables III and IV. Figures 5 and 6 show the effect on modulus and strength of changing the ratio of BBB/PBI at constant processing conditions (475°C, 20,000 psi, 20 minutes). It can be seen that the modulus changes by a factor of 3 between pure BBB and pure PBI with the most rapid increase being between 0 and 50% PBI. There is a much larger increase in strength (about 10 fold) with the change being almost linear with composition for the 0.93 I.V. PBI. The 75% level of the 0.59 I.V. PBI shows a rather low strength but the possibility that this is an artifact cannot be ruled out.

Figures 7 and 8 show the effect on modulus and strength of varying the temperature while keeping the composition constant (80% BBB/20% 0.59 I.V. PBI, 20,000 psi, 20 minutes) together with results on pure BBB. They show that the modulus and strength of the blend is greater than that of the pure BBB at all temperatures up to about 500°C when the properties become indistinguishable.

In Tables III and IV, two point comparisons of the effect of dwell time and load are given. Increasing the dwell time increases both strength and modulus in all cases except for the modulus of the pure BBB at 475°C which falls slightly. Increasing the load leads to a decrease in properties except for the modulus of 0.93 I.V. PBI blend.

Table V lists results for the co-precipitated materials. These samples were very fragile and it was difficult to cut good test specimens from them. Comparison of the modulus values with those of the pure material or blends show that the moduli are at the level of the blends, e.g. 0.5×10^6 psi for 475°C and 10,000 psi. However, the strengths are close to the values exhibited by the pure BBB in agreement with the difficulties encountered in cutting the samples. Again,poorer properties were found at the higher pressure level.

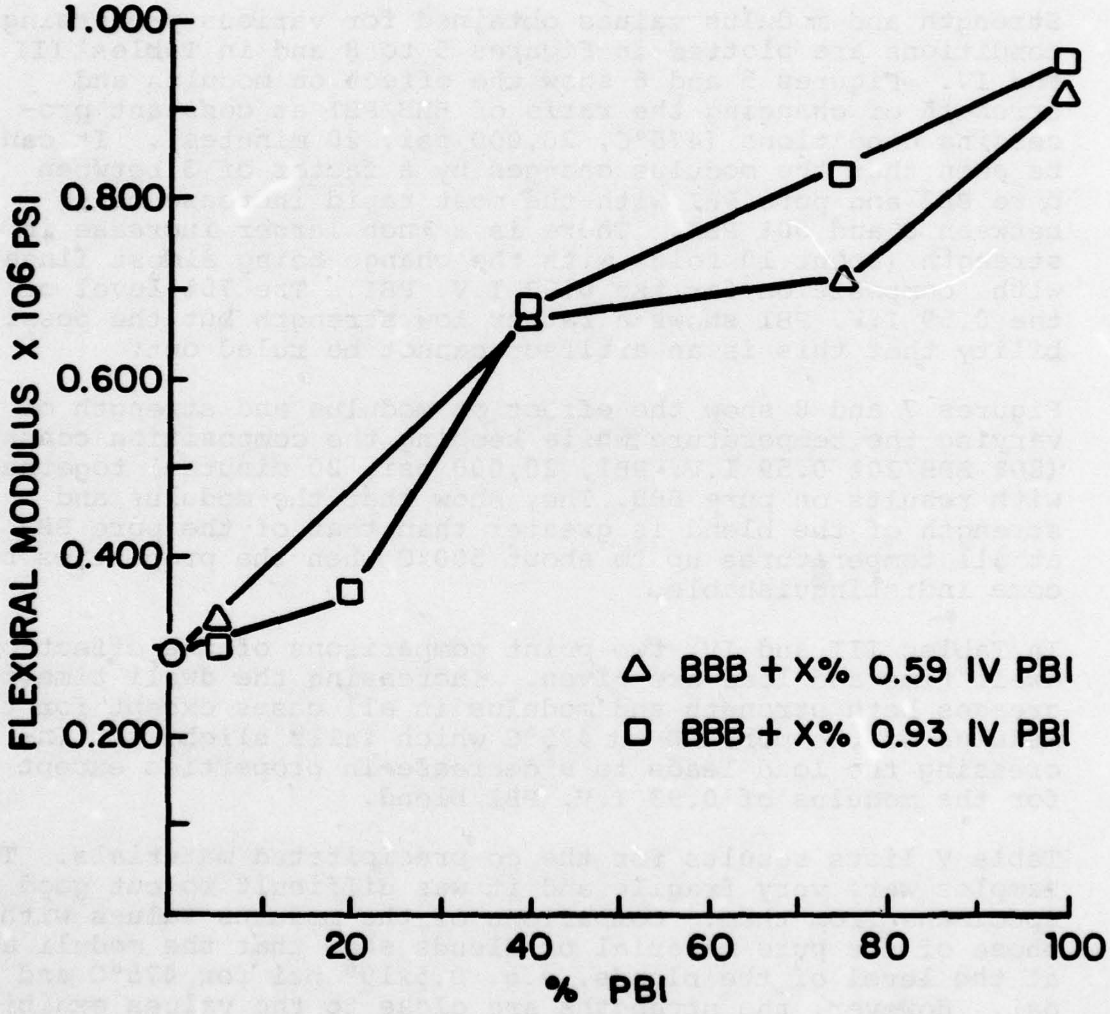


Fig. 5. Modulus vs. Composition of BBB/PBI Polymer Alloys

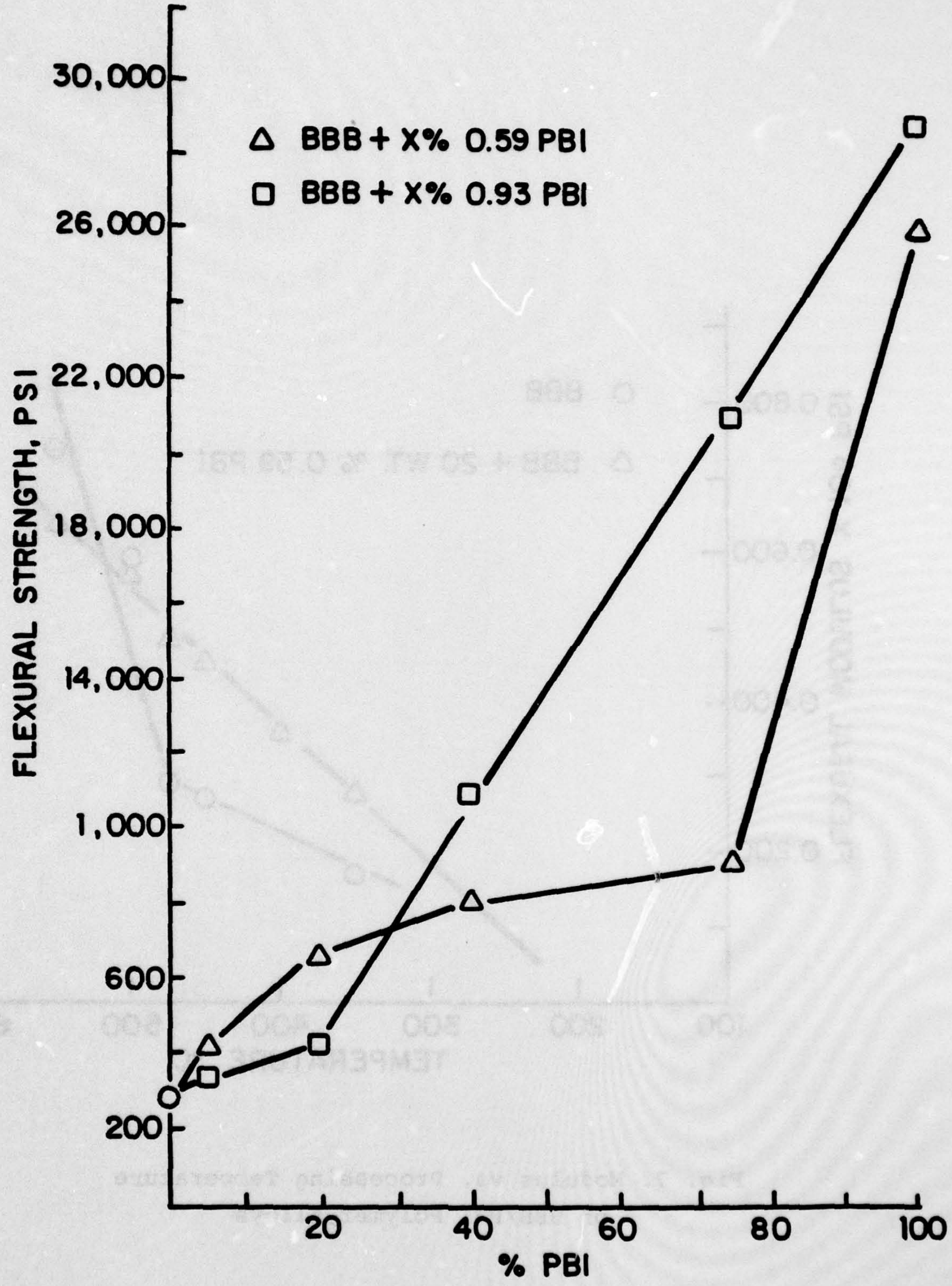


Fig. 6. Strength vs. Composition of BBB/PBI Polymer Alloys

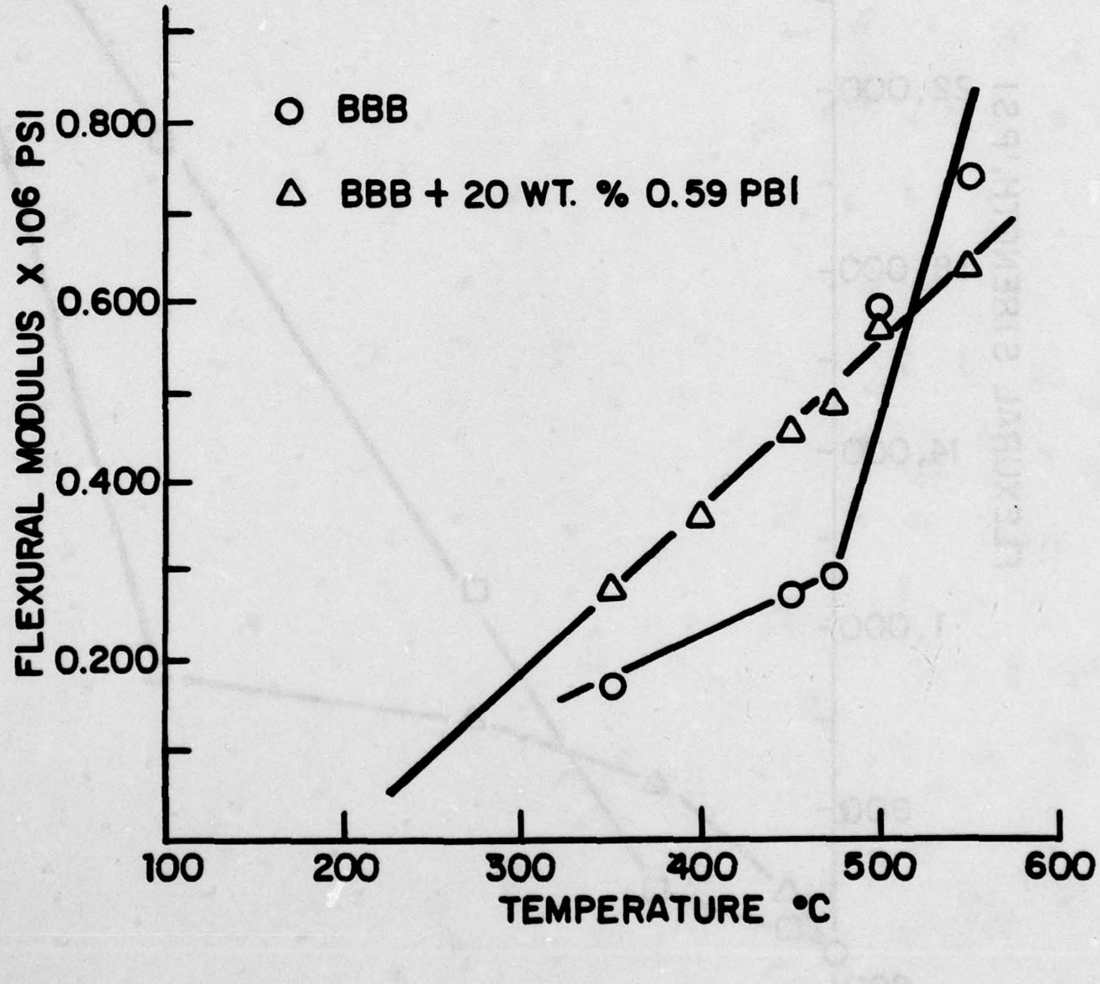


Fig. 7. Modulus vs. Processing Temperature of BBB/PBI Polymer Alloys

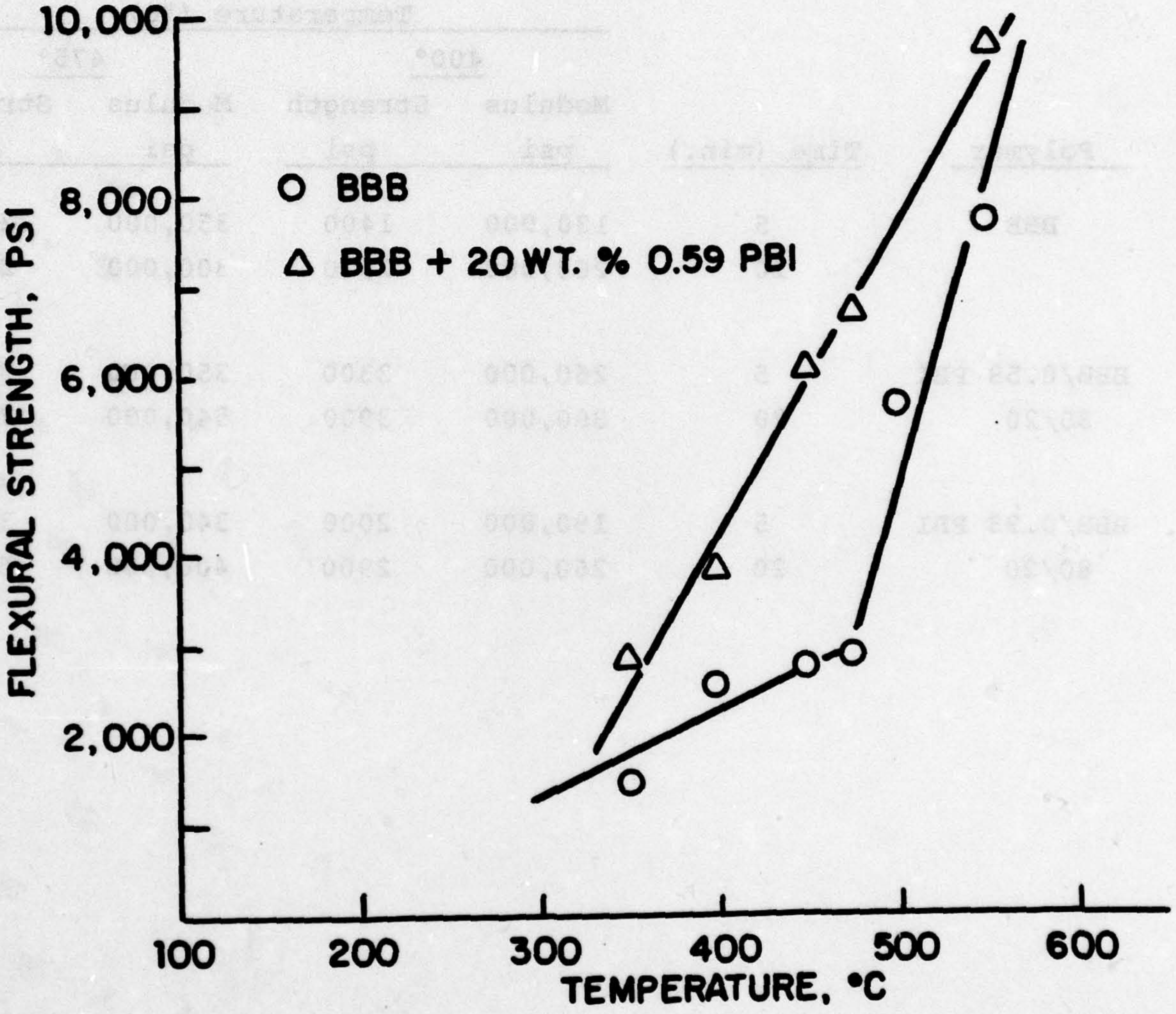


Fig. 8. Strength vs. Processing Temperature of BBB/PBI Polymer Alloys

TABLE III

MODULUS AND STRENGTH VS. TEMPERATURE AND TIME FOR BBB/PBI BLENDS

		Temperature (°C)			
		400°		475°	
Polymer	Time (min.)	Modulus psi	Strength psi	Modulus psi	Strength psi
BBB	5	130,000	1400	350,000	2600
	20	260,000	2500	300,000	2900
BBB/0.59 PBI	5	260,000	3300	350,000	3600
80/20	20	360,000	3900	540,000	7300
BBB/0.93 PBI	5	190,000	2000	340,000	3600
80/20	20	260,000	2900	400,000	5300

TABLE IV

MODULUS AND STRENGTH VS. APPLIED LOAD

Polymer	Load (lbs.)	Modulus (psi)	Strength (psi)
BBB	10,000	290,000	2800
	20,000	210,000	2400
BBB/0.59 PBI 80/20	10,000	530,000	7300
	20,000	420,000	5100
BBB/0.93 PBI 80/20	10,000	400,000	5300
	20,000	430,000	4200

TABLE V

PROPERTIES OF CO-PRECIPITATED 80/20 BBB/PBI BLEND

	Load Pressure (lbs.)			
	10,000		20,000	
Temp (°C)	Modulus (psi)	Strength (psi)	Modulus (psi)	Strength (psi)
350°	-	266	298,000	724
475°	519,000	3430	342,000	1750
550°	426,000	3530 (1)	(2)	

(1) Best value

(2) Samples fractured in cutting

2. X-ray Diffraction

Wide angle x-ray diffraction of the pure BBB before and after pressing showed two very diffuse reflections with the inner one being at about 8.0Å and the outer one at 3.5Å. In the sample which had been pressed at 20,000 psi and 475°C, the 3.5Å ring showed some orientation indicatating a planar orientation, i.e., one in which the appropriate reflecting planes are aligned perpendicular to a particular axis, in this case, the compression axis. The 8.0Å ring, on the other hand, showed no preferred orientation. In addition, the pressed sample exhibited a sharp unoriented reflection, at about 3.12Å.

The 0.93 I.V. PBI showed only a very diffuse ring at about 4.7Å before and after pressing with no orientation effects. The 0.59 I.V. PBI was highly crystalline (see list of spacings in Table VI) both before and after pressing. This again showed no orientation effects on treatment.

X-ray patterns from the blends essentially showed a superpositioning of these observations. With BBB and 0.93 I.V. PBI, only the BBB reflections were observed, with the orientation similar to that for straight BBB and with the additional sharp reflections at 3.12Å. With BBB and 0.59 I.V. PBI, the crystalline PBI was observed super-imposed on the BBB pattern.

Different treatment conditions (temperature, time, pressure) gave almost identical x-ray patterns, the only difference being the intensity of the sharp additional BBB reflections. At 400°C and 5 minutes, the 3.12 Å reflection was barely visible. At 475°C for 20 minutes, the 3.12Å reflection was strong and some additional reflections at about 2.2 Å were observed.

The co-precipitated BBB-0.59 I.V. PBI differed in that the orientation of the BBB 3.5Å reflection was much less. Furthermore, no extra crystalline reflection appeared after the heat treatment and no PBI reflections were observed.

Only some of the early samples were examined at low angle. The straight BBB sample was compared with BBB/PBI blends. In each case, there was a strong, diffuse central scatter which usually can be associated with voids. The scatter was asymetrical, being elongated preferentially along the compression axis, i.e. taking into account the reciprocal relationship in scattering,

TABLE VI

SPACINGS FOR 0.59 I.V. PBI

No.	Spacing Å	Comments
1	6.32	Very strong
2	4.93	Doublet weak/medium
3	4.17	Strong
4	3.75	Strong
5	3.01	Medium

this could be due to voids elongated in the plane of the flat test piece. The intensity and extent of the scattering increased with temperature and time suggesting that the voids get smaller and/or some degradation is occurring giving rise to additional small voids.

3. Optical Microscopy

Pure BBB samples treated at 350, 450 and 550°C were examined (Figure 9 of a 450°C sample is representative). Each showed a texturing which appeared to correspond with the original particles with a flattening of the texture perpendicular to the compression axis. The 550°C sample appeared to be better compacted than did the 350°C sample. The color of the samples also changed with temperature being golden for 350°C and almost silver for the sample treated at 550°C.

Pure 0.59 I.V. PBI showed a fine texture (Fig. 10), about 10μ or so, which corresponded to a slight color difference within the sample. The samples were silver-colored in general. Comparison of the pressed sample with the SEM of the powder suggests that the mottling corresponds to the finest particles visible in the SEM. It is to be noted that the particle size analysis indicates about 10μ.

Pure 0.93 I.V. PBI has a much coarser texturing than is the case for the 0.59 PBI large particles. The 0.93 I.V. PBI particles were of the order of 200μ and appeared to be cemented together (Figure 11) by a darker material. Again, comparison with the SEM of the untreated powder shows that the large particles are of the same order of size as the large particles in the powder. In this case, the smaller particles appear to have fused together to form the darker phase.

In the BBB/PBI blends, two distinct phases were apparent, with the BBB having a golden tinge and the PBI a silvery hue. In the optical micrographs (Figures 12 and 13), the PBI shows up as the darker phase. At low concentrations of BBB (Figures 12a and 13a), the PBI phase is continuous and has the texture of the corresponding pure material. At high BBB concentrations, the BBB phase is continuous (Figures 12c and 13c), again with the texture of pure BBB. The transition between continuous phases occurs at about 40% (Figures 12b and 13b).

Mixtures of BBB/0.59 I.V. PBI were processed at 350°, 450°, and 550°C. As with the pure BBB, the color of the BBB changed giving less contrast between the BBB and PBI phases. It also appeared as if the total area of the darker, PBI-rich phase, was greater as the temperature was increased.

Fig. 9. (200X) Optical Micrograph:
Pure BBB
Pressed @ 450°C, 20,000 psi, 20 min

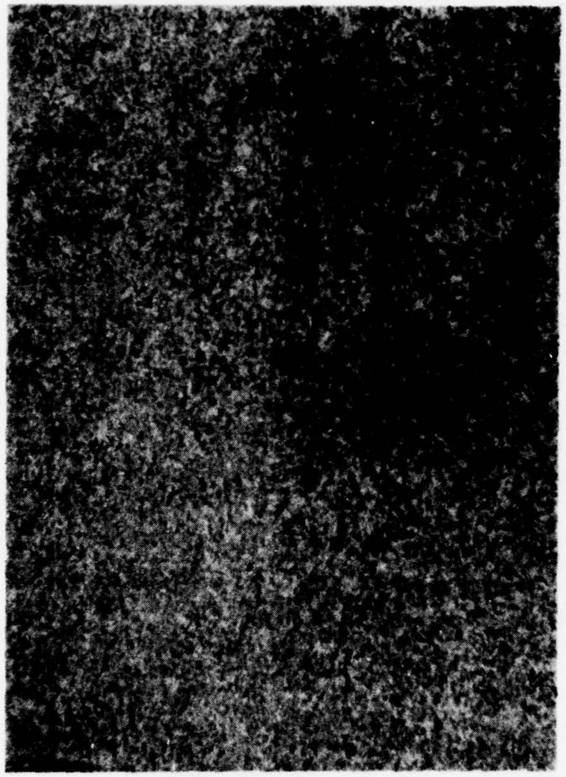


Fig. 10. (200X) Optical Micrograph:
Pure 0.59 I.V. PBI
Pressed @ 450°C, 20,000 psi, 20 min

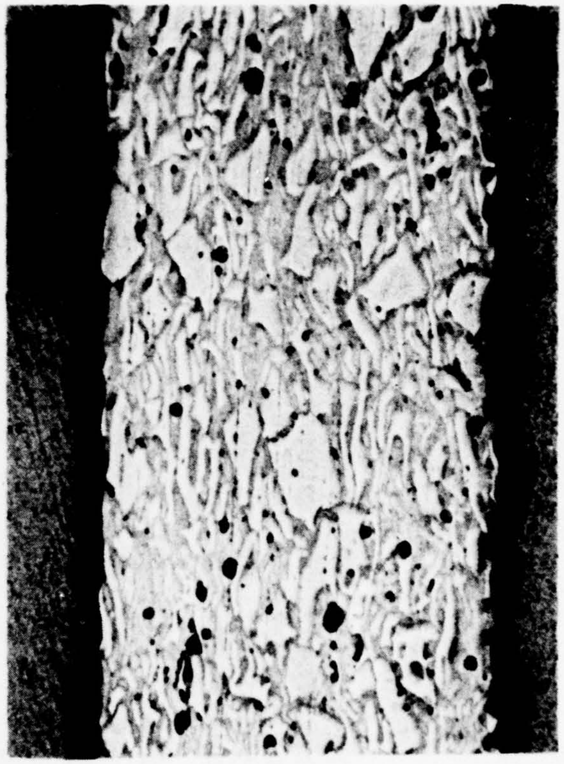


Fig. 11. (50X) Optical Micrograph:
Pure 0.93 I.V. PBI
Pressed @ 450°C, 20,000psi, 20 min

OPTICAL MICROGRAPHS

Fig. 12a. (50X) 25 BBB/75 0.59 PBI

Fig. 12b. (50X) 60 BBB/40 0.59 PBI

Fig. 12c. (50X) 95 BBB/5 0.59 PBI

OPTICAL MICROGRAPHS

Fig. 13a. (50X) 25 BBB/75 0.93 PBI

Fig. 13b. (50X) 60 BBB/40 0.93 PBI

Fig. 13c. (50X) 95 BBB/5 0.93 PBI

When the two polymers were co-precipitated, the optical micrographs confirmed that a true co-precipitation had taken place. The two phases could be distinguished in individual particles with the PBI appearing as silver flecks in the golden BBB matrix. The size of the PBI inclusions was of the order 1-5μ.

After processing, the boundaries of the individual particles could still be distinguished (Figures 14a and b), with cracks between particles in the lower temperature sample (Figure 14a). At higher magnification (Figures 15a and b), the two phases are still clearly visible, again with the size of the PBI being in the range of a few microns. As with the dry blends, the tint of the BBB changes with processing temperature, becoming more silvery while the total area of the PBI (darker phase in the micrographs) appeared to increase (compare Figures 15a and 15B).

4. Transmission Electron Microscopy

Sections of pressed discs of the pure polymer, the dry blends and the co-precipitated materials were examined together with sections of the untreated polymers. As indicated earlier (Section tion IIA) there were distinctive textural differences between the three untreated polymers. The BBB had a very open porous structure, Figure 16, whereas the 0.93 I.V. PBI was compact and featureless (Figure 2b). The 0.59 I.V. PBI sample had a mottled texture in the size range of a few hundred Angstrom units (Figure 3b).

The pure BBB treated at 475°C, 20 minutes, 10,000 psi (Figure 16) is much more compact and shows a nodular texture in the range of a few 100 Angstrom units. The 0.93 I.V. PBI remained quite featureless with occassional inclusions, as seen in Figure 17. These inclusions have not yet been identified. In the 0.59 I.V. PBI, the texture observed in the unprocessed material was again apparent (Figure 18).

In the dry blended mixture, the individual phases could still be detected. Figure 19 is a photomicrograph of an 80/20 BBB/0.59 I.V. PBI blend treated at 475°C, 10,000 psi and 20 minutes. It shows a PBI particle embedded in the BBB matrix and individual particle boundaries of the BBB can be identified.

The co-precipitated material was examined after treatment at 350°C, 475°C and 550°C at 10,000 psi. As with the optical microscopy distinct changes in texture were observed. At 350°C, the

CO-PRECIPITATED BBB/PBI

Fig. 14a. (200X) Pressed @ 350°C, 10,000 psi, 20 min

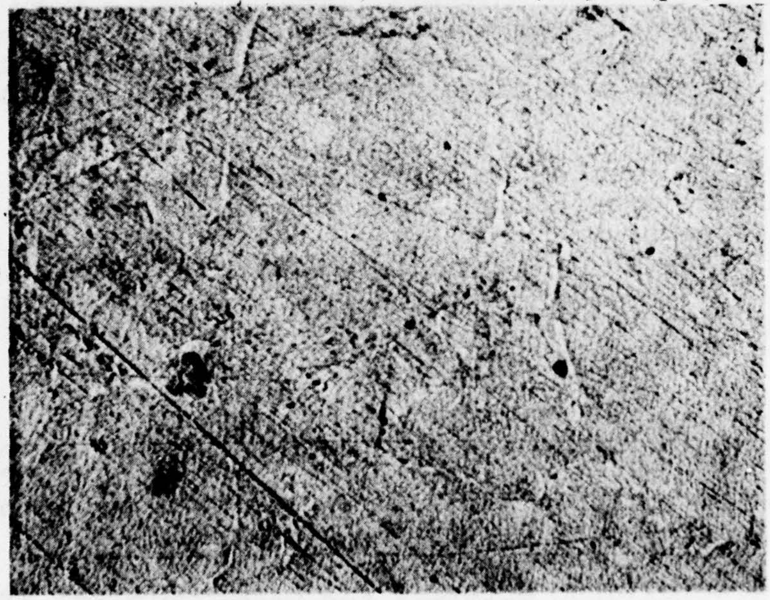


Fig. 14b. (200X) Pressed @ 475°C, 10,000 psi, 20 min

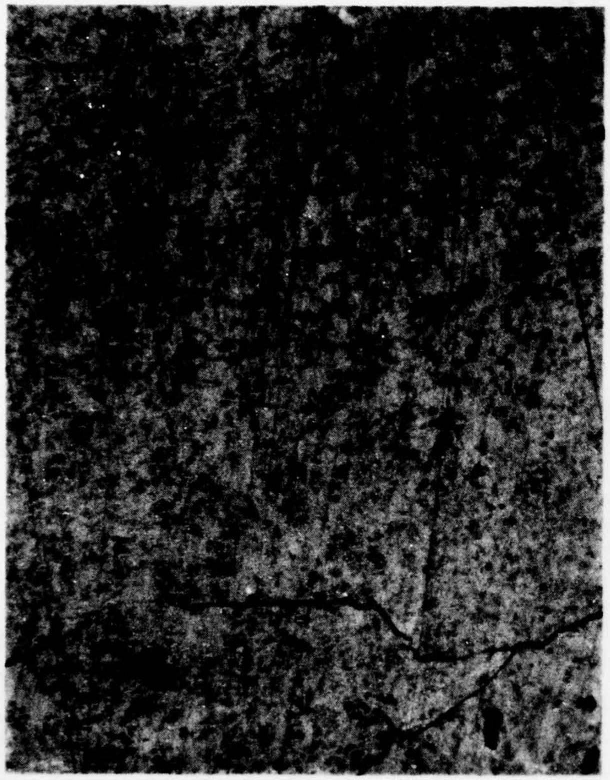


Fig. 15a. (500X) Co-precipitated BBB/PBI
Pressed @ 350°C, 10, 000 psi, 20 min

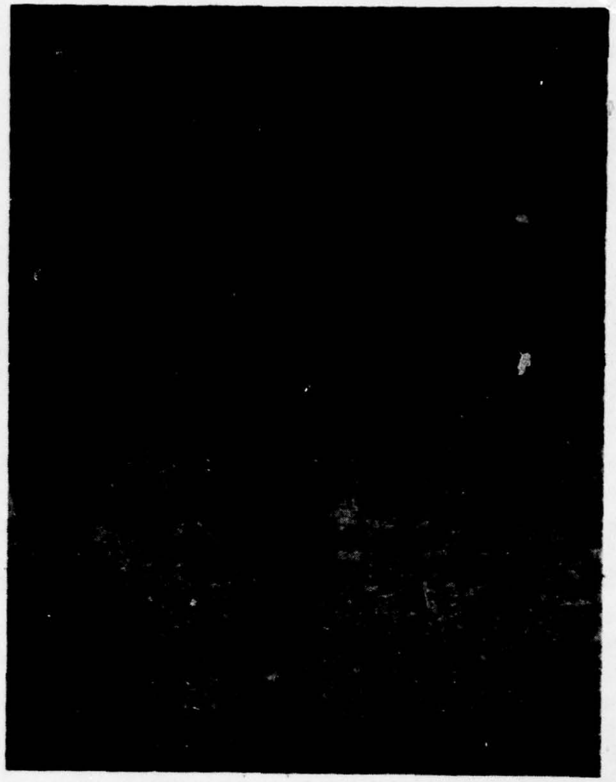


Fig. 15b. (500X) Co-precipitated BBB/PBI
Pressed @ 550°C, 10, 000 psi, 20 min

Fig. 16. (18,400)

TEM: BBB Pressed @ 475°C, 10,000 psi, 20 min

TABLE VII

THERMAL EXPANSION OF BBB AND BLENDS BETWEEN 23°C and 600°C

Polymer	Temperature (°C)	Time (min)	Load (lbs.)	Coefficient of Thermal Expansion ($°C^{-1} \times 10^5$) Thickness	Width
BBB	475°	5	10,000	10.7	0.4
	475°	20	10,000	10.2	0.2
	475°	20	20,000	5.1	2.3
BBB/0.59 PBI 80/20	475°	5	10,000	7.1	0.4
	475°	20	10,000	7.0	0.8
	475°	20	20,000	3.8	0
BBB/0.93 PBI 80/20	475°	5	10,000	6.4	0.6
	475°	20	10,000	2.1	0
	475°	20	20,000	2.3	1.9

400°C, at which point the change was much more rapid with increasing temperature, reaching a peak at about 600-650°C. The total expansion at 600°C was measured for both directions and the results are listed in Table VII. The expansion in thickness was generally much greater than the change in width. The change in thickness was lower for the blends, at similar processing conditions, than for the pure BBB. Increasing time and pressure also tends to decrease the expansion. No clear trend of expansion versus processing conditions was observed for the width.

7. Infrared Studies

The initial BBB powder sample was found to exhibit weak carbonyl absorptions at 1785 and 1747 cm^{-1}. These absorptions were associated with anhydride groups by means of comparison with naphthalic anhydride. The naphthalic anhydride was found to have absorptions at 1772 and 1740 cm^{-1}, differing by approximately 10 cm^{-1} from the polymer. It is likely that these were end group absorptions in the polymer and that such end groups might react further upon heat treating the polymer. A series of samples of various compositions and heat treatments were examined and the data are reported in Table VIII.

It was found that heat treatment at 475°C (20 min.) of the BBB reduced the carbonyl absorptions to trace levels. Similar heating of mixtures of BBB with PBI to 475°C also reduced the intensity of the absorptions to trace levels. However, heating such a mixture to 350°C did not change the absorptions relative to the parent BBB sample. Thus, for the anhydride groups to react further, the sample must be heated above 350°C.

Carboxylic acid absorptions may also occur, but this region of the spectrum is dominated by the carbonyl absorption of the polymer repeat unit.

8. Mass Spectral Analysis

As shown later in the discussion there are several possible reactions for BBB end groups. The anhydride end groups can react with amine end groups or amine groups in partially cyclized rings in the main chain. In this case, the reaction product would be water.

The ester end groups on PBI can react with amines to produce water and phenol. The water or phenol can in turn react with the BBB anhydride end group to produce the carboxylic acid group and phenolic ester, and these groups can subsequently react with amines, again producing water and phenol.

TABLE VIII

FOURIER TRANSFORM INFRA-RED RESULTS ON SELECTED SAMPLES

Sample	Treatment	Relative Intensity of 1785, 1747 cm^{-1} Carbonyl Absorption
Naphthalic Anhydride	Powder	Absorption at 1772 and 1740cm^{-1}
26050-49 (100% BBB)	Powder	Weak absorption
25975-11-D (100% BBB)	Pressed at 475°C for 20 min.	Trace absorption substantially reduced from 26050-49.
25975-22-A 1,2 (80% BBB, 20% PBI, 0.59 I.V.)	Pressed at 350°C for 20 min.	Similar to 26050-49
25975-11-H (80% BBB, 20% PBI, 0.93 I.V.)	Pressed at 475°C for 20 min.	No detectable carbonyl absorption
25975-19-11A,B (60% BBB, 40% PBI, 0.59 I.V)	Pressed at 475°C for 20 min.	Trace absorption

Accordingly, the evolution of water and phenol was studied by mass spectral analysis, as a function of temperature, from four samples: 100% BBB, 100% PBI, 50% BBB/50% PBI dry blended mixture as-is and a 60% BBB/40% PBI which had been previously heat treated at 475°C for 20 minutes at 10,000 psi. Each sample was heated through three cycles without removing it from the system. It should further be noted that the mass spectral technique used gives only a qualitative comparison between one sample and another but is more quantitative within a single sample. That is to say that differences in the shapes of curves are real when comparing one sample with another but differences in magnitude should be treated with caution. However for a single sample, differences in magnitude between successive runs are significant.

The data shown in Figures 24-33 are plots of the peak heights of the evolved species as measured in the mass spectrometer. In Figures 24 & 25 are plotted the data for water evolution from 100% PBI. On the first heating (Figure 24), there is a peak at about 200°C which is completely absent in the subsequent runs (Figure 25). This is probably due to absorbed water. There is a suggestion of a second peak at about 400°C on the first run and it is at about this temperature that there is a rise in water evolution on subsequent cycles. The phenol evolution for the *100% PBI is shown in Figures 26 & 27.* This also shows a peak on the first run (Figure 26) at about 400°C. The second and third runs (Figure 27) show only trace amounts of phenol until temperatures are reached which are close to the highest temperature previously seen by the sample, i.e. at about 400°C. No phenol was evolved with the pure BBB.

The results for the 50/50 blend are shown in Figures 30, 31,32. Again the water evolution (Figure 30) falls off rapidly on the first run with only trace amounts up to 400°C on subsequent cycles (Figure 32). The phenol evolution (Figure 30) however is quite significant even at relatively low temperatures and shows a peak at about 200°C with a secondary peak at about 400°C. No phenol was detected on the second run until the highest temperatures were reached (Figure 31).

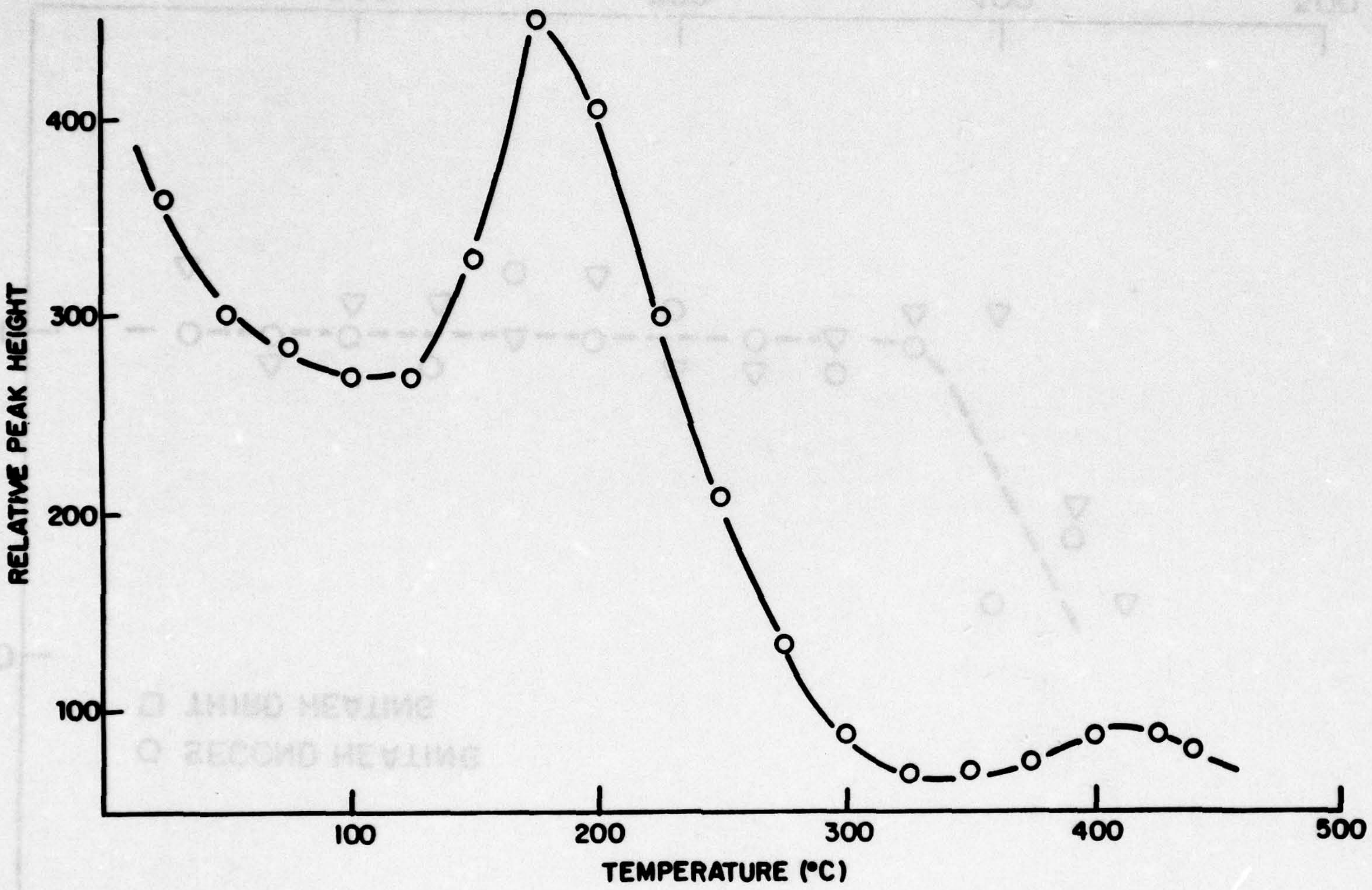


Fig. 24. Water Evolution for PBI (P915A). 1st Heating

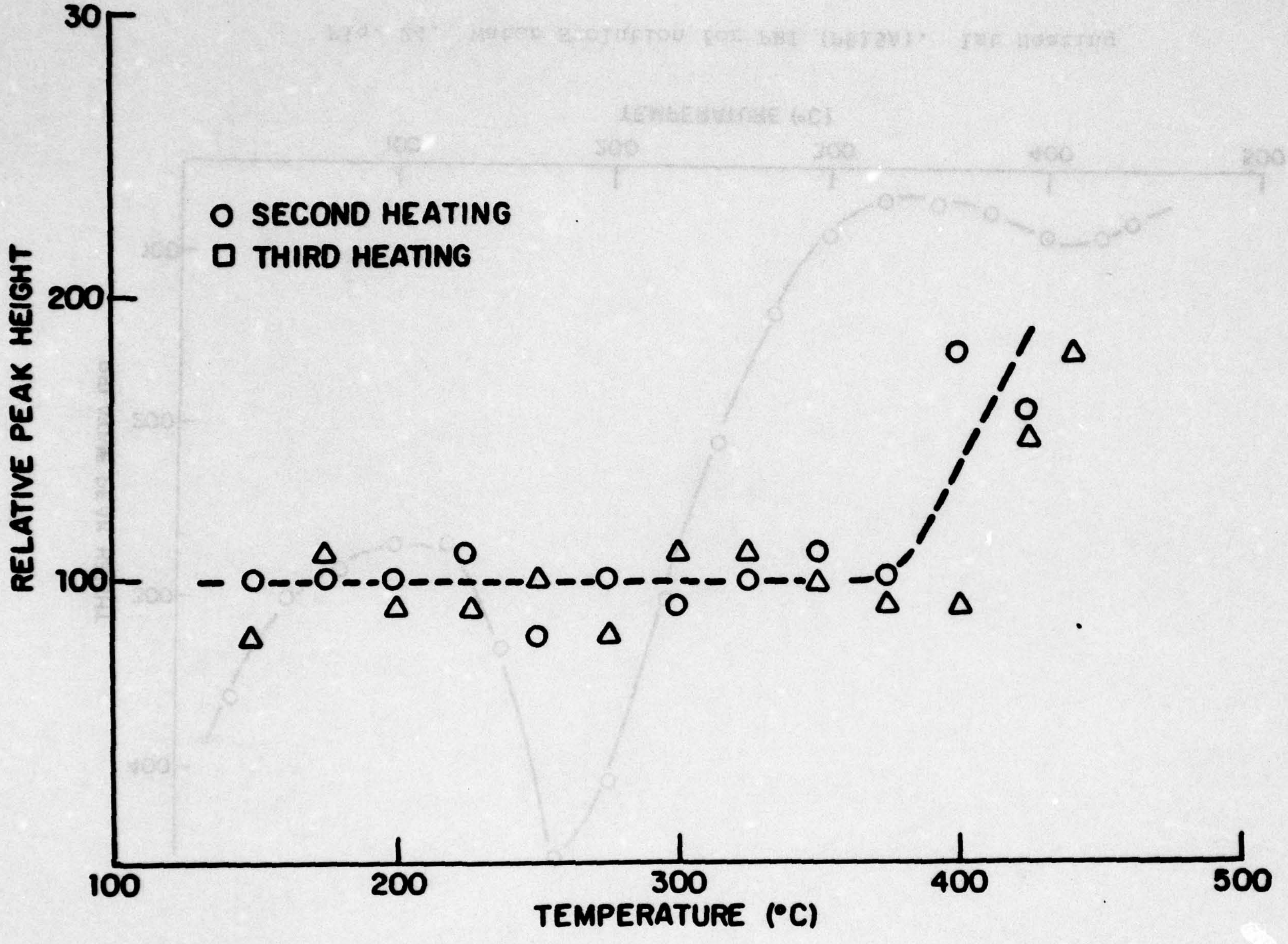


Fig. 25. Water Evolution for PBI (P915A). 2nd and 3rd Heating

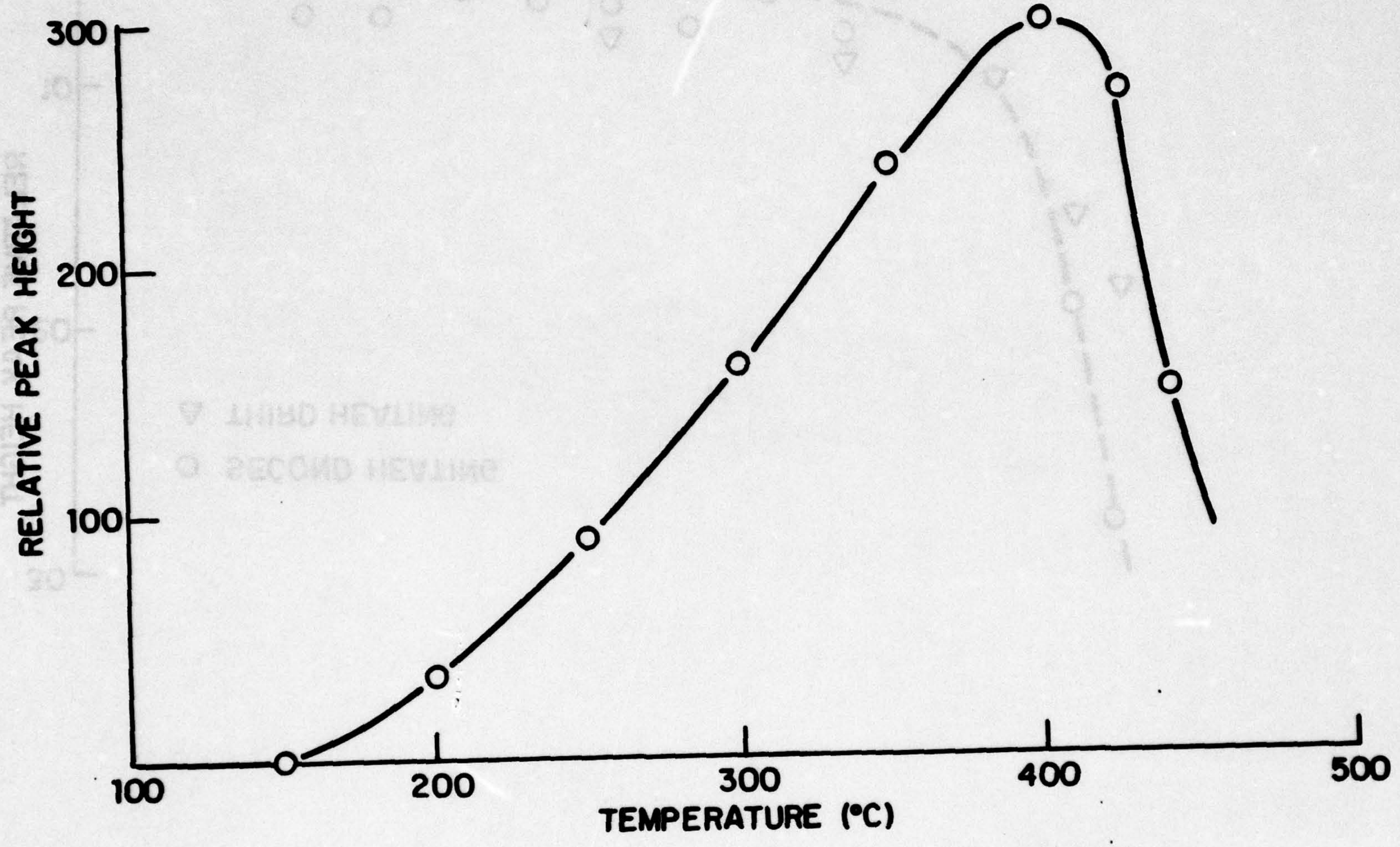


Fig. 26. Phenol Evolution for PBI (P915A). 1st Heating

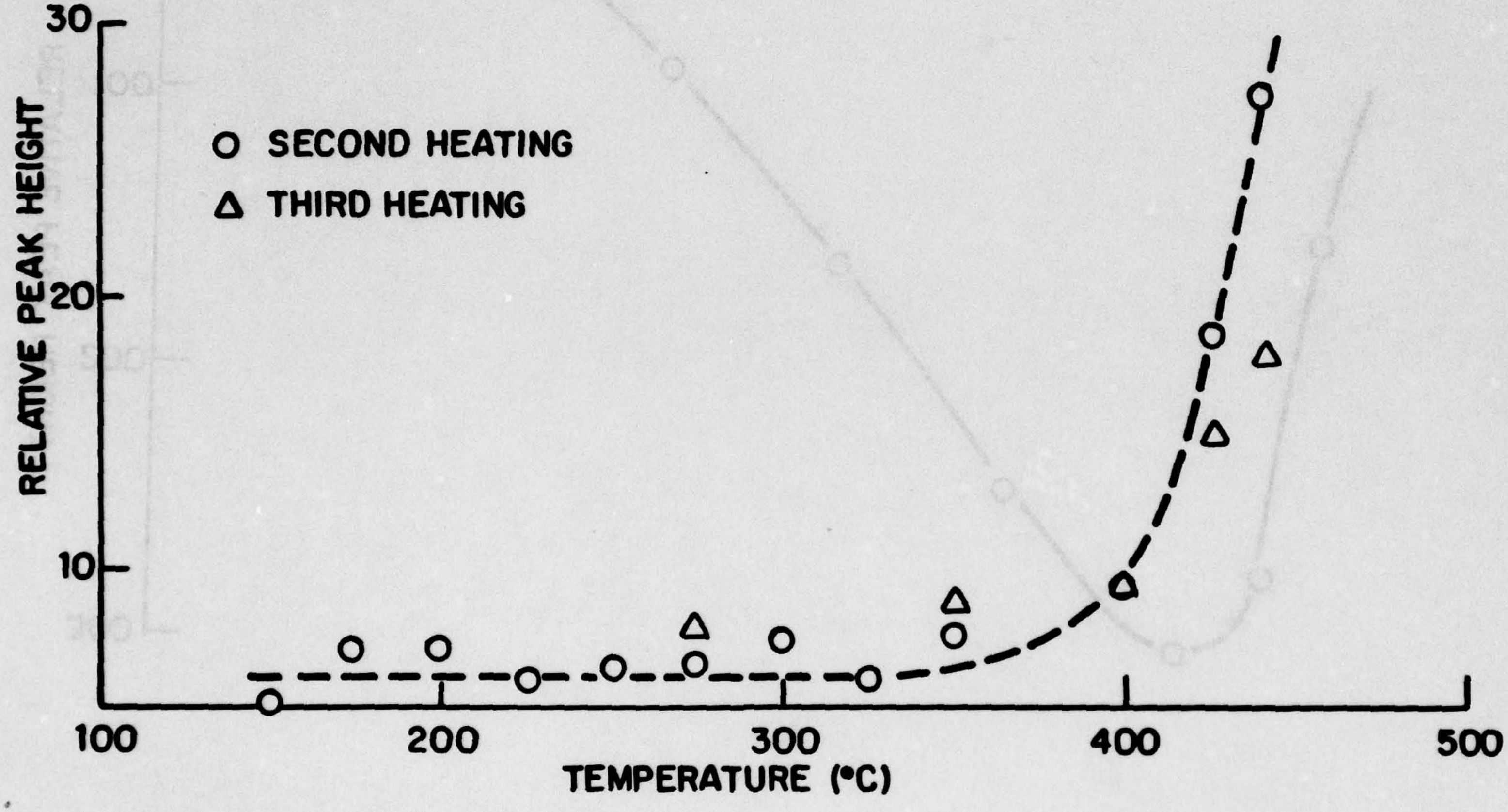


Fig. 27. Phenol Evolution for PBI (P915A). 2nd and 3rd Heating.

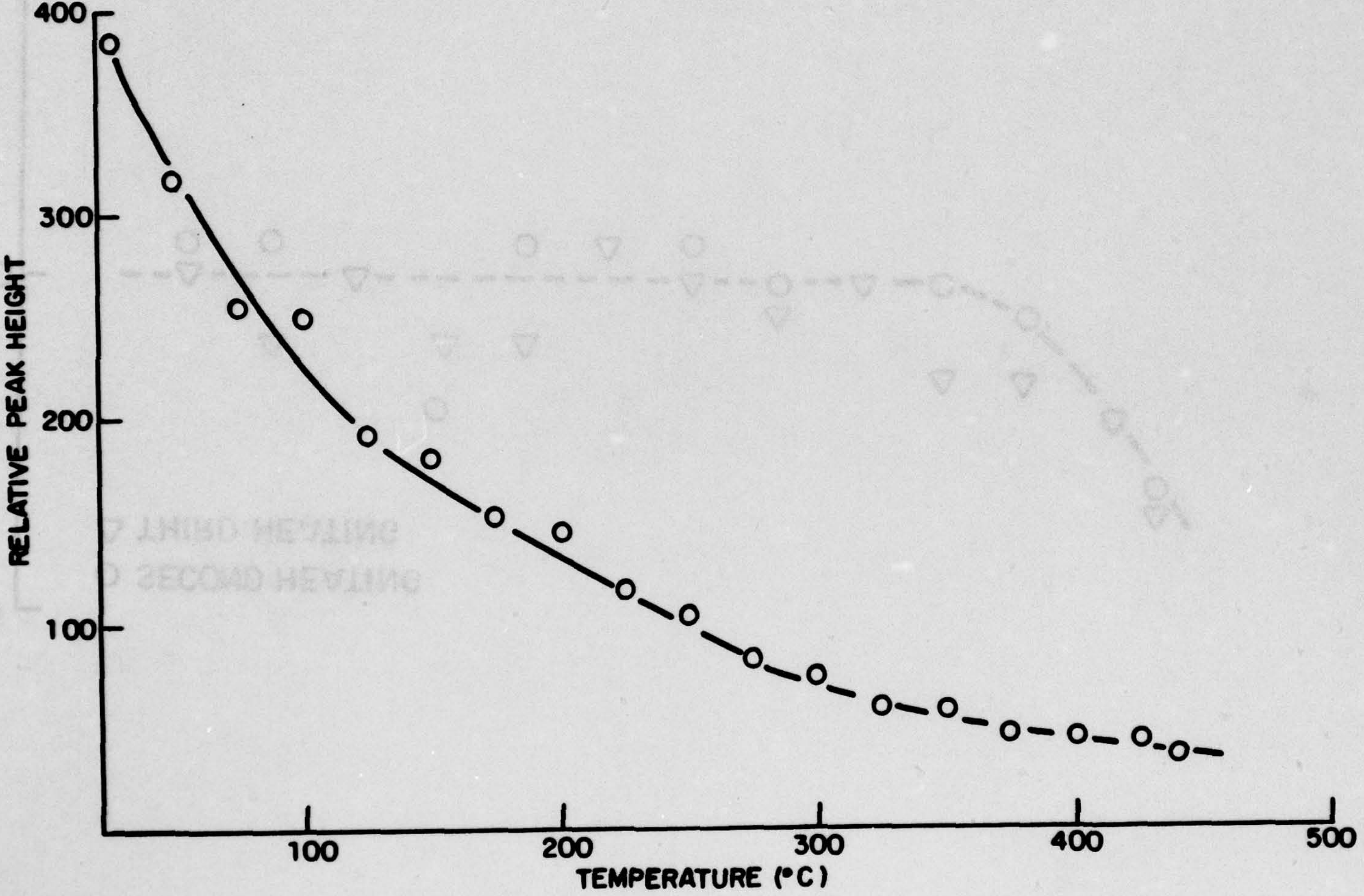


Fig. 28. Water Evolution for BBB (26050-49). 1st Heating

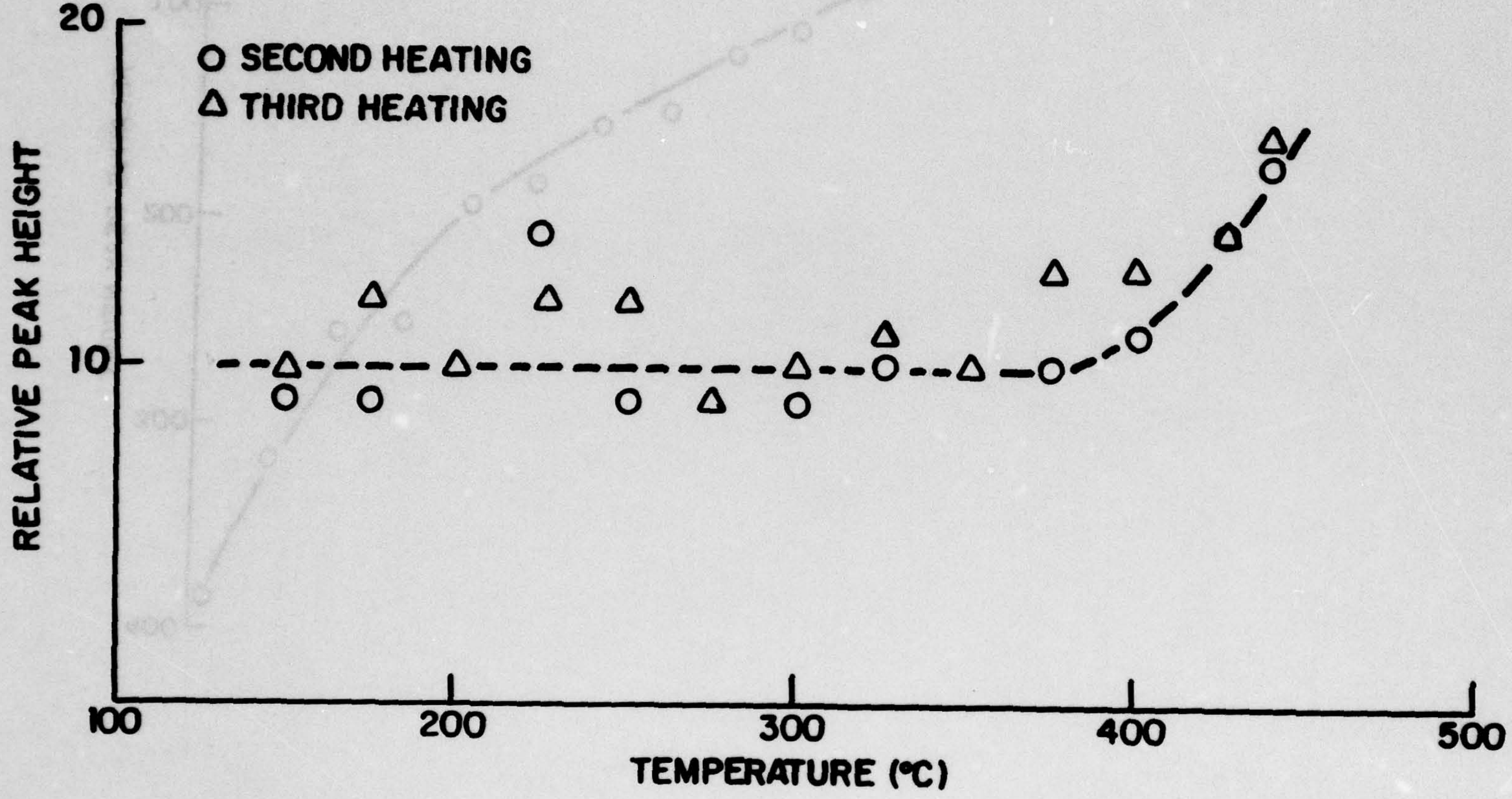


Fig. 29. Water Evolution for BBB (26050-49). 2nd and 3rd Heating

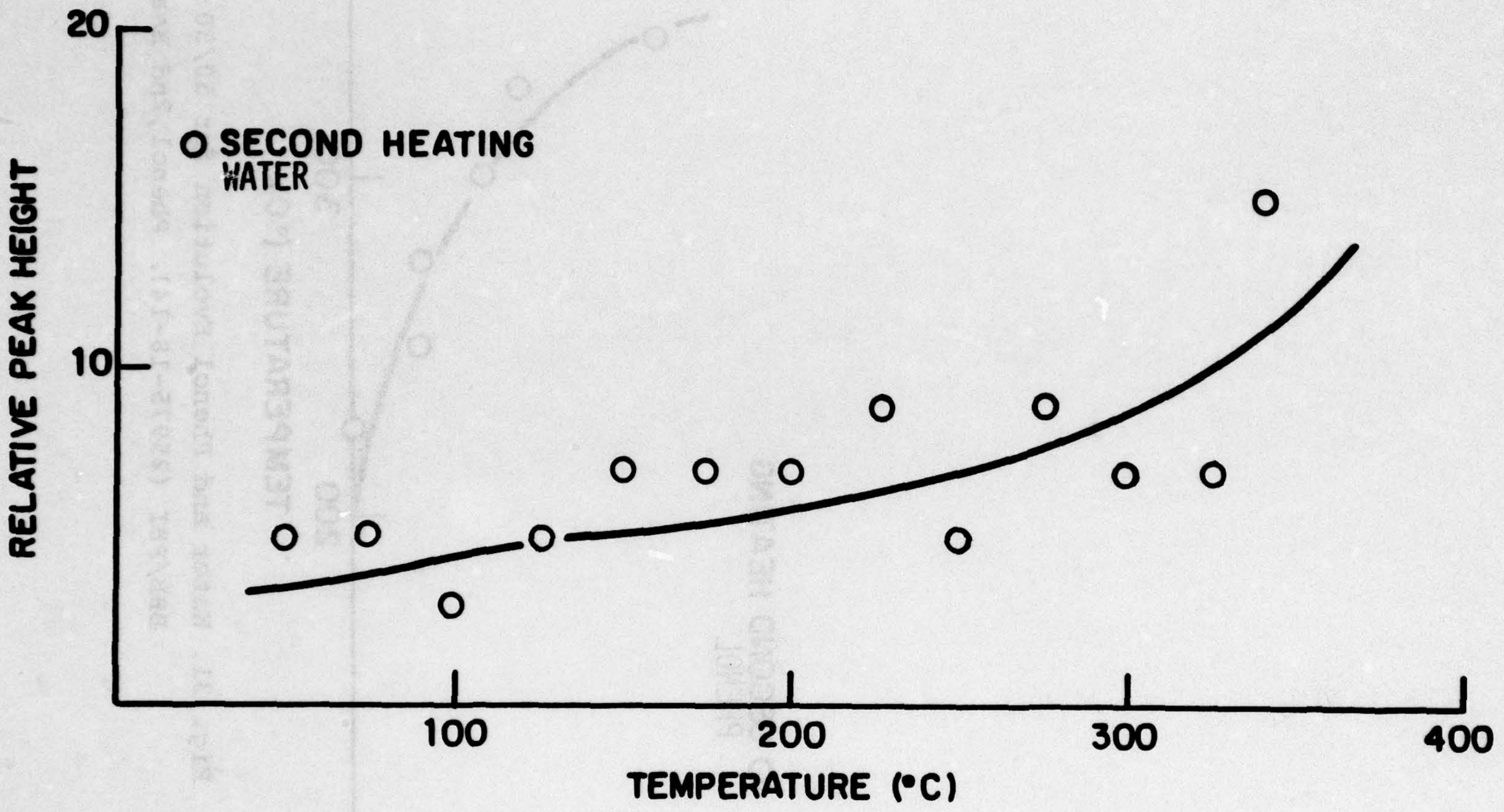


Fig. 32. Water and Phenol Evolution for 50/50 Mixture BBB/PBI (25975-18-4). Water, 2nd Heating

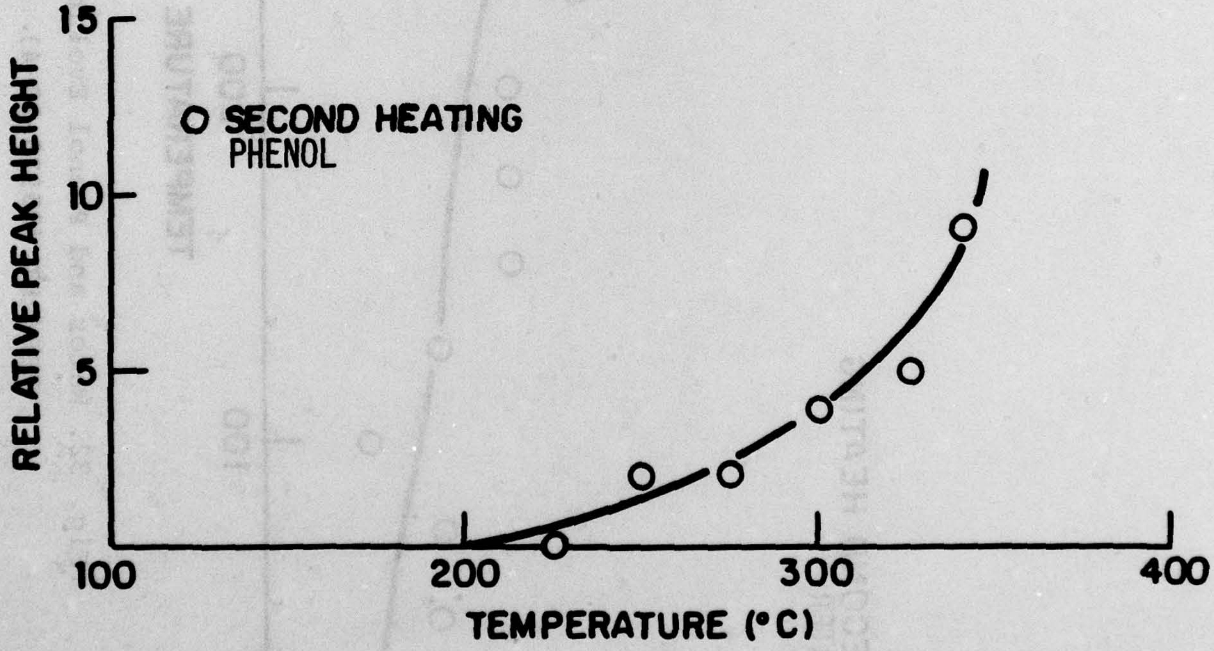


Fig. 31. Water and Phenol Evolution for 50/50 Mixture BBB/PBI (25975-18-14). Phenol,2nd Heating

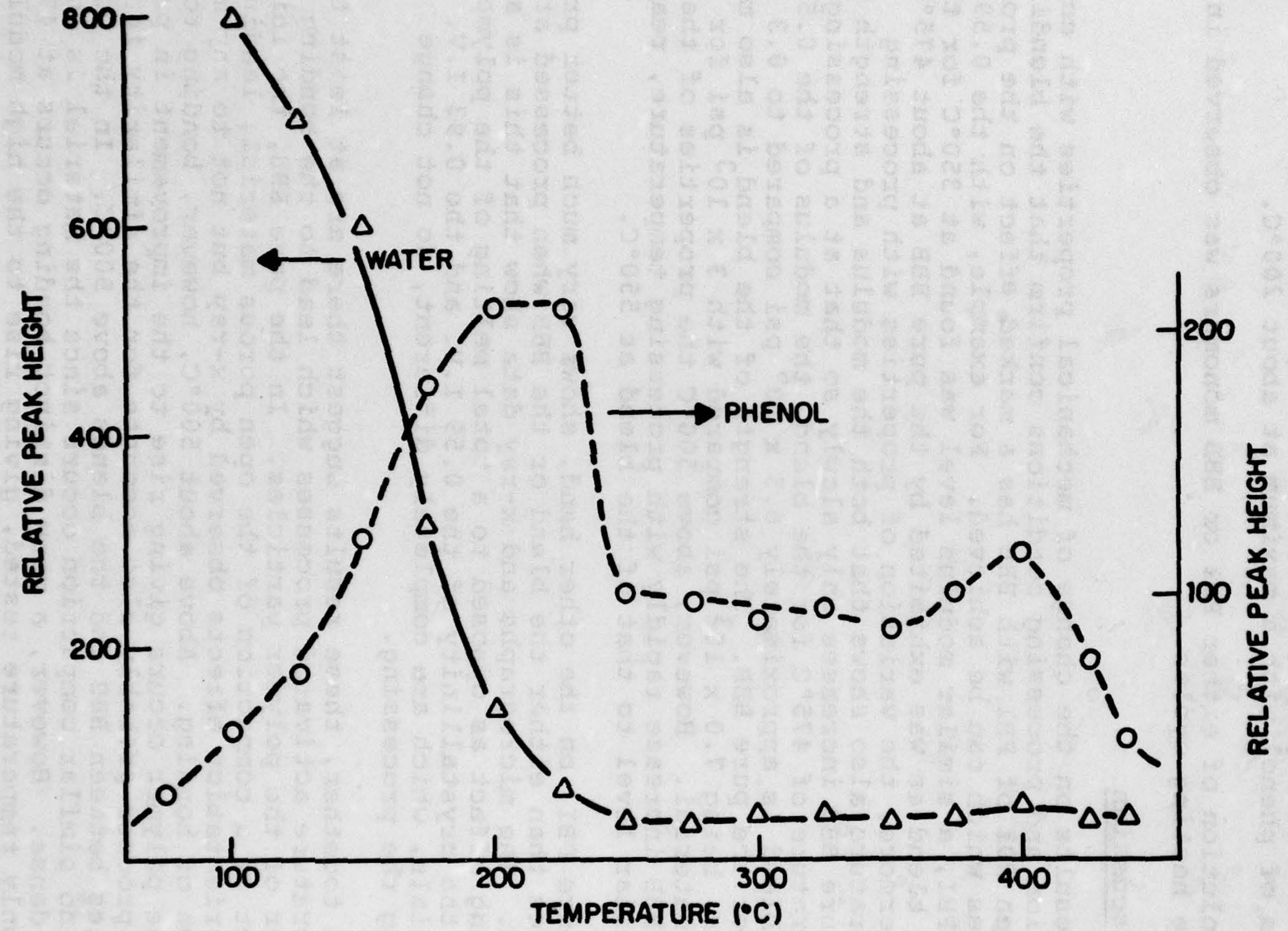


Fig. 30. Water and Phenol Evolution for 50/50 Mixture BBB/PBI (25975-18-4). 1st Heating

For the 60/40 blend, which had previously been heated to 475°C, there was a large water evolution (Figure 33) and trace quantities of phenol with a maximum at about 200°C.

No evolution of either PBI or BBB monomers was observed in any of the heating cycles.

B. Discussion

The results on the change of mechanical properties with composition and processing conditions confirm that the blending of even 20% of PBI with BBB has a marked effect on the properties which can be achieved. For example, with the 0.59 I.V. PBI, a similar modulus level was found at 350°C for the 80/20 blend as was exhibited by the pure BBB at about 475°C. Furthermore, the variation of properties with processing temperature also shows that both the modulus and strength of the pure BBB increases only slowly so that at a processing temperature of 475°C for the blend, the modulus of the 0.59 I.V. blend is approximately 0.5×10^6 psi compared to 0.3×10^6 psi for the pure BBB. The strength of the blend is also much higher, being 7.0×10^3 psi compared with 3×10^3 psi for the pure material. However, above 500°C the properties of the pure BBB increase rapidly with processing temperature, reaching a similar level to that of the blend at 550°C.

The pure PBI, on the other hand, shows very much better properties than either the blend or the BBB when processed at 475°C. The micrographs and x-ray data show that this is a bonding effect as opposed to a total melting of the polymer, e.g. the crystallinity of the 0.59 I.V. and the 0.93 I.V. materials, which are completely different, do not change during the processing.

Taken together, these results suggest there are at least two temperature activated processes which lead to the bonding together of the polymer particles. In the pure BBB, the initial effect is a compaction of the open porous material, leading to the orientation effects observed by x-ray but not to any marked degree of bonding. Above about 500°C, however, bonding together of the polymer occurs giving rise to the improvement in properties. This process probably also accounts for the similarity in properties between BBB and the blends above 500°C. In the pure PBI, no similar compaction occurs since the material is initially more dense. However, a very distinct bonding occurs at 475°C, the only temperature tested, giving rise to the high modulus and strength of these materials.

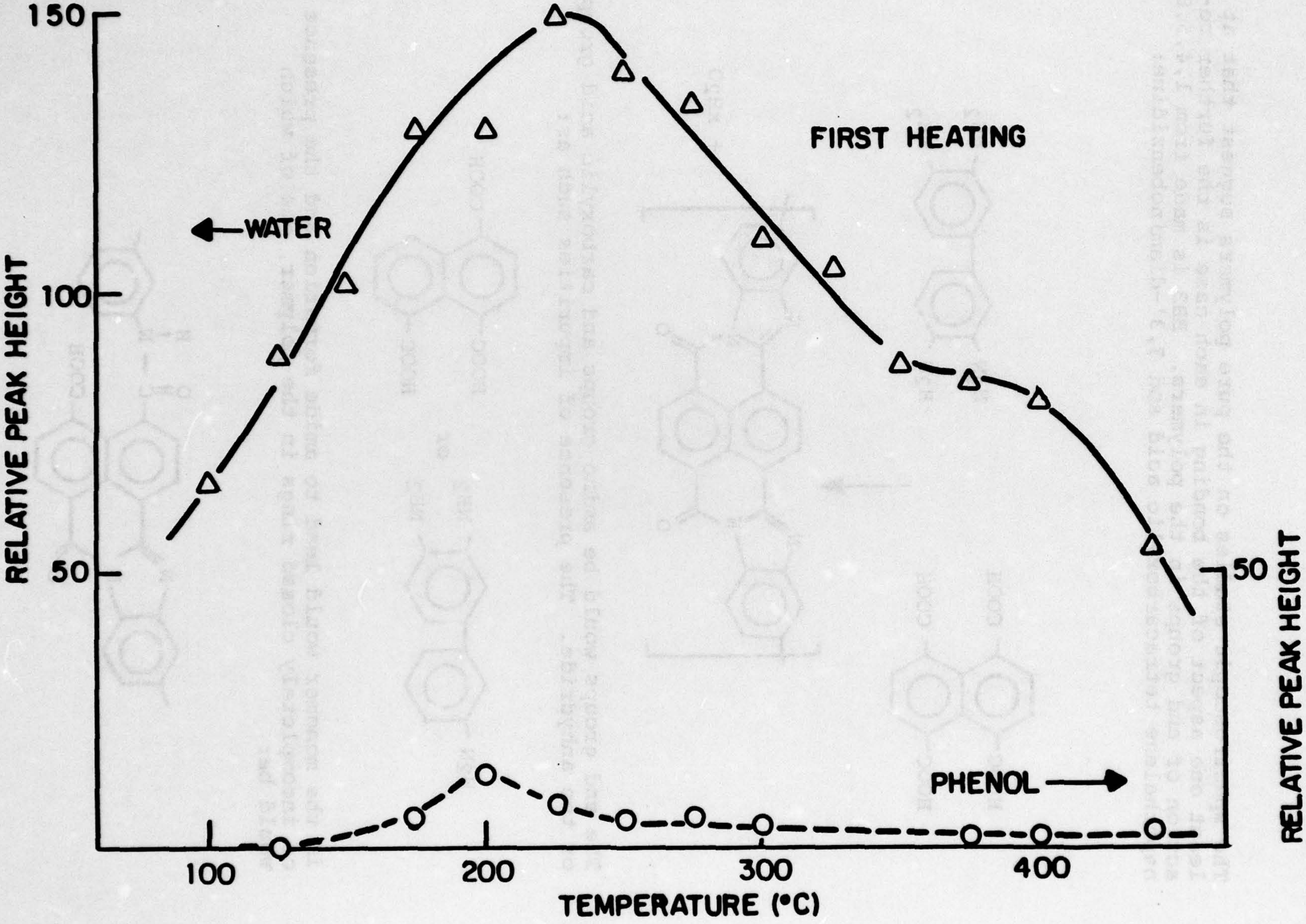
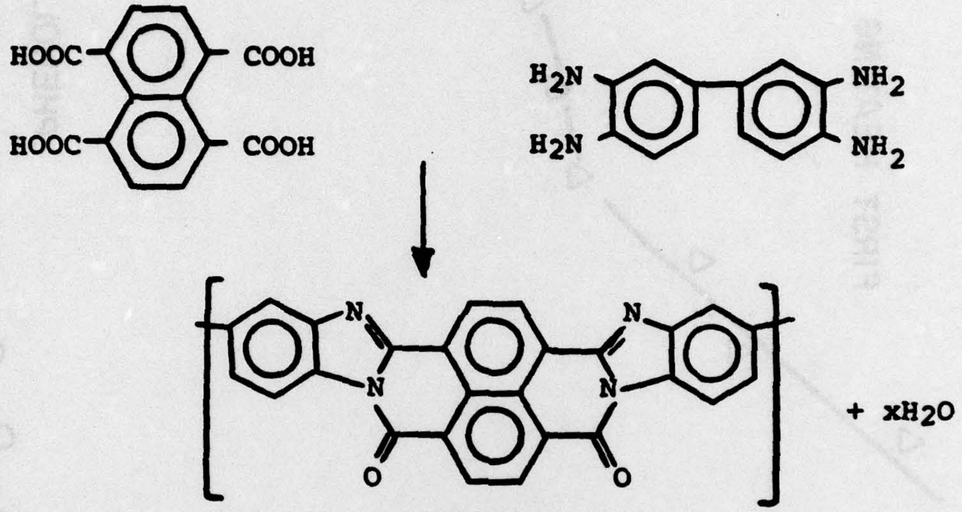
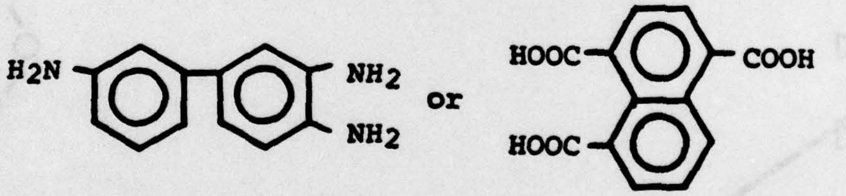


Fig. 33. Water and Phenol Evolution for 60/40 Mixture BBB/PBI (25975-19-11) Sample Pressed at 475°C

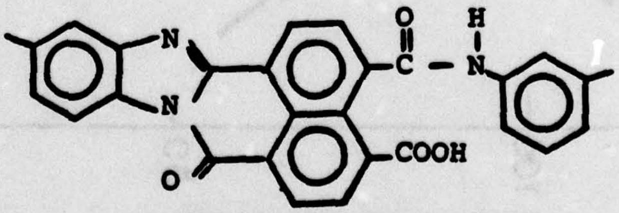
The spectroscopic studies on the pure polymers suggest that at least one aspect of the bonding in each case is the further reaction of end groups in the polymers. BBB is made from 1,4,5,8,-naphthalene tetracarboxylic acid and 3,3'-diaminobenzidine:



The end groups would be amino groups and carboxylic acid groups or the anhydride. The presence of impurities such as:

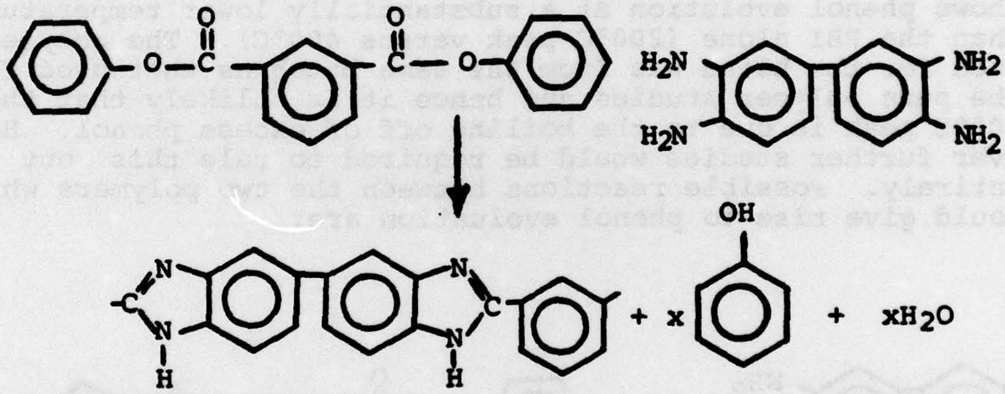


in the monomer would lead to amide formation and the presence of incompletely closed rings in the polymer, one of which would be:



As already stated, further reaction of the end groups would liberate water. The fact that the carbonyl absorption, as shown by infra-red analysis, disappears after heat treatment of the BBB to 475°C is suggestive of an end group reaction taking place. Unfortunately the mass spectroscopic data cannot be used to confirm this since on the first cycle - when most of the reaction would be expected to occur - the evolution of absorbed water is masking the evolution of "reactive" water. Furthermore the limitation of the scan to less than 450°C does not bring the sample up to the temperatures at which the greatest change in BBB properties were observed (i.e. 500°C). However the upturn in water evolution at about 400°C on the second and third runs may also be indicative of end group reactions at these temperatures (Figures 25, 29).

PBI is also made from 3,3'-diaminobenzidine, but condensed with diphenylisophthalate:

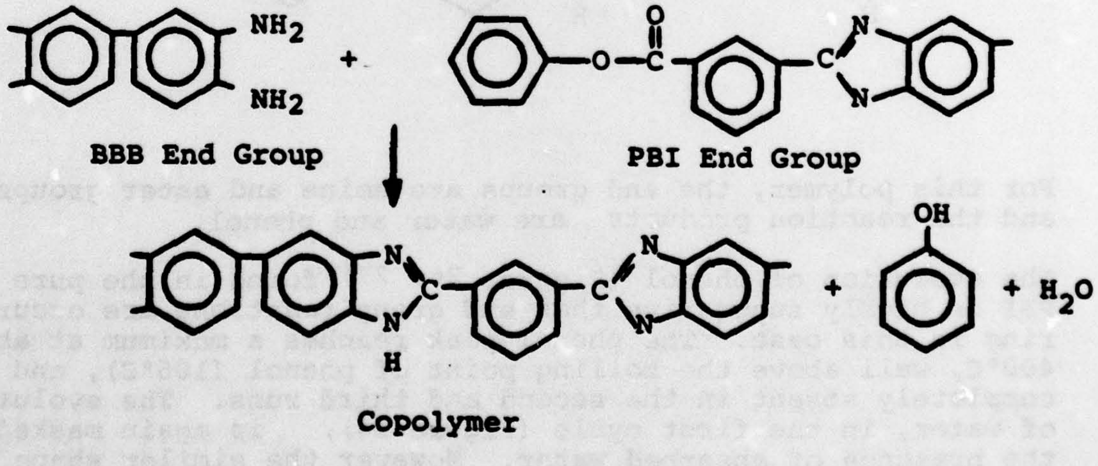


For this polymer, the end groups are amine and ester groups, and the reaction products are water and phenol.

The evolution of phenol (Figures 26, 27) found in the pure PBI is highly suggestive that end group reactions are occurring in this case. The phenol peak reaches a maximum at about 400°C, well above the boiling point of phenol (185°C), and is completely absent in the second and third runs. The evolution of water, in the first cycle (Figure 24), is again masked by the presence of absorbed water. However the similar shape of the curves for water and phenol on subsequent cycles (Figures 25 & 27), is again at least consistent with further end group reactions occurring when temperatures close to the original processing temperature are reached.

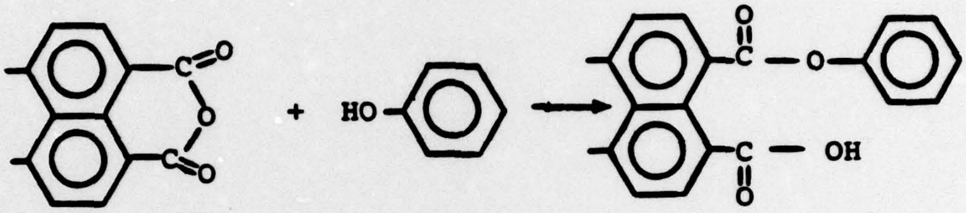
The results with blends do not clearly indicate whether the third process, namely BBB/PBI interaction, is occurring. However each individual technique used to study these samples does show some evidence that such reactions do take place. The fact that the properties are substantially improved at the 20% PBI level is one indication for this since it is not until the 40% PBI level that a PBI matrix is set up. Secondly the optical micrograph evidence, which shows that the PBI-rich phase grows with increasing processing temperature. Thirdly, the higher moduli exhibited by the co-precipitated material could imply that a PBI-BBB interaction was occurring within the particles. The low strengths of these latter materials probably arises because the interparticle boundaries are principally BBB/BBB. Fourthly the transmission electron micrographs show a "softening" of the boundaries between PBI and BBB phases (at 475°C) as if at least in this region some bonding is occurring.

Finally, the first heating cycle of the 50/50 blend (Figure 30) shows phenol evolution at a substantially lower temperature than the PBI alone (200°C peak versus 400°C). The polymer used for the blend was from the same batch as that used for the pure polymer studies and hence it is unlikely that the 200°C peak is due to the boiling off of excess phenol. However further studies would be required to rule this out entirely. Possible reactions between the two polymers which could give rise to phenol evoluation are:



Similar reactions can occur wherever the amine group occurs, such as in partially cyclized rings in the main chain.

The anhydride end groups on the BBB are susceptible to attack from phenol, water or amine groups. For example, with free phenol, the reaction would be:



BBB End Group

These groups can in turn react with available amines to form water and phenol.

The positive effect of increasing time, particularly at higher temperature (Table III) is consistent with a temperature-activated process and suggests that temperatures greater than 400°C are preferred. The effect of increasing pressure is to raise the glass transition temperature. The lower properties at higher processing pressures may be accounted for by the decrease in mobility of the molecules which serves to suppress the temperature-activated processes. This means that a balance may have to be struck between compaction, which requires a high pressure, and bonding which progresses more readily at a lower pressure.

Thus the studies indicate that the improved properties of high temperature processed BBB, PBI and blends are contributed to, at least in part, if not in total,by three temperature activated processes. Firstly,end group reactions within the PBI which peak at temperatures of about 400°C. Secondly,end group reactions within the BBB which probably occur at temperatures close to 500°C. Thirdly,reactions between the polymers, possibly of end groups on the PBI with partially

cyclized BBB at lower temperatures (200-300°C). The temperature ranges in which the reaction products were evolved are certainly consistent with the temperatures at which improved properties could be observed. However, the best properties observed were produced at temperatures higher than those at which the peak evolution of reactive products occur. Thus, other processes may be occurring, e.g. improving the compaction and hence contact between the polymer particles.

SECTION IV

RECOMMENDATIONS

It is recommended that further studies be directed at confirming the phenol evolution, at low temperatures, observed in the 50/50 mixture of BBB and PBI. The identification of end group reactions or reactions with partially cyclized rings as a major source of property improvement suggests that other additives may be identified with suitable end groups, which could also improve the processability of BBB.

Another area which may be studied is that the phenol acts as a plasticizing agent leading to a lowering of the compaction temperature in the BBB-PBI mixtures. Various plasticizing agents have been examined previously but phenol itself has not been used.

Finally, all of the samples heated in the mass spectrometer showed some evolution of CO_2. This could be due to decarboxylation reactions of the carboxylic acid end groups. This reaction would be in competition with the polymerization reactions and, if it could be suppressed, improved processability may be achieved.

SECTION V

REFERENCES

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SECTION VI

LIST OF PERSONNEL

During the course of this effort, the following members of the Celanese Research Company professional scientific staff have contributed to the progress of the investigation:

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At the Celanese Research Company, the work was performed within the Materials and Engineering Research Department under the direction of Dr. G. Farrow, Research Director and managed by Dr. C. V. Evins, Manager, Physics Section. Contract Administration was the responsibility of Dr. Joseph R. Leal, Senior Staff Associate.