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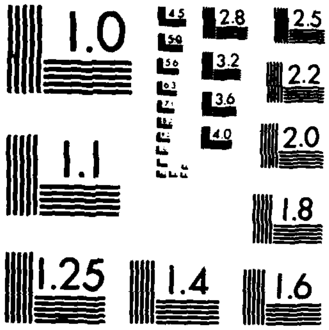
CHEMICAL ENGINEERING T A SPECKHARD ET AL FEB 86 TR-9
UNCLASSIFIED N00014-83-K-0423 F/G 11/9 NL



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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER 9	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Ultimate Tensile Properties of Segmented Polyurethane Elastomers: Factors Leading to Reduced Properties of Polyurethanes based on Non Polar Soft Segments		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Thomas A. Speckhard and Stuart L. Cooper		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K0423
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemical Engineering University of Wisconsin, Madison, WI 53706		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy St. Arlington, VA 22217		12. REPORT DATE Oct. 11, 1986 13. NUMBER OF PAGES 51
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

To be published in Rubber Chemistry and Technology.

18. SUPPLEMENTARY NOTES

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NOV 04 1986
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Ultimate Tensile Properties, Non Polar Soft Segment, Premature Phase Separation, Strain Induced Crystallization, Compositional Heterogeneity.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

See next page.

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ABSTRACT

Polyurethane block copolymers based on non-polar soft segments such as polyisobutylene, polybutadiene, and polydimethylsiloxane possess some desirable chemical and transport properties compared with conventional polyether or polyester polyurethanes. Unfortunately, the reported tensile properties of non-polar soft segment based polyurethanes are poor relative to those of conventional polyurethanes. Several explanations for this behavior have been suggested based on differences in soft segment functionality, molecular weight, glass transition temperature, crystallizability, and compatibility with the hard segment. These explanations are examined in light of the literature and some new experimental results. All of the above factors can lead to poor tensile properties; however, the [illegible] properties of polyurethanes based on non-polar soft [illegible] appear to be a lack of soft segment crystallizability [illegible] possibly an excessively high degree of phase [illegible]. Additional work is needed to more fully understand [illegible] listed above.

ULTIMATE TENSILE PROPERTIES OF SEGMENTED POLYURETHANE ELASTOMERS: FACTORS LEADING TO REDUCED PROPERTIES FOR POLYURETHANES BASED ON NON-POLAR SOFT SEGMENTS

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May 1985
Revised February 1986

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ABSTRACT

Polyurethane block copolymers based on non-polar soft segments such as polyisobutylene, polybutadiene, and polydimethylsiloxane possess some desirable chemical and transport properties compared with conventional polyether or polyester polyurethanes. Unfortunately, the reported tensile properties of non-polar soft segment based polyurethanes are poor relative to those of conventional polyurethanes. Several explanations for this behavior have been suggested based on differences in soft segment functionality, molecular weight, glass transition temperature, crystallizability, and compatibility with the hard segments. These explanations are examined in light of the literature and some new experimental results. All of the above factors can lead to poor tensile properties; however, the only inherently limiting factors on the tensile properties of polyurethanes based on non-polar soft segments appear to be a lack of soft segment crystallizability under strain and possibly an excessively high degree of phase separation. Additional work is needed to more fully understand the effects of the variables listed above.

I. Introduction

The wide range of physical properties and morphologies that can be obtained by changing the chemical components, composition and processing history of segmented polyurethane elastomers has generated a great interest in understanding the structure-property relationships of these materials with the ultimate goal of being able to tailor materials to meet specific applications. Thus, since their introduction[1], linear segmented polyurethane elastomers have been the subject of numerous studies using a wide variety of experimental techniques[2-6]. Two properties of commercial importance are the high tensile strength and toughness of many polyurethane elastomers especially in contrast to other elastomers (see Table 1). Therefore, factors giving rise to high strength and toughness have been extensively investigated[2-14], and deformation mechanisms have been proposed by several authors[7,8,15-20].

Conventional polyurethane elastomers are $(AB)_n$ block copolymers in which the soft segments are polyether or polyester macrodiols. Recently, polyurethane elastomers incorporating soft segment diols based on polyisobutylene (PIB), polybutadiene (PBD), and polydimethylsiloxane (PDMS) have been introduced and their properties have been investigated[14,21-35]. When compared with polyester polyurethanes, these materials demonstrate superior hydrolytic stability and lower moisture permeability. Other advantageous properties of one or more of these families of materials include higher oxidative stability, improved low temperature flexibility, and increased or decreased gas permeability. Structure-property studies have also indicated that these materials exhibit a higher degree of phase separation than conventional polyurethanes which is not surprising since they have no potential for soft segment-hard segment hydrogen bonding and have an increased segmental polarity difference.

Despite the increased degree of phase separation which is generally thought to improve mechanical properties[2-8], a review of the literature indicates that the tensile strength and toughness of PBD, PIB, and PDMS polyurethanes are inferior compared with conventional polyurethanes. Table 2 contains tensile data from the literature of typical and 'exceptional' properties for polyurethanes based on different soft segment types. Several explanations have been advanced for the observed difference in tensile properties based on the differences in soft segment glass transition temperature (T_g), crystallizability, functionality, molecular weight, and compatibility with the hard segments[14,21-27,33]. In this contribution these explanations are discussed and examined in light of the polyurethane and related elastomer literature along with recent experimental results from this laboratory. The discussion is divided into sections concerning the effects on tensile properties of the soft segment functionality and molecular weight, soft segment glass transition temperature, strain-induced crystallization of the soft segments, overall molecular weight and compositional heterogeneity, and the degree of phase separation and other morphological factors.

II. Strengthening and Deformation Mechanisms in Polyurethanes

Befor examining explanations of the relatively poor tensile properties of PIB, PBD and PDMS based polyurethanes it is appropriate to briefly discuss the processes that have been identified as leading to high strength in conventional polyurethane elastomers along with the deformation mechanisms of these materials. Smith[7,8,36] has noted that for a material to exhibit toughness and strength it must contain two phases. In the case of elastomers these two phases normally consist of a rubbery amorphous matrix containing glassy or crystalline domains or filler particles. Accordingly, Smith[7] has identified the following strengthening processes: in the matrix - viscoelastic dissipation of energy near the tip of a crack, strain-induced crystallization, and development of highly oriented chains; for filler particles or plastic domains - deflection or bifurcation of cracks, cavitation, and plastic deformation of domains. These concepts are based on a three step model for fracture involving an initiation step, slow crack growth, and catastrophic crack propagation[7]. Since initiation is largely controlled by flaws or heterogeneities in the sample and catastrophic propagation occurs once a crack reaches a certain size, strengthening processes are generally thought to retard slow crack growth or to prevent cracks from reaching catastrophic size. In the rubbery phase crack growth can be retarded by energy dissipation through viscoelastic processes near the crack tip particularily in the narrow temperature region of leathery viscoelastic response. Highly oriented chains tend to impede the growth of cracks transverse to the applied load while strain-induced crystallization generates plastic domains which retard and deflect growing cracks. Filler particles or plastic domains may also deform plasticly in high stress regions thereby relieving stress concentrations and dissipating energy. Small particles also tend to induce the formation of small cavities which due to surface effects are more stable than large cavities. Several or even all of these processes can operate simultaneously depending on the structure of the elastomer and the test conditions. For a more detailed discussion of processes leading to high strength in polyurethanes and other elatomers, the reader is referred to the appropriate literature[7,8,36].

In the specific area of polyurethane block copolymers, several investigators have measured the deformation response of the hard and soft segments and the domain structure, primarily by infrared dichroism, infrared adsorption as a function of strain, wide angle x-ray scattering (WAXS), small angle light and x-ray scattering (SALS and SAXS), and birefringence measurements[15-19,37-42]. Bonart and coworkers[15,16,42] have proposed the following mechanism for deformation in polyurethane block copolymers with crystallizable hard segments. At relatively low strains (200%), strain-induced crystallization of the positively oriented (chain backbone aligned with the stretch direction) soft segments can occur depending on the soft segment type while the hard segments exhibit an overall negative orientation. Fibrillar hard segments for which the long axis dimension coincides with the polymer chain axis will assume a positive orientation while chains in lamellar hard segment domains whose long axes are perpendicular to the polymer chain backbone will be negatively oriented due to the torques applied by the soft segments. At higher elongations (500%), the lamellar domains are disrupted and all of the hard segments assume a positive orientation.

Subsequently, other authors have confirmed the general features of this model for various polyurethane materials. It has also been suggested that the observation of negative hard segment orientation could be explained by deformation mechanisms inherent in spherulite deformation[18]. Recently, Falabella et al.[20] have constructed constitutive equations for the orientation response in polyurethane elastomers by assuming that the hard and soft segments act in series under load.

III. Polyol Functionality and Molecular Weight

In some investigations of the properties of polyurethane elastomers based on relatively non-polar soft segments such as PIB, PBD, and PDMS, the authors have suggested that the observed reduction in tensile properties relative to conventional polyurethanes may be due to the use of polyols whose molecular weight or functionality precludes the attainment of optimum properties[24,25,30]. The effects of soft segment molecular weight on the properties of conventional polyurethanes have been investigated extensively[2,11,12]. In most cases polyurethanes possessing soft segment molecular weights in the range of 2000-3000 were found to have optimum properties. Materials based on lower soft segment molecular weights suffered from a lower degree of phase separation and an inability of the soft segments to crystallize under strain. Smith[8] has suggested that smaller hard segment domains at equivalent volume fractions should be more effective at stopping catastrophic crack growth through the soft segment matrix. At equivalent hard segment contents, lower soft segment molecular weight materials have shorter average hard segment sequence lengths and might be expected to have smaller hard segment domains. Recent work using small angle x-ray scattering (SAXS) has supported this concept[12,14,31]. Thus, materials with large soft segment molecular weights would tend to possess poorer tensile properties. As a result of these competing processes, optimum tensile properties are observed at soft segment molecular weights of

2000-3000.

Ono et al.[22] and Petrov and Lykin[23] studied the effect of polybutadiene molecular weight on the properties of the corresponding polyurethanes. Ono et al. found that many properties improved as molecular weight decreased from 3000 to 1350, including a doubling of tensile strength from 5 to 10 MPa (6.9 MPa = 1000 PSI). This could be a significant factor since most of the reported work, including the studies reporting optimum properties (Table 2), has been done on materials with PBD soft segments with molecular weights greater than 2000. However, it should be noted that the materials studied by Ono et al. were prepared at a constant molar ratio of hard segment to soft segment. Thus while the soft segment molecular weight decreased from 3000 to 1350 the hard segment content increased from approximately 25 to 75%. This large change in hard segment content casts doubt upon the attempt to interpret the variation in properties solely in terms of an effect of soft segment molecular weight. It should also be noted that the increase in tensile strength was accompanied by a decrease in elongation at break (600 to 200%). This tradeoff behavior between tensile strength and elongation at break is customary with changes in hard segment content. Similar results have been presented by Petrov and Lykin[23], Zapp et al.[28] and Tyagi et al.[32] on PBD, PIB and PDMS based polyurethanes respectively. In all of these studies hard segment content varied inversely with soft segment molecular weight.

Recently, Speckhard et al.[14,31] have investigated the effects of soft segment molecular weight at constant hard segment content on the properties of PIB polyurethanes. Over the molecular weight range studied (1800-11000), tensile properties decreased with increasing soft segment molecular weight. Thus, it appears that some improvement in tensile properties may be obtained by using lower soft segment molecular weights (<1500) than have generally been reported in the literature. The fact that optimum properties appear to be obtained for these polyurethanes in a lower molecular weight range than for conventional polyurethanes is not surprising, since unlike conventional polyurethanes they do not demonstrate a marked improvement in either the degree of phase separation or the ability to crystallize under strain with increasing soft segment molecular weight. The effects of strain-induced crystallization and phase separation will be discussed further in later sections.

The average functionality and functionality distribution of soft segment polyols can also markedly affect the tensile properties of the resulting polyurethane. Segments with less than two functional groups inhibit chain extension and thus lead to lower molecular weight material. Schollenberger and Dinbergs[13,43] have shown that decreasing the total molecular weight below a certain threshhold value leads to a dramatic reduction in tensile properties. Segments with functionalities greater than two promote crosslinking and network defects which result in increased phase mixing and lead to poorer tensile properties[2]. It should be noted that a small amount of crosslinking may actually lead to improved properties (for further discussion see section VII). Soft segments with a number average functionality of 2.0 but a broad distribution of functionalities contain many segments with functionalities both greater and less than two and therefore suffer from a combination of the effects described above. Polyether and polyester soft segments normally possess a narrow distribution of functionalities with an average functionality close to 2.0, and thus the effects of soft segment functionality in conventional polyurethanes have not been extensively studied.

Problems associated with the functionality of hydroxy-terminated PBD and its effects on mechanical properties have been investigated by Petrov and Lykin[23] and Schneider et al.[24-26]. Petrov and Lykin studied materials based on soft segment polyols with functionalities less than two and found, as expected, that the mechanical properties improved as the average functionality of the polyol approached two. It is interesting to note that in the range of functionalities examined (1.65-1.98), the tensile strength tripled while the elongation at break only increased slightly. Similar results have been obtained on PIB polyurethanes[28]. Schneider et al.[24,25] first studied materials based on a hydroxy-terminated PBD that had an average functionality greater than two with a broad distribution of functionalities[44]. They suggested that the properties of the material suffered from some gel formation during synthesis due to the presence of soft segments with functionalities greater than two, network defects, and possibly low molecular weight because of the presence of monofunctional oligomers. In a later study[26], the PBD macroglycol used had a narrow distribution of functionality with an average functionality of 1.97. However, there was not a dramatic improvement in tensile properties. Compared to their previous work the authors observed lower values of tensile strength and higher values of elongation at break, a result that might be expected on the basis of fewer crosslinks in the material.

In studies of PIB polyurethanes, Speckhard et al.[14,30,31] reported results similar to those of Schneider and his coworkers. In the initial study[30] the PIB oligomer used had an average functionality of 1.9. The materials exhibited poor tensile properties which were ascribed to an overall low molecular weight of the polyurethane due to the low soft segment functionality. Later studies[14,31] using a PIB diol with an average functionality of 2.0 and a narrow functionality distribution[45,46] showed only small increases in tensile properties. (Recently, questions concerning the functionality of the PIB oligomer have been raised[47].)

Although, soft segment molecular weight and functionality do influence mechanical properties it does not appear that optimizing these parameters will produce properties comparable with those of conventional polyurethanes. However, the effects of soft segment molecular weight and functionality should be carefully noted in studies examining the effects of other variables on the tensile properties of polyurethane elastomers especially when conclusions are drawn by comparison with the results of other studies.

IV. Soft Segment Glass Transition Temperature

It is well known that tensile properties of polyurethane block copolymers are dependent on temperature[48]. Samples tested below the soft segment glass transition are brittle and behave like plastics. Above the glass transition or melting point of the hard segments the material behaves like an amorphous uncrosslinked rubber. Between transition temperatures of the hard and soft segments the material exhibits behavior typical of a thermoplastic elastomer with increasing modulus and strength as the temperature is lowered. Thus, tensile properties reflect the viscoelastic state of the material at the test conditions. For example, Lilaonitkul and Cooper[6] have explained differences in the room temperature tensile properties of polyether and polyester polyurethanes by observing, based on dynamic mechanical analysis, that at room temperature the polyether polyurethanes were in the rubbery plateau region whereas the polyester samples were in the leathery region of viscoelastic behavior. Smith[36,48] has noted that to unambiguously compare the ultimate tensile properties of different elastomers it is necessary to remove factors related only to experimental conditions. Therefore, to compare the properties of different elastomers, Smith has developed the failure envelope concept[7,36] which compensates for the effects of test temperature and strain rate on the ultimate properties of elastomers. While the failure envelope is only applicable for materials to which time-temperature superposition applies, and is therefore generally not applicable to phase separated elastomers due to strain induced changes in morphology, some of the associated concepts are still applicable to polyurethane block copolymers[7,8]. Thus, Smith suggests comparing properties of polyurethane block copolymers at equivalent values of $T-T_g$, where T is the test temperature and T_g is the soft segment glass transition temperature.

In light of the above discussion the question arises as to whether the poorer tensile properties of non-polar soft segment based polyurethanes in comparison with conventional polyurethanes are at least partly attributable to differences in the soft segment glass transition temperatures. That this could be the case is illustrated by looking at typical soft segment glass transition temperatures for polyurethanes based on different soft segments (Table 3). Generally, the non-polar soft segments have lower glass transition temperatures, especially those based on PDMS. It should be noted that the glass transition temperatures of conventional polyurethanes can change markedly with hard segment content, soft segment molecular weight, and other factors because of changes in the degree of phase separation. Non-polar based polyurethanes because of their greater segmental incompatiblity generally exhibit a relatively constant T_g with respect to changes in hard segment content, soft segment molecular weight, and hard segment type[14]. In order to more fully examine the effects of the soft segment T_g on the tensile properties of polyurethanes we have performed tensile experiments on conventional and non-polar soft segment based polyurethanes at several temperatures both above and below room temperature. The results of these tests which allow for comparison of samples at equivalent values of $T-T_g$ are discussed below.

IV.A. Experimental

Stress-strain tests were performed on several families of polyurethane block coplymers as a function of temperature. Poly(tetramethylene oxide) (PTMO)[49,50], PIB[14,30] and PDMS[33] based materials previously investigated were tested along with PTMO and PBD based samples prepared by a two-step prepolymer approach in solution similar to that described previously[33,51-53]. Except where noted the hard segments of these materials and those described from the literature are based on 4,4'-diphenylmethane diisocyanate (MDI) and butanediol (BD). One series of polyurethane zwitterionomers based on poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), PTMO and PBD soft segments[52] was also investigated. The sample nomenclature used is as follows: sample PTMO-1000-50 refers to a sample based on PTMO/MDI/BD with 50 weight percent MDI/BD and a 1000 molecular weight PTMO soft segment.

Uniaxial stress-strain data were taken on an Instron table model tensile testing device at a constant rate of strain, based on the initial gage length, of 23 percent per minute. Samples were prepared using an ASTM D1708 standard die. Tests were performed at temperatures from -70 to 80°C with the aid of an Instron Environmental Testing Chamber. Values for stress were calculated based on the initial cross-sectional area.

IV.B. Results and Discussion

Tensile properties at different temperatures for selected polyurethane block copolymers are displayed in Table 4. Room temperature properties were similar to previously reported values except for the PIB based sample which was from a different synthesis batch and exhibited improved properties[14]. The variation of properties due to changes in polymerization conditions will be discussed in section V. Table 4 shows that comparing non-polar polyurethanes with the PTMO based sample at roughly equivalent values of $T-T_g$ (60-70°C) indicates that PTMO-1000-50 has 2-3 times greater strength and extensibility. However, it should be noted that particularly in the case of the PDMS based materials, the non-polar based samples exhibited room temperature properties of a typical nature (see Table 2) whereas the properties of PTMO-1000-50 would fall closer to the exceptional category. Furthermore, on a percentage basis, the increase in modulus and strength of the non-polar based materials as the temperature is lowered could be significant if non-polar based materials exhibiting exceptional properties at room temperature showed similar increases. For example, the roughly threefold increase in modulus and strength of sample PDMS-2000-25 when the temperature is lowered from 25 to -50°C would translate to a tensile strength at $T-T_g = 70^\circ C$ of 63 Mpa for one of the PDMS based samples with a room temperature tensile strength of 21 MPA listed in Table 2. The PIB and PBD based materials however, only show about a 50% increase in modulus and strength when going from room temperature values to data at $T-T_g$ of $60-70^\circ C$. This is primarily due to the smaller change in test temperature ($20^\circ C$) which is a result of the higher T_g of PIB and PBD relative to PDMS. A careful examination of the data in Table 4 (and other results not shown) indicates that for all soft segment types a reduction of $35^\circ C$ in the test temperature roughly doubles the strength and modulus of the material. Thus, it is possible in light of the results shown here and the limited data available on PDMS based polyurethanes in the literature to attribute their low room temperature tensile properties to their correspondingly low soft segment T_g. However, a similar explanation for PBD and PIB based materials would not seem to be warranted.

The data in Table 4 (as well as other data not presented) exhibit three other interesting aspects that should be noted. First, at equivalent values of $T-T_g$ all of the materials have roughly equivalent moduli. This indicates that the processes leading to better strength and extensibility in certain polyurethanes do not necessarily produce changes in the modulus of the sample. Second, for all of the samples changes in temperature did not appreciably affect the elongation at break. Finally, one major difference between the conventional and non-polar soft segment based materials is the lower elongation at break of the latter. In fact, many although not all polyurethanes based on non-polar soft segments studied previously have exhibited low extensibility, even in cases where soft segment functionality should not be a problem[14]. These aspects will be discussed further in the sections which follow.

V. Strain-Induced Crystallization

As noted above, conventional and non-polar soft segment based polyurethanes have similar moduli at equivalent hard segment content and $T-T_g$ but quite different ultimate tensile properties. These effects can be seen graphically in Figure 1 which displays room temperature stress-strain curves for some of the better conventional (PTMO and PCL) polyurethanes and the exceptional non-polar based materials of Table 2. The nomenclature is the same as described previously except two samples are based on a 20/80 mixture of the 2,6 and 2,4 isomers of toluene diisocyanate (TDI), and one sample is based on hydrogenated MDI (H_{12}MDI, 4,4'dicyclohexylmethane diisocyanate). Figure 1 also shows that the better conventional polyurethanes have higher hard segment content than the exceptional non-polar based materials. Higher hard segment content materials based on PIB and PBD soft segments have been examined but generally exhibit very brittle behavior with elongations at break of less than 100% and often less than 50%[14,24,25]. On the other hand, non-polar soft segment based materials that do exhibit high elongations at break have relatively low tensile strength. In particular they do not exhibit the upturn in the stress-strain curve with increasing elongation that is observed for good conventional polyurethane elastomers.

Figure 1 also shows data on a typical PPO based polyurethaneurea made with ethylene diamine (ED) as the chain extender instead of BD[54].

It is interesting to note that the PPO based sample exhibits behavior similar to that of the exceptional non-polar based materials. Low tensile strength for most PPO based polyurethanes and polyurethaneureas compared with good conventional polyurethane elastomers is well documented[1-4,11,55-58] and is generally attributed to the inability of the atactic polypropylene oxide soft segments to crystallize under strain. It is possible that in some cases the lower properties of PPO based materials are due to lower overall molecular weight because PPO glycols often contain secondary hydroxyl groups which are less reactive than primary hydroxyl groups[1]. Shibatani et al.[53] have shown that the ability of isotactic PPO segments to crystallize under strain can improve the tensile properties of the corresponding polyurethanes relative to atactic PPO based materials. In general, pendant groups on the backbone of polyether or polyester soft segments lead to reduced tensile properties due to inhibition of strain-induced crystallization and increased interchain separation which reduces viscous effects[1-4,58,59]. Also, it is important to note that strain-induced crystallization usually results in an upturn in the stress-strain curve. This is a characteristic feature of good conventional polyurethanes that as noted above is not generally observed for polyurethanes based on non-polar soft segments. Speckhard et al. in a study of polyurethane zwitterionomers[52] attributed the superior ultimate tensile properties of PTMO and PEO based materials compared with those of PBD and PPO based samples to the effects of soft segment strain-induced crystallization since the crystallizable PEO and PTMO based systems exhibited an upturn in the stress-strain curve while the PPO and PBD based materials did not exhibit an upturn.

The fact that PPO and other non-crystallizable polyether and polyester based polyurethanes generally exhibit properties comparable with exceptional non-polar soft segment based polyurethanes suggests that the ability of non-polar soft segments to crystallize under strain should be examined. A review of the literature indicates that while under proper conditions PIB, PBD and PDMS based elastomers can exhibit strain-induced crystallization, when incorporated in polyurethane block copolymers they apparently do not crystallize under strain, at least at the reported conditions. PIB homopolymers and ionomers are known to exhibit strain-induced crystallization[60-62]; however, the behavior was generally observed below room temperature or at higher elongations than normally achieved with PIB polyurethanes. High molecular weight PDMS has also been reported to exhibit strain-induced crystallization, again however below room temperature[9,63,64]. The crystallizability of PBD depends on the relative proportion of its various isomers (cis, trans, vinyl). For example, high cis content PBD elastomers[65] exhibit strain-induced crystallization below room temperature to a greater extent than most commercially available polybutadiene based materials. Thus, since the tensile properties of non-polar soft segment based polyurethanes have been reported at room temperature, it is not surprising that strain-induced crystallization has not been observed.

From the above discussion it would appear that the inability of non-polar soft segments in polyurethane block copolymers to crystallize under strain could be a major factor leading to reduced tensile properties. In order to more fully examine the extent to which strain-induced crystallization is responsible for the improved tensile properties of conventional polyurethanes compared with non-crystallizable soft segment based materials, we have performed stress-strain tests on several series of conventional crystallizable and non-crystallizable, and non-polar soft segment based polyurethanes. Before discussing the results of these studies a more detailed review of the phenomenon of strain-induced crystallization in polyurethane and other elastomers is warranted.

The phenomenon of strain-induced crystallization in crosslinked natural and other crystallizable rubbers is well known and the high strength of crystallizable rubbers has been attributed to it[66-69]. In fact Flory[67] and Mark[68] have attributed the upturn in the stress-strain curves and Mooney-Rivlin plots of natural and other crystallizable rubbers to the occurrence of strain-induced crystallization. However, other authors[70-72] have commonly attributed the upturns in stress-strain curves and Mooney-Rivlin plots to effects related to the finite extensibility of the polymer chains. In this concept, as the rubber is stretched some chains reach the limit of their extensibility and further elongation is only possible by deforming bond angles and bond lengths or by chain rupture. All of these processes require considerably more energy than simple configurational rearrangements and thus lead to increases in the stress. Mark in a later study[73] using specially designed model PDMS networks did observe upturns in the Mooney-Rivlin plots that he attributed to the effects of limited chain extensibility. However, he noted that the upturn was more gradual than that observed for crystallizing systems and occurred at 60-70% of the maximum elongation which is approximately twice what had been expected by theory[71,74]. Mark and Flory had previously argued that any upturn in stress due to finite chain extensibility should be gradual due to reapportionment of the stress from an extended chain to neighboring chains in the network structure[68]. In summary, it appears that under appropriate conditions both strain-induced crystallization and limited chain extensibility can lead to an upturn in the stress strain curve. However, practically only crystallizable rubbers exhibit high tensile strengths (20 MPa)[67,72], and strain-induced crystallization is probably the major factor leading to increased strengths in these materials[74].

Direct evidence for strain-induced crystallization in polyurethanes and other elastomers is normally obtained by wide angle x-ray scattering (WAXS), although other techniques such as density and birefringence measurements, differential scanning calorimetry, and small angle light scattering have been used[7,67,75]. In polyurethane block copolymers, Clough and Schneider[76] have reported strain-induced crystallization of poly(butylene adipate) and poly(tetramethylene oxide) based polyurethanes at 100-200% elongation based on WAXS. Bonart[15,77] has also observed strain-induced crystallization in polyether and polyester polyurethanes by calorimetry and WAXS and has included the phenomenon in his well known model of deformation in polyurethane systems[15]. Llorente and Mark[75] however, have noted that calorimetry and x-ray scattering are relatively insensitive to small amounts of crystallinity and recommended the measurement of the strain optical coefficient (SOC) as a function of temperature. As noted above, indirect evidence for strain-induced crystallization normally consists of an increase in the slope of the stress-strain curve at higher elongation. In addition to being indirect, this method is somewhat arbitrary because normally engineering stress and not true stress values are reported. Therefore, samples which show an increase in true stress may not demonstrate an increase in engineering stress due to the reduction of the cross-sectional area upon elongation. However, since the present interest is with the increase in properties resulting from strain-induced crystallization, more direct evidence for the existence of strain-induced crystallization in the experiments discussed below was not obtained.

V.A. Experimental Results

The experimental procedure and materials studied were described in section IV.A. Crystallization in unoriented samples has been reported for high molecular weight crosslinked rubbers based on PIB, cis PBD, and PDMS at 5[78], 1[79], and -55°C[62] respectively while strain induced crystallization has been observed at temperatures of up to approximately 50 and -20°C for PIB[61] and PDMS[62] based materials. Since incorporation as low molecular weight segments in polyurethane block copolymers would be expected to reduce the crystallizability[16], samples based on PIB and PBD were investigated from room temperature to -40°C while PDMS based samples were studied at temperatures as low as -70°C. Stress-strain curves at several temperatures for samples PIB-3400-27 and PDMS-2000-25 (chain extended with MDEA - see Table 4) are shown in Figure 2. Both samples show an increase in strength and modulus with decreasing temperature as noted in the previous section. The elongation at break however, is not markedly influenced by changes in temperature. Most important, the shape of the stress-strain curve, particularly for the PIB sample, is not altered appreciably by temperature variation. If strain-induced crystallization was occurring to any appreciable extent, one would expect to see some indication of an upturn in the stress-strain curve. The behavior of sample PIB-3400-27 was typical of all the PIB and PBD based samples investigated. The PDMS samples tended to exhibit an almost linear stress-strain curve at low temperatures as opposed to a plot of gradual decreasing slope at higher temperatures similar to that exhibited by the PIB and PBD based materials. This could be an indication that some strain-induced crystallization is occurring; however, in no case did a sample exhibit a clear upturn in the stress-strain curve as is typical of polyether and polyester polyurethanes (Figure 1). Furthermore, Smith[7,8] has argued that if strain-induced crystallization is a major strengthening factor in a material, then at temperatures above which crystallization can occur the material should exhibit a sudden large reduction in properties. Although the properties of polyurethanes based on non-polar soft segments do decrease with increasing temperature, the change is gradual and can probably be better explained on the basis of viscoelastic ($T-T_g$) effects discussed previously.

To further investigate the role of strain-induced crystallization in the tensile properties of conventional polyurethanes, stress-strain data for PTMO based polyurethanes were taken as a function of temperature from 25-80°C. Results for two samples, which were also studied in a similar fashion by Smith[7], are shown in Figure 3. Sample PTMO-1000-50 (ET-38-1) shows the typical upturn in stress at room temperature and to a lesser extent at higher temperatures with a gradual reduction in properties. Other samples based on PTMO generally showed similar behavior. However sample PTMO-2000-28 (ET-24-2) shows a great reduction in properties between 40 and 60°C that Smith[7] suggested was due to a lack of strain-induced crystallization at the higher temperature. Smith cited small angle light scattering data as evidence for strain induced crystallization in PTMO-2000-28 at room temperature. Since PTMO-1000-50 and other PTMO based samples did not display a similar reduction in properties, Smith asserted that strain-induced crystallization was not the major factor leading to high strength in most polyurethane block copolymers. To support this assertion Smith also noted that some poly(propylene oxide) polyurethanes[80] do exhibit relatively good tensile properties.

It should be noted however, that the fact that the other PTMO based samples in Figure 3 and Smith's study[7] do not show a rapid reduction in properties with increasing temperature does not mean that strain-induced crystallization is not occurring in those samples. In fact, as noted previously, WAXS results indicate that strain-induced crystallization does occur in samples of this type[15,76,77]. The other samples in Smith's study had a higher hard segment content or lower soft segment molecular weight which tend to inhibit strain-induced crystallization. Furthermore, the effects of forming crystalline soft domains on the tensile properties of samples with a higher hard segment content will be proportionately less. Also, the fact that some reinforcement is provided by the hard segment domains may allow samples of higher hard segment content to elongate sufficiently such that strain-induced crystallization can occur, although to a lesser extent and probably at higher strains as the temperature is raised. This last effect along with viscoelastic effects ($T-T_g$) could lead to a gradual reduction in properties with increasing temperature as is observed. The more rapid decrease in properties of sample PTMO-2000-28 can be attributed to its low hard segment content which effectively magnifies any strengthening effects due to strain induced crystallization.

Figure 4 displays room temperature stress-strain curves for a family of PTMO based materials[6], an SBS (styrene-butadiene-styrene) triblock copolymer[81] and a PPO based polyurethaneurea with hard segments based on TDI and 4,4' methylene bis(2-chloro aniline)(MOCA)[55]. The PPO based sample exhibits behavior similar to that of the PTMO based samples including a noticeable upturn in the stress-strain curve. However, it should be noted that the PPO based samples with good properties[80] referred to by Smith[7] (and most other PPO based samples with superior properties reported in the literature) and the PPO based sample shown in Figure 4 are both polyurethaneureas that are presumably crosslinked due to the presence of excess isocyanate in the reaction mixture. For example, the sample shown in Figure 4 contains about 12% excess TDI compared to the stoihciometric amount. Therefore, it would be possible to attribute the upturn in the stress-strain curve for the PPO based sample in Figure 4 to the effect of limited chain extensibility in the network structure.

However, Figure 4 also shows that the SBS triblock copolymer[81] exhibits an upturn in the stress-strain curve. In fact this behavior is typically observed for triblock elastomers[81-86]. Also in general, the upturn in the stress-strain curve gradually decreases as the temperature is raised in a manner similar to sample PTMO-1000-50 in Figure 3[82,83],and like polyurethane elastomers, the upturn in the curve occurs at lower strains for materials of higher hard segment content (note the PTMO based samples in Figure 4)[81]. Non-crystallizing filled rubbers can also exhibit upturns in the stress-strain curve that occur at lower strains with increasing filler content[87]. This behavior is attributed to a strain amplification effect. Since the filler does not deform, the local strain in the matrix exceeds the macroscopic strain resulting in an increase in stress due to the finite extensibility of the polymer chains. Because SBS materials display tensile behavior similar to that of good conventional polyurethane elastomers and like polyurethanes they are not chemically crosslinked but possess a phase separated domain structure[2-6], explanations for the tensile behavior of SBS materials may have some validity for polyurethanes and thus merit consideration.

As might be expected because of the complex nature of the materials, different investigators have emphasized the effects of different factors or processes when interpreting the tensile properties of ABA block copolymers. Fischer and Henderson[83] and Bishop and Davison[88] noted the role of the hard domains as multifunctional crosslinks and in creating trapped entanglements. Both the trapped entanglements and the crosslinks serve to distribute the stress allowing the attainment of high elongation and strength. On the other hand, Smith and Dickie[82] and Mojaher et al.[85] have emphasized the role of the domains in stopping crack growth and providing high strength by plastic deformation. In fact, Smith and

Dickie suggest that the existence of covalent bonds between the matrix and the domains is inconsequential, and Smith has presented data that show that different families of elastomers that contain either filler particles or plastic domains (at greater than 20 volume percent) exhibit roughly equivalent toughness[7,8]. Beecher et al.[86] have studied the morphology of a deformed SBS block copolymer by electron microscopy. In the initial region of the stress-strain curve (up to about 100-200% elongation) any continuous polystyrene structures were broken up and the individual domains were deformed into ellipsoids with the long axis in the direction of stretch. From 200-800% elongation no further deformation of the polystyrene domains occurred; this corresponds to the relatively flat portion of the stress-strain curve comparable with the data between 50 and 450% elongation for the SBS sample shown in Figure 4. At about 800% elongation the polystyrene domains began to deform drastically with rupture occurring in the polystyrene phase. This behavior was accompanied by a large increase in the measured stress.

The observations of Beecher et al.[86] would tend to support Smith's view[7,82] that plastic deformation of domains is the major factor leading to high strength in phase separated elastomers. However, conclusions drawn from work on SBS systems may not be directly applicable to polyurethane elastomers for several reasons. First, Bonart's[15] x-ray work suggests a somewhat different morphological behavior for polyurethanes during deformation. In particular the hard segment domains seem to be disrupted in a more gradual manner beginning at lower extension. Second, there is no evidence that fracture in polyurethane block copolymers occurs in the hard phase. In fact the differences in properties with soft segment type discussed previously might suggest that fracture occurs in the soft segment rich phase especially in weaker materials. Cella[89] in work on segmented polyether polyesters, which should be even more similar to segmented polyurethanes than triblock copolymers, suggested that fracture in his samples occurred in the soft segment matrix. Third, effects due to trapped entanglements should be much more prevalent in the triblock materials due to their much higher soft block molecular weight. Obviously, Smith's concept in its simplest form will not be able to explain differences in properties with soft segment type since it does not take into account the properties of the matrix. While failure processes in the soft segment domains are important, it does appear that deformation of hard segment domains is probably the major factor leading to high strength in polyurethane and other phase separated elastomers. Apparently, however, other factors are at work that either supplement this effect or provide reinforcement which prevents rupture until a high enough elongation is achieved for significant plastic deformation of domains to occur.

One process that could function in a supplementary or complementary fashion with domain deformation is strain-induced crystallization. Even if actual crystallization did not occur the cohesiveness and thus the viscous strengthening effect of the matrix is probably greater for crystallizable soft segments[58,59]. Obviously, additional tests are needed on both non-polar and conventional polyurethane elastomers, especially as a function of extension rate and temperature and at high strains to adequately understand the effects of strain-induced crystallization on ultimate tensile properties. Yet, the inability of these materials to crystallize under strain is probably not the cause of the low elongation and brittle behavior exhibited by many non-polar based polyurethanes. Potential factors leading to brittle behavior include the effect of soft segment functionality noted previously and compatibility problems during synthesis resulting in low overall molecular weight and compositional heterogeneity which are discussed in the next section.

VI. Molecular Weight and Compositional Heterogeneity

The effect of the overall molecular weight on the mechanical properties of polymers generally assumes the form of an increase in properties with increasing molecular weight that gradually levels off[2,43]. This trend has been confirmed for polyurethane block copolymers[13,43], although relatively little work has been done because of the difficulty in measuring the molecular weight of the materials and the relative insensitivity of the mechanical properties to changes in molecular weight except at the lowest levels. Figure 5 shows stress-strain curves at room temperature for three PTMO based polyurethane block copolymers with the same chemistry (50 wt.% hard segment, 3/2/1 molar ratio of MDI/BD/PTMO-1000). Sample A[49] was prepared in bulk while samples B and C were prepared in solution as described previously[33,51]. Molecular weights for these samples were measured by gel permeation chromatography in THF at room temperature, and are given as relative values in terms of the equivalent molecular weight polystyrene standard with the same peak retention volume. Values computed in this manner were 130,000; 44,000; and 27,000 for samples A, B, and C respectively. Thus, Figure 5 shows as expected a large decrease in tensile strength and elongation with decreasing molecular weight. It is interesting to note that the initial part of the the curves are identical and that decreasing molecular weight effectively reduces the slope of the curve at higher elongations. Similar behavior has been reported for polyester polyurethanes[13].

This behavior would suggest that the number of bonds in the interfacial area and/or the number of domains through which a single polymer chain passes are important since those are the factors that are primarily being decreased by a reduction in molecular weight. The reduction in properties may simply be due to a higher number of chains in which only one end is anchored in the hard segment domains. This would result in property differences similar to those between AB and ABA block copolymers[86]. Yet, even at a number average molecular weight of 10,000 the average chain would contain about 5 hard and 5 soft segments. However, the addition of only 5 wt.% of an AB block copolymer to the corresponding ABA material has been shown to reduce the tensile strength by 20%[90]. Camargo et al.[91] in a study of reaction injection molded polyurethane elastomers attributed the lower mechanical properties and brittle behavior of non-catalyzed samples, as opposed to the better properties of conventional materials, to the lower molecular weight of the non-catalyzed systems resulting in fewer links between hard segment domains.

Low molecular weight has often been cited as a cause of low mechanical strength in non-polar based polyurethane systems[14,30,31,33,34]. Often, as discussed previously, low molecular weight is a result of poor functionality of the soft segment polyol. Recently, several studies have indicated that polymerization conditions can markedly affect the molecular weight, composition distribution and morphology of the resulting polyurethane elastomer[27,34,92-98]. Macknight and coworkers[27,97] have shown that PBD based polyurethanes reacted in bulk can suffer from phase separation of the reactants leading to a bimodal distribution of hard segment lengths and a broad composition distribution. The samples were of relatively low molecular weight, probably because after phase separation the reactants in each phase are not in stoichiometric ratios[98]. These materials often exhibited two hard segment glass transitions and when fractionated in N-dimethylformamide (DMF) produced hard segment rich and soft segment rich sol and gel fractions respectively. Recently, Macknight and coworkers[34] have studied similar materials polymerized in solution. The solution polymerized materials had higher molecular weight, no evidence of a bimodal hard segment length distribution, and 2-7 times greater tensile strength when compared with the corresponding bulk polymerized samples. The properties of the solution polymerized samples were still low compared to conventional polyurethanes; tensile strengths were below 20 MPa except for one sample with 76 wt.% hard segment. The difference in tensile strength between the bulk and solution polymerized samples are probably due mainly to the differences in molecular weight[99]. The effect of a bimodal hard segment length distribution on tensile properties is not clear although recent work in this laboratory with blends of polyether polyurethanes of different hard segment content, and thus different hard segment length distributions, indicate that the blend of two copolymers exhibits lower tensile properties than a single block copolymer with the same average hard segment content[100].

We have also recently begun to study the effects of polymerization conditions on the molecular weight and composition distribution of the polyisobutylene polyurethane systems whose mechanical properties were investigated previously[14,30,31]. Figure 6 shows stress-strain curves for two series of PIB (2450 MW) based polyurethanes polymerized with (W) and without (WO) catalyst in solution and subsequently poured into a mold at 75°C while the solvent evaporated[14]. Obviously, the samples polymerized in the presence of catalyst have superior tensile properties although again in comparison with conventional polyurethanes the properties are poor. Molecular weights determined in the manner described above are approximately 30,000 and 10,000 for the catalyzed and uncatalyzed samples respectively. In our previous work[14,30,31], we studied samples polymerized in solution[31], polymerized in solution and cured in a heated mold[14] and polymerized in bulk[30]. Preliminary work indicates that in agreement with Bengston et al.[34] the solution polymerized samples have the highest molecular weight and superior tensile properties. We have also fractionated some of these samples in DMF in a manner similar to Xu et al.[27]. The resulting sol and gel fractions are hard segment and soft segment rich respectively although the differences in composition are generally not as large as those observed by Xu et al. This would be expected since in the PIB systems there was no evidence of two hard segment glass transitions. All polyurethane block copolymers would be expected to show some compositional heterogeneity even under ideal conditions (equal reactivity of all isocyanate and hydroxyl functionalities in the system) because of the nature of the reaction at finite molecular weights[101]. Since many of the non-polar based materials have relatively low molecular weights this 'natural' heterogeneity would be magnified, and it is not clear to what extent if any the observed compositional heterogeneity exceeds that predicted under ideal conditions[99,101]. Chen et al.[97] described the large compositional heterogeneity of their PBD based polyurethanes in terms of reactant incompatibility effects; other potential sources of 'excess' heterogeneity would include differences in reactivity of the polyol (soft segment diol) and chain extender either intrinsically or because of differences in mobility in, for example, a bulk polymerization[102]. Recently, polymerization models based on Monte Carlo methods have been developed to simulate the polymerization of polyurethanes under various conditions and distinguish between "natural" and other sources of compositional heterogeneity[99,101,102].

From the above discussion, it is clear that an overall low molecular weight can significantly reduce the properties of polyurethane block copolymers. Excessive compositional heterogeneity is also likely to result in lower properties. Both of these effects are likely to be magnified in non-polar soft segment based polyurethanes due to the greater incompatibility of the reactants. Polymerizing samples in solution appears to lessen these problems; however, the tensile properties are still low compared to conventional polyurethanes. It should be noted that in conventional polyurethanes the opposite behavior is usually observed with the highest molecular weight and tensile properties obtained in bulk polymerizations (for example, note the discussion concerning figure 5.) Thus, in the sense that the high degree of reactant incompatibility in non-polar soft segment based polyurethanes limits the utility of bulk polymerization, reactant incompatibility could be considered as a factor limiting the tensile properties. Since the molecular weight of most of the conventional polyurethane materials whose properties are described in the literature is not reported, it is not clear whether the improved properties obtained in bulk polymerization can be attributed solely to molecular weight effects or if crosslinking or other morphological effects (see section VII) are also important. Again, more studies in which the effects of molecular weight and compositional heterogeneity are explicitly investigated for both conventional and non-polar soft segment based polyurethanes are needed. In particular, careful characterization of conventional polyurethanes polymerized under conditions leading to optimum properties (i.e. bulk polymerization) is warranted. Yet it is apparent that in many of the studies to date on non-polar soft segment based polyurethanes, low molecular weight and excessive compositional heterogeneity have led to low tensile properties.

VII. Phase Separation and Morphological Effects

The two phase structure of polyurethanes is the major morphological factor leading to high strength in linear polyurethane block copolymers[103]. It is well known that polyurethane block copolymers can exhibit differences in domain morphology, degree of phase separation, and superstructure such as spherulites or globules depending on chemical composition and processing and polymerization history[91-96]. However, the effects of these factors on tensile and other mechanical properties is in many cases not well understood. For example, samples that exhibit a very low degree of phase separation often exhibit much poorer properties than materials with a higher degree of phase separation[104]. On the other hand, polyester polyurethanes generally possess better properties than polyether based samples[1,3,4,94] although polyether polyurethanes normally have a higher degree of phase separation[77,94,105]. In this case, as usual, other factors besides phase separation such as differences in the soft segment T_g may be responsible for the difference in tensile properties. In a recent study of polyether polyurethanes with different hard segment length distributions[95], materials with fewer single MDI hard segments exhibited a higher degree of phase separation. These same materials however, possessed lower ultimate tensile properties; the authors suggested that the better phase separated morphology restricted the ability of the soft segments to crystallize under strain because of increased hard segment crystallinity and domain interconnectivity. Macosko and coworkers[91,98] have noted that in reaction injection molded (RIM) polyurethanes rapidly reacting systems result in poorer phase separation but better tensile properties. However, the poorer phase separation is also accompanied by higher molecular weight which should at least partially account for the increase in properties.

Results that suggest that too high a degree of phase separation leads to lower properties are obviously significant for non-polar soft segment based polyurethanes since they normally exhibit a higher degree of phase separation than conventional polyurethanes. Schneider and Matton have suggested[24] that PBD polyurethanes may suffer from poor adhesion between the hard and soft segments. Although there are covalent bonds between the two phases, it may be that the adhesive process occurs primarily through physical bonds; a concept that would be supported by Smith's data[82] discussed earlier. Paul[106] has recently suggested that in order to obtain good interfacial adhesion and consequently superior mechanical properties in two phase polymer blends, one should try to select systems on the 'edge of miscibility'. It has also been noted that in filled rubber better properties are obtained if there is a modulus gradient between the matrix and the filler presumably because the localization of shear stresses is avoided[107]. All of these concepts suggest that broad interfacial zones would be preferable to sharp phase boundaries in order to produce high mechanical strength. The interfacial thickness of a polyurethane block copolymer would be expected to increase with the polarity of the soft segment; this assertion is supported by the available SAXS data[12,14,31,94,108]. Thus, the sharp interfaces in non-polar based polyurethanes may be one inherent factor leading to lower strength when compared with conventional polyurethanes. To test this hypothesis, PDMS based polyurethanes have recently been investigated in this laboratory that incorporate a small amount of polar groups (chloropropyl or cyanoethyl) as side chains or in the PDMS backbone[109,110]. Incorporating cyanoethyl or chloropropyl groups should lead to a lower degree of phase separation and in particular a broader interfacial zone because of the increased polarity of the soft segment and the potential for intersegmental hydrogen bonding. Infrared spectroscopy data indicate the existence of intersegmental hydrogen bonding in the substituted materials which should promote interfacial adhesion[109,110]. Figure 7 displays stress-strain curves of a conventional PDMS based polyurethane (29 weight percent MDI/BD)[33] and the corresponding sample (PCEMS)[110] in which one-fourth of the methyl groups in the siloxane backbone have been replaced by cyanoethyl groups. The cyanoethyl substituted sample clearly has improved tensile properties in accordance with the suggestion that sharp interfaces or lack of interfacial adhesion can lead to reduced tensile properties. However, it should be noted that the cyanoethyl substituted material has a considerably higher soft segment T_g which should also give rise to improved room temperature tensile properties as previously noted. Still, the relatively large increase in extensibility which, as noted in section IV, is not normally associated with a change in the value of test temperature minus the soft segment T_g $(T-T_g)$ suggests that at least some of the improvement in properties is attributable to the differences in interfacial morphology.

Since the morphology of polyurethanes at scales larger than the domain structure (termed superstructure) can be dramatically influenced by processing and polymerization conditions, several investigators have recently sought to understand the effects of changes in the superstructure on mechanical properties[91-98,111]. Camargo et al.[91] have noted that in reaction injected molded systems the formation of large spherulites results in poorer properties because of the tendency for cracks to propagate along spherulite boundaries. A similar explanation could apply to the gross macrophase structure observed by Macknight and coworkers[27,97] in polybutadiene polyurethanes[24]. On the other hand Vallance et al.[96] have attributed the superior properties of a series of as-polymerized polyether polyurethanes compared with identical materials cast from solution to their higher degree of organization of the superstructure. Since changes in the superstructure are also likely to influence the degree of phase separation and other factors, it is unclear to what extent superstructure influences mechanical properties in polyurethane elastomers and whether the superstructure of non-polar based polyurethanes could be inherently unfavorable for the realization of good tensile properties.

Besides effects at scales larger than the domain structure it is known that the interior organization of, in particular, the hard segment domains can influence mechanical properties. Nierzwicki and Wysocka[112] have noted that samples with the highest hard segment glass transition temperatures also have the highest tensile strength. They varied the hard segment T_g by varying the NCO/OH ratio which leads to different amounts of chemical crosslinking of the hard segments. Of course, the differences in properties could simply be attributed to the differences in crosslinking, but the authors were trying to explain the well known phenomenon of a maximum in tensile properties at low levels of crosslinking. Apparently, a slight degree of crosslinking improves the cohesion of the hard segment domains while too much crosslinking may inhibit the phase separation process[113]. A series of studies on polyurethane ionomers[51-54] in which the hard segments contain ionic groups has shown that even in cases where the degree of phase separation was unaffected by ion incorporation, mechanical properties were increased. Recently, work on PDMS based polyurethanes and polyurethane ionomers has indicated that hard segment domain cohesion is a more important factor than hard segment content in determing the tensile properties of these materials[33]. Although it is not clear if hard segment domain cohesion is affected by changes in soft segment type, it should be noted that the results of SAXS have indicated that much of the phase mixing in PIB polyurethanes occurs in the hard segment domains[14]. Incorporating soft segments in the hard segment domain would of course be expected to reduce the hard segment domain cohesion. However, Bonart and Muller[114] have suggested that much of the phase mixing in conventional polyurethanes also occurs in the hard domains, and thus it is questionable if this effect could explain differences in tensile properties between conventional and non-polar based polyurethanes. In fact, the higher degree of segmental incompatibility in non-polar based polyurethanes would lead one to conclude that they should exhibit less phase mixing in both the hard and soft domains.

From the results cited above it is obvious that the degree of phase separation and other morphological factors can affect the mechanical properties of polyurethane block copolymers. Again, further studies are needed to determine to what extent these factors may be responsible for the lower tensile properties of non-polar soft segment based polyurethanes. In particular, the effect of a sharp interface between phases, which is probably inherent in non-polar based materials, on mechanical properties warrants further investigation.

VII. Conclusions

Factors that could explain the lower tensile properties of non-polar soft segment based polyurethane block copolymers relative to those of conventional polyether or polyester polyurethanes have been examined. Many of the materials studied in the literature have suffered from the use of soft segments with poor functionality which has led to low molecular weight, network defects, and an unfavorable amount of crosslinking. Additionally, most of the materials have been based on soft segments whose molecular weight appears to be too high to obtain optimum properties. Polyurethanes based on non-polar soft segments are also likely to suffer from premature phase separation during polymerization leading to low molecular weight and compositional heterogeneity especially if the reaction is done in bulk. The lower soft segment glass transition temperature of in particular the polydimethylsiloxane polyurethanes can also contribute to their lower room temperature tensile properties. However, if differences in the soft segment glass transition temperatures are accounted for by comparing samples at equivalent values of $T-T_g$ and other parameters are optimized, it appears that only a lack of soft segment crystallizability under strain and possibly an excessively high degree of phase separation are inherently limiting the tensile properties of non-polar soft segment based polyurethane block copolymers. The limited amount of available information concerning the effects of many of these factors suggests a need for additional work in this area.

Acknowledgements

The authors would like to acknowledge partial support of this research by the Office of Naval Research and the Naval Air Systems Command. We would like to thank Dr. V.S.C. Chang and Dr. J.P. Kennedy of the University of Akron for providing the polyisobutylene polyurethanes.

REFERENCES

1. P. Wright and A.P.C. Cumming, Solid Polyurethane Elastomers, Mclaren and Sons Ltd., London (1969).
2. J.H. Saunders, Rubber Chem. Tech.,33, 1259 (1960).
3. C. Hepburn, Polyurethane Elastomers, Applied Science Publ., New York (1982), Chap. 3.
4. D.C. Allport and A.H. Mohajer, Block Copolymers. D.C. Allport and W.H. Janes, Eds., Wiley, New York (1973), Chap 8C.
5. P.E. Gibson, M.A Vallance, and S.L. Cooper, Developments in Block Copolymers, I. Goodman, Ed, Applied Science Publ., London, (1982), p. 217.
6. A. Lilaonitkul and S.L. Cooper, Adv. Ureth. Sci. Tech., 7, 163 (1979).
7. T.L. Smith, J. Polym. Sci.-Phys., 12, 1825 (1974).
8. T.L. Smith, Polym. Engr. Sci., 17, 129 (1977).
9. T.L. Smith, J. Appl. Phys., 35, 27 (1964).
10. Y.S. Lipatov, Adv. Ureth. Sci. Tech., 4, (1976).
11. R.J. Zdrahala, S.L. Hager, R.M. Gerkin, and F.E. Critchfield, J. Elast. Plas., 12, 225 (1980).
12. J.W.C. Van Bogart, P.E. Gibson, and S.L. Cooper, J. Polym. Sci.-Phys., 21, 65 (1983).
13. C.S. Schollenberger and K. Dinbergs, J. Elast. Plas., 11, 58 (1979).
14. T.A. Speckhard, P.E. Gibson, S.L. Cooper, V.S.C. Chang, and J.P. Kennedy, Polymer, 26, 55 (1985).
15. R. Bonart, J. Macomol. Sci.-Phys., 2,115 (1968).
16. R. Bonart, L. Morbitzer, and G. Hentze, J. Macromol. Sci.-Phys., 3, 337 (1969).
17. G.M. Estes, R.W. Seymour, and S.L. Cooper, Macromolecules, 4, 452 (1971).
18. I. Kimura, H. Ishihara, H. Ono, N. Yoshihara, S. Nomura, and H. Kawai, Macromolecules, 7,355 (1974).

19. Y.J.P. Chang and G.L. Wilkes, J. Polym. Sci.-Phys., 13, 455 (1975).

20. R. Falabella, R.J. Farris, and S.L. Cooper, J. Rheology, 28, 123 (1984).

21. P.W. Ryan, J. Elastoplastics, 3, 57 (1971).

22. K. Ono, H. Shimada, T. Nishimura, S. Yamashita, H. Okamoto, and Y. Minoura, J. Appl. Polym. Sci., 21, 3323 (1977).

23. G.N. Petrov and A.S. Lykin, Polym. Sci. USSR., 20, 1351 (1979).

24. N.S. Schneider and W. Matton, Polym. Engr. Sci., 19, 1122 (1979).

25. C.M. Brunette, S.L. Hsu, W.J. Macknight, and N.S. Schneider, Polym. Engr. Sci., 21, 163 (1981).

26. C.M. Brunette, S.L. Hsu, M. Rossman, W.J. Macknight, and N.S. Schneider, Polym. Engr. Sci., 21, 668 (1981).

27. M. Xu, W.J. Macknight, C.H.Y. Chen, and E.L. Thomas, Polymer, 24, 1327 (1983).

28. R.L. Zapp, G.E. Serniuk, and L.S. Minckler, Rubber Chem. Tech., 43, 1154 (1970).

29. B. Ivan and J.P. Kennedy, ACS Org. Coat. Plas. Preprints, 43, 909 (1980).

30. T.A. Speckhard, G. Ver Strate, P.E. Gibson, and S.L. Cooper, Polym. Engr. Sci., 23, 337 (1983).

31. T.A. Speckhard, K.K.S. Hwang, S.L. Cooper, V.S.C. Chang, and J.P. Kennedy, Polymer, 26, 70 (1985).

32. D. Tyagi, I. Yilgor, G.L. Wilkes, and J.E. Mcgrath, Polymer, 25, 1807 (1984).

33. Y. Xuehai, M.R. Nagarajan, T.G. Grasel, P.E. Gibson, and S.L. Cooper, J. Polym. Sci.-Phys., 23, 2319 (1985).

34. B. Bengston, C. Feger, and W.J. Macknight, submitted to Polymer.

35. V.S.C. Chang and J.P. Kennedy, Polym. Bull., 8, 69 (1983).

36. T.L. Smith, Rheology, 5, F.R. Eirich, Ed., Academic, New York, (1969), Chap. 4.

37. G.M. Estes, R.W. Seymour, D.S. Huh, and S.L. Cooper, Polym. Engr. Sci., 9, 383 (1969).

38. R.W. Seymour, A.E. Allegrezza, Jr., and S.L. Cooper, Macromolecules, 6, 896 (1973).

39. H.W. Siesler, Polym. Bull., 9, 382, 471, 557 (1983).

40. H. Ishihara, I. Kimura, K. Saito, and H. Ono, J. Macromol. Sci.-Phys., 10, 591 (1974).

41. C. Wang and S.L. Cooper, Macromolecules, 16, 775 (1983).

42. R. Bonart and K. Hoffmann, Coll. Polym. Sci., 260, 268 (1982).

43. C.S. Schollenberger and K. Dinbergs, J. Elastoplastics, 5, 222 (1973).

44. H. Inagaki, N. Donkai, A. Saitoh, and Y. Zenitani, J. Appl. Polym. Sci., 29, 3741 (1984).

45. J.P. Kennedy and R.A. Smith, J. Polym. Sci.-Chem., 18, 1523 (1980).

46. B. Ivan, J.P. Kennedy, and V.S.C. Chang, J. Polym. Sci.-Chem., 18, 3177 (1980).

47. R. Musch, Rubber Chem. Tech., 58, 45 (1985).

48. T.L. Smith, J. Poly. Sci., A1, 3597 (1963).

49. D.S. Huh and S.L. Cooper, Polym. Engr. Sci., 11, 369 (1971).

50. K.K.S. Hwang, T.A. Speckhard, and S.L. Cooper, J. Macromol. Sci.-Phys., 23, 153 (1984).

51. K.K.S. Hwang, C.Z. Yang, and S.L. Cooper, Polym. Engr. Sci., 21, 1027 (1981).

52. T.A. Speckhard, K.K.S. Hwang, C.Z. Yang, W.R. Laupan, and S.L. Cooper, J. Macromol. Sci.-Phys., 23, 175 (1984).

53. C.Z. Yang, K.K.S. Hwang, and S.L. Cooper, Makromol. Chem., 184, 651 (1983).

54. K. Shibatani, D.J. Lyman, D.F. Shieh, and K. Knutson, J. Polym. Sci.-Chem., 15, 1655 (1977).

55. S.E. Berger and W. Szukiewicz, I+EC Prod. Res. Dev., 3, 129 (1964).

56. K.W. Rausch, R.F. Martel, and A.H.R. Sayigh, I+EC Prod. Res. Dev., 3, 125 (1964).

57. J.M. Buist and R. Hurd, Adv. Ureth. Sci. Tech., 2, 29 (1973).

58. L.B. Weisfeld, J.R. Little and W.E. Wolstenholme, J. Polym. Sci., 56, 455 (1962).

59. T. Tanaka, T. Yokoyama, and Y. Yamaguchi, J. Polym. Sci., A1, 2153 (1968).

60. C.Y. Jiang, J.E. Mark, V.S.C. Chang, and J.P. Kennedy, Polym. Bull., 11, 319 (1984).

61. R.F. Storey and J.P. Kennedy, Polym. Bull., 8, 281 (1982).

62. M. Kato and J.E. Mark, Rubber Chem. Tech., 49, 85 (1976).

63. E.L. Warrick, J. Polym. Sci., 27, 19 (1958).

64. V.Y. Levin, G.L. Slonimskii, K.A. Andrianov, A.A. Zhdanov, Y.K. Godovskii, V.S. Papkov, and Y.A. Lyubavskaya, Vysokomol. Soyed, A15, 224 (1973).

65. G. Sylvester and W. Wieder, "Elastomers and Rubber Elasticity", J.E. Mark and J. Lai, Eds., ACS Sympos. Ser., 193, Washington D.C. (1982).

66. P.J. Flory, J. Chem. Phys., 15, 397 (1947).

67. P.J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, N.Y. (1953).

68. J.E. Mark, Polym. Engr. Sci., 19, 255 (1979).

69. J.E. Mark, Polym. Engr. Sci., 19, 409 (1979).

70. L. Mullins, J. Appl. Poly. Sci., 2, 257 (1959).

71. L.R.G. Treloar, The Physics of Rubber Elasticity, 3rd Ed., Clarendon Press, Oxford (1975).

72. F.W. Billmeyer, Textbook of Polymer Science, 2nd Ed., Wiley, New York (1971).

73. A.L. Andrady, M.A. Llorente, and J.E. Mark, J. Chem. Phys., 73, 1439 (1980).

74. J.E. Mark, J. Chem. Educ., 58, 899 (1981).

75. M.A. Llorente and J.E. Mark, J. Polym. Sci.-Phys., 19, 1107

(1981).

76. S.B. Clough and N.S. Schneider, J. Macromol. Sci.-Phys., 2, 555 (1968).

77. L. Morbitzer, G. Hentze, and R. Bonart, Kolloid-Z., 216-217, 137 (1967).

78. R.M. Kell, B. Bennett, and P.B. Stickney, Rubber Chem. Tech., 31, 499 (1958).

79. G. Natta and G. Moraglio, Makromol Chem., 66, 218 (1963).

80. S.L. Axelrood and K.C. Frisch, Rubber Age, 88, 465 (1960).

81. M. Morton, J.E. McGrath, and P.C. Juliano, J. Polym. Sci., C26, 99 (1969).

82. T.L. Smith and R.A. Dickie, J. Polym. Sci., C26, 163, (1969).

83. E. Fischer and J.F. Henderson, J. Polym. Sci., C26, 149 (1969).

84. G.R. Kraus, Science and Technology of Rubber, F.R. Eirich, Ed., Academic, New York (1978), Chap. 8.

85. Y. Mojaher, G.L. Wilkes, I.C. Wang, and J.E. McGrath, Polymer, 23, 1523 (1982).

86. J.F. Beecher, L. Marker, R.D. Bradford, and S.L. Aggarwal, J. Polym. Sci., C26, 117 (1969).

87. J.V. Dawkins, Block Copolymers, D.C. Allport and W.H. Janes, Eds., Wiley, New York (1972), Chap. 8B.

88. E.T. Bishop and S. Davison, J. Polym. Sci., C26, 59 (1969).

89. R.J. Cella, J. Polym. Sci. Sympos., 42, 727 (1973).

90. M. Morton, Block Polymers, S.L. Aggarwal, Ed., Plenum Press, New York, (1970) p. 1.

91. R.E. Camargo, C.W. Macosko, M.V. Tirrell, and S.T. Wellinghof, Polym. Engr. Sci., 22, 719 (1982).

92. I. Fridman, E.L. Thomas, L.J. Lee, and C.W. Macosko, Polymer, 21, 393 (1980).

93. A.L. Chang, R.M. Briber, E.L. Thomas, R.J. Zdrahala, and F.E. Critchfield, Polymer, 23, 1060 (1982).

94. S. Abouzahr and G.L. Wilkes, J. Appl. Polym. Sci., 29, 2695 (1984).

95. J.A. Miller, S.B. Lin, K.K.S. Hwang, K.S. Wu, P.E. Gibson, and S.L. Cooper, Macromolecules, 18, 32 (1985).

96. M.A. Vallance, J.L. Castles, and S.L. Cooper, Polymer, 25, 1734 (1984).

97. C.H.Y. Chen, R.M. Briber, E.L. Thomas, M. Xu, and W.J. Macknight, Polymer, 24, 1333 (1983).

98. P. Kolodzies, C.W. Macosko, and W. E. Ranz, Polym. Engr. Sci., 22, 388 (1982).

99. T.A. Speckhard, J.G. Homan, J.A. Miller, and S.L. Cooper, Polymer, submitted for publication.

100. M.R. Nagarajan, Y. Xuehai, P.E. Gibson, and S.L. Cooper, to be submitted.

101. T.A. Speckhard, J.A. Miller, and S.L. Cooper, Macromolecules, accepted for publication.

102. J.A. Miller, T.A. Speckhard, J.G. Homan, and S.L. Cooper, Polymer, submitted for publication.

103. S.L. Cooper and A.V. Tobolsky, J. Appl. Polym. Sci., 10, 1837 (1966).

104. T.A. Speckhard, K.K.S. Hwang, S.B. Lin, S.Y. Tsay, M. Koshiba, Y.S. Ding, and S.L. Cooper, J. Appl. Polym Sci., 30, 647 (1985).

105. V.W. Srichatrapimuk and S.L. Cooper, J. Macromol. Sci.-Phys., 15, 267 (1978).

106. D.R. Paul, ACS Polym. Matl. Sci. Engr. Preprints, 50, 1 (1984).

107. A.E. Oberth, Rubber Chem. Tech., 40, 1337 (1967).

108. Z. Ophir and G.L. Wilkes, J. Polym. Sci.-Phys., 18, 1469 (1980).

109. Y. Xuehai, M.R. Nagarajan, C. Li., P.E. Gibson, and S.L. Cooper, submitted for publicaton.

110. C. Li, T.A. Speckhard, Y. Xuehai, and S.L. Cooper, to be submitted.

111. J.A. Miller and S.L. Cooper, J. Polym. Sci.-Phys., 23, 1065 (1985).

112. W. Nierzwicki and E. Wysocka, J. Appl. Polym. Sci., 25, 739 (1980).

113. W. Nierzwicki, J. Appl. Polym. Sci., 30, 761 (1985).

114. R. Bonart and E.H. Muller, J. Macromol. Sci.-Phys., 10, 345 (1974).

Table 1

Typical Tensile Properties of Elastomers

Elastomer Type	Engineering Tensile Strength σ_b PSI (MPa)	Elongation at Break ϵ_b %
SBS	4500 (31)	900
Vulcanized rubber (natural)	3000 (21)	600
Vulcanized SBR	2000 (14)	900
EVA Copolymer	2000 (14)	700
Segmented Polyurethane	6-7000 (41-48)	500

Table 2

Typical (T) and 'Exceptioral' (E) Properties of Segmented Polyurethane Elastomers with Different Soft Segments

Soft Segment Type	(Reference)	Engineering Tensile Strength σ_b PSI,(MPa)	Elongation at Break ε_b %
PTMO	(6,8)	4500 , (31)	1000 (E)
PTMA		6-7000 (T), (41-48)	500 (T)
PCL		9000 (E), (62)	500
PPO	(3)	2000 (T), (14)	800 (T)
	(55)	5000 (E), (34)	300
PIB	(14)	1000 (T), (7)	100 (T)
	(31)	3000 (E), (21)	200
PBD	(25)	1400 (T), (10)	200 (T)
	(26)	600 , (4)	1600 (E)
	(22)	3000 (E), (21)	200
	(34)	3000 (E), (21)	300
PDMS	(33)	1000 (T), (7)	200 (T)
	(32)	3000 (E), (21)	400
	(32)	1000 , (7)	900 (E)

PTMO - poly(tetramethylene oxide)
PTMA - poly(tetramethylene adipate)
PCL - polycaprolactone
PPO - poly(propylene oxide)
PIB - polyisobutylene
PBD - polybutadiene
PDMS - polydimethylsiloxane

Table 3

Typical Soft Segment Glass Transition Temperatures in Polyurethane Block Copolymers

Soft Segment Type (approximate number average molecular weight)	T_g* (°C)	Reference
PCL (2000)	-50	12
PTMA (1000)	-35	6
PTMO (1000)	-45	6
PTMO (2000)	-70	6
PPO (2000)	-50	11
PIB (2000)	-60	14
PBD (2000)	-75	24
PBD - High vinyl (2000)	-55	26
PDMS (2000)	-120	33

* Measured by Differential Scanning Calorimetry (DSC). Depending on the test conditions and the method of determination (onset or midpoint etc.), temperatures may vary ± 5-10 degrees.

Table 4

Tensile Properties of Selected Polyurethane Block Copolymers at Different Temperatures

	ROOM TEMPERATURE (24°C)					OTHER TEMPERATURES				
Sample[A]	T_g °C	$T-T_g$ °C	E_{100} PSI	σ_b PSI	ϵ_b %	Test Temp. °C	$T-T_g$ °C	E_{100} PSI	σ_b PSI	ϵ_b %
PTMO-1000-50 (ET-38-1)	-46	70	1100	8200	650	59	115	650	3100	670
PDMS-2000-25	-120	145	550	700	170	-50	70	1600	2300	240
PDMS-2000-25*	-120	145	230	500	270	-50	70	1100	1900	180
PIB-3400-27	-57	81	1100	1900	270	3	60	1300	2800	340
						-12	45	1800	4000	370
PBD-2000-38	-55	79	1800	2000	150	5	60	2700	3000	150
						-10	45	3700	4200	150

* - chain extended with MDEA (methyldiethanol amine) instead of BD

A - sample nomenclature described in text

E_{100} - secant modulus at 100% elongation

Figure Captions

Figure 1 Stress-strain curves of polyurethane elastomers based on different soft segments

Figure 2 Stress-strain curves as a function of temperature for a polyisobutylene polyurethane and a polydimethylsiloxane polyurethaneurea

Figure 3 Stress-strain curves as a function of temperature for two polyether polyurethanes

Figure 4 Stress-strain curves for a styrene-butadiene-styrene triblock copolymer, a poly(propylene oxide) polyuretheneurea, and a series of poly(tetramethylene oxide) polyurethanes with different hard segment contents

Figure 5 The effect of molecular weight on the stress-strain curves of a polyether polyurethane

Figure 6 The effect of the use of catalyst on the stress-strain curves of two polyisobutylene polyurethanes

Figure 7 Stress-strain curves for a polydimethylsiloxane based polyurethane and a corresponding material (PCEMS) containing cyanoethyl groups on the siloxane backbone

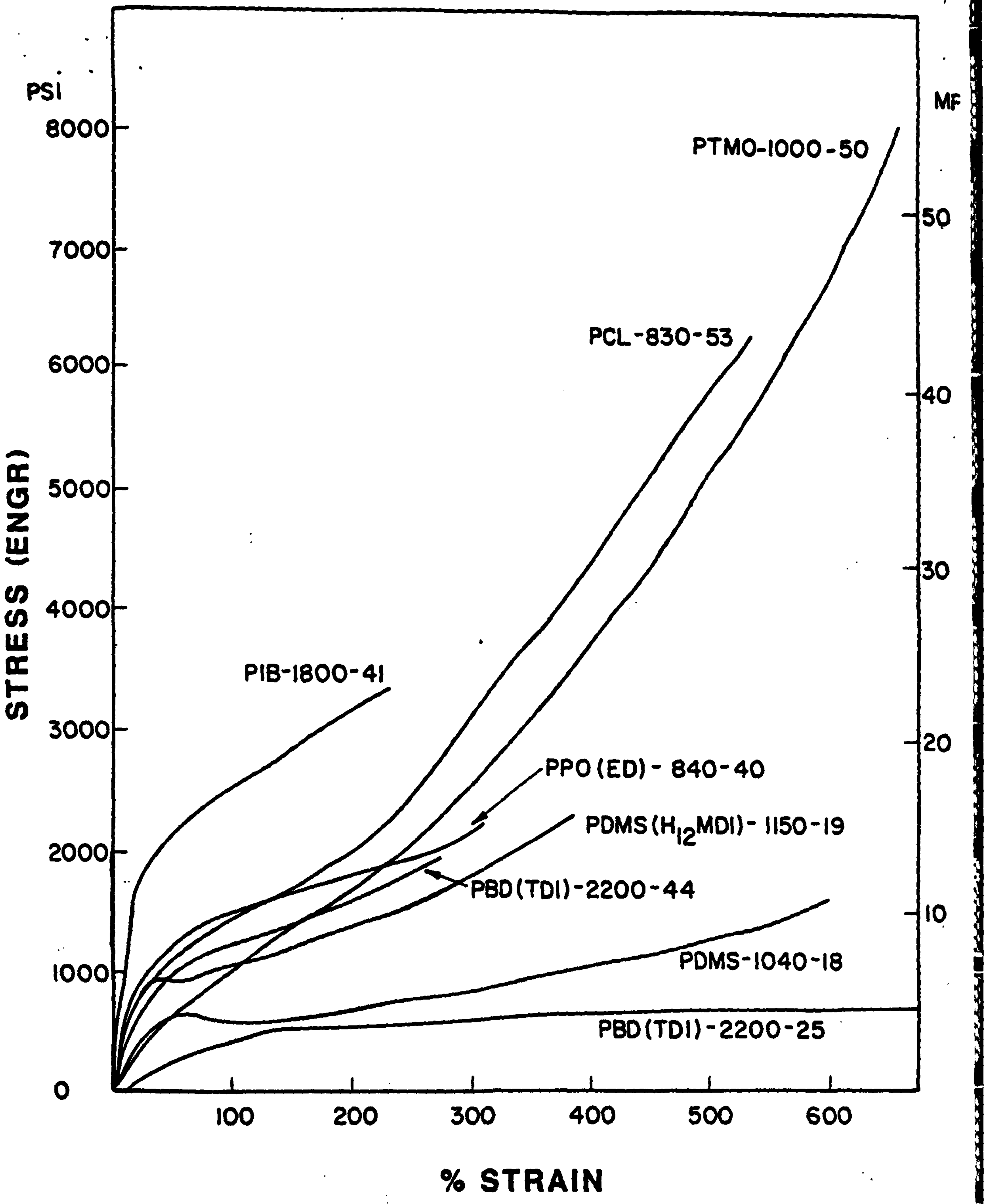

PSI
STRESS (ENGR)
8000
7000
6000
5000
4000
3000
2000
1000
0
MF
50
40
30
20
10
100
200
300
400
500
600
% STRAIN
PTMO-1000-50
PCL-830-53
PIB-1800-41
PPO (ED) - 840-40
PDMS (H12MDI) - 1150-19
PBD (TDI) - 2200-44
PDMS-1040-18
PBD (TDI) - 2200-25

FIGURE 1

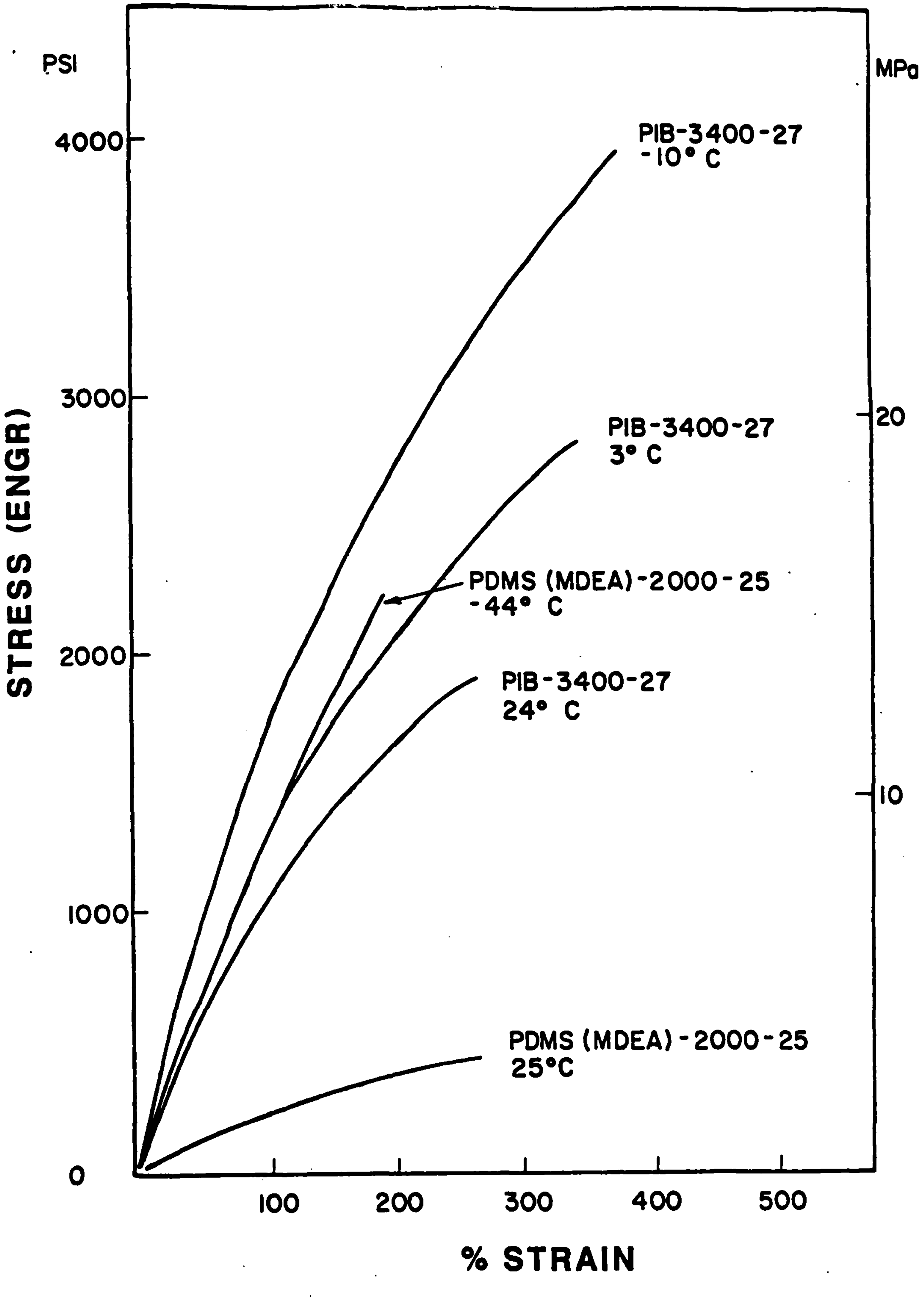

PSI
MPa
STRESS (ENGR)
4000
3000
2000
1000
0
20
10
100
200
300
400
500
% STRAIN
PIB-3400-27
-10° C
PIB-3400-27
3° C
PDMS (MDEA)-2000-25
-44° C
PIB-3400-27
24° C
PDMS (MDEA)-2000-25
25°C

FIGURE 2

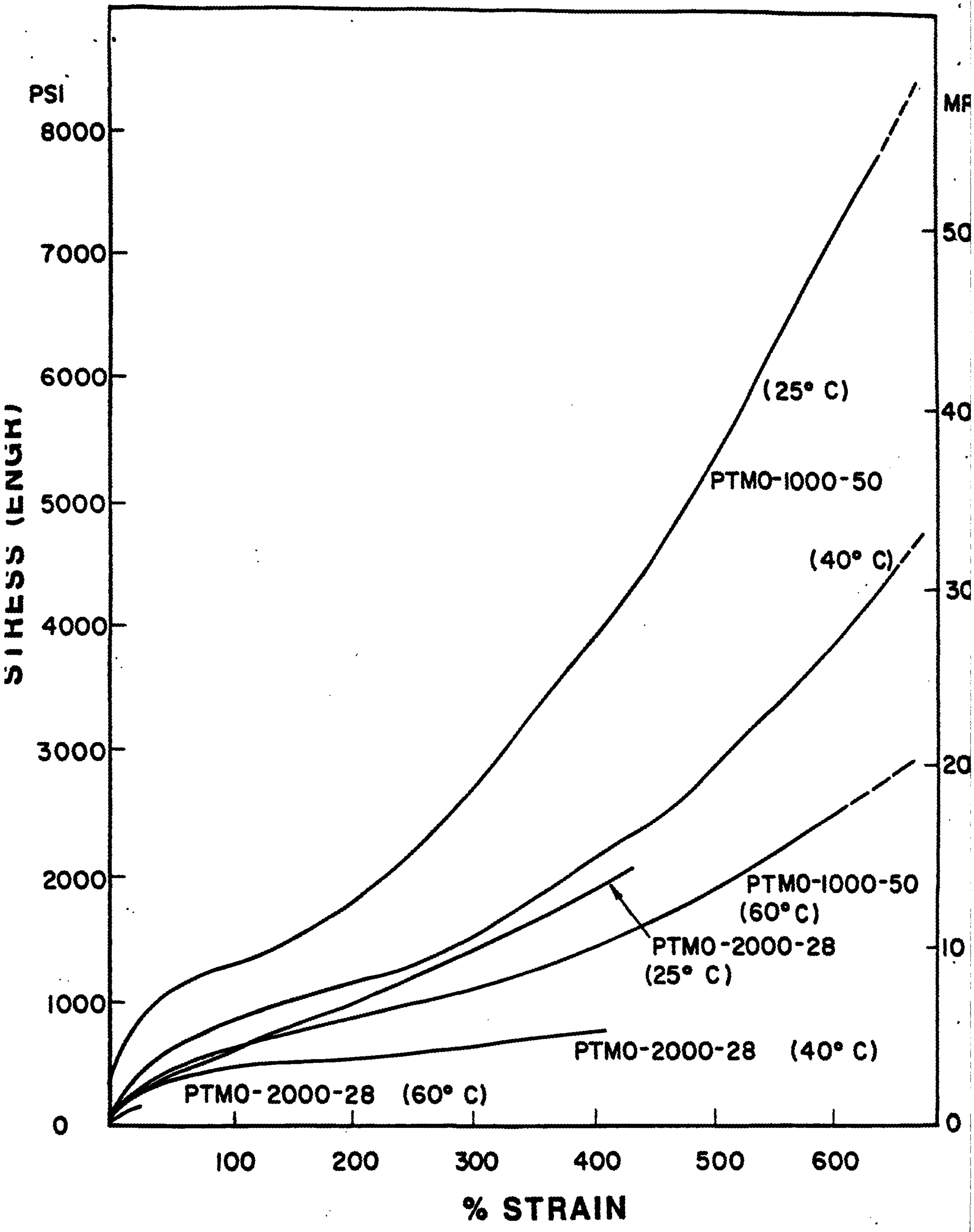

PSI
8000
7000
6000
5000
4000
3000
2000
1000
0
STRESS (ENGR)
MP
50
40
30
20
10
0
100
200
300
400
500
600
% STRAIN
(25° C)
PTMO-1000-50
(40° C)
PTMO-1000-50
(60°C)
PTMO-2000-28
(25° C)
PTMO-2000-28 (40° C)
PTMO-2000-28 (60° C)

FIGURE 3

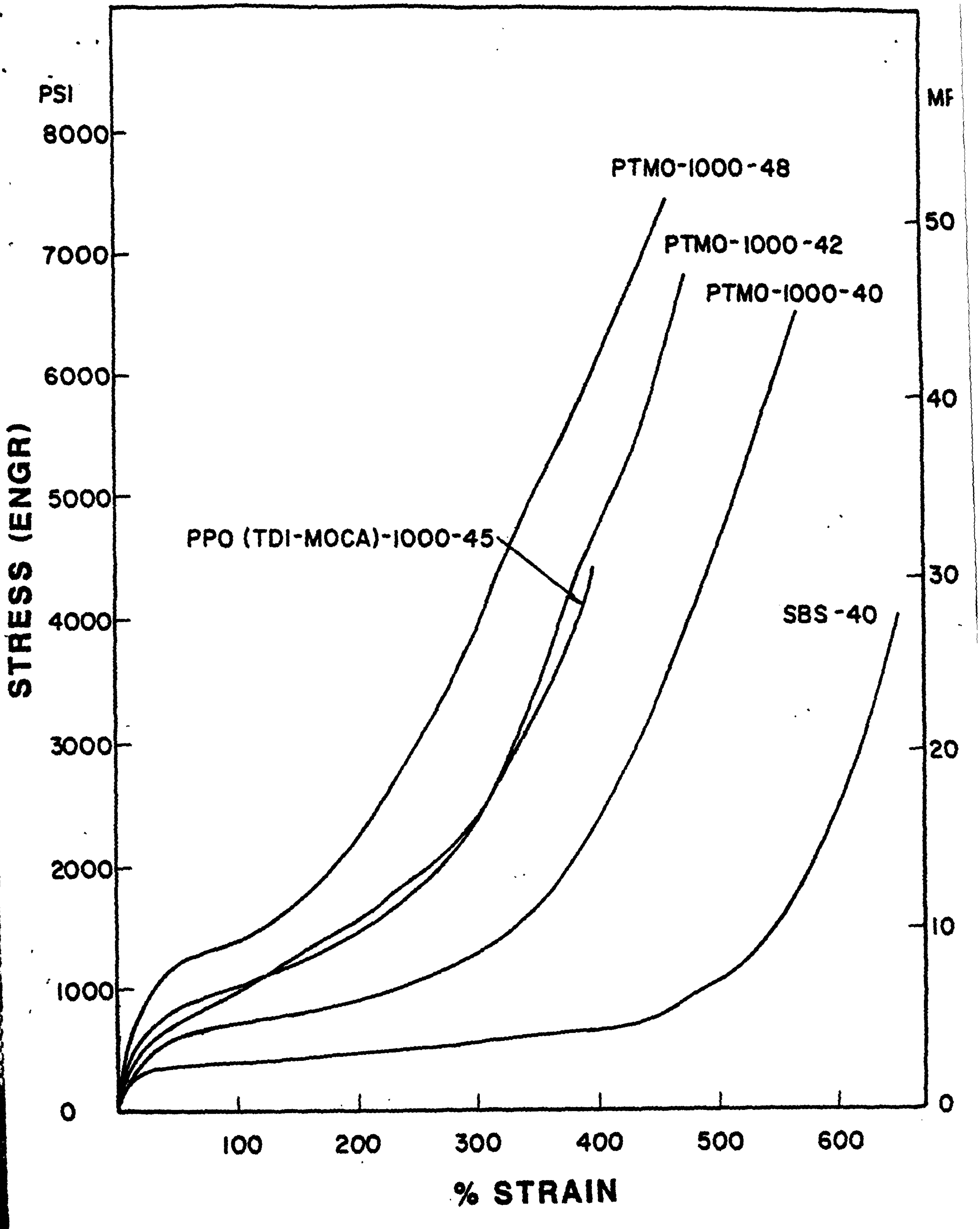

PSI
MP
8000
7000
6000
5000
4000
3000
2000
1000
0
STRESS (ENGR)
50
40
30
20
10
0
100
200
300
400
500
600
% STRAIN
PTMO-1000-48
PTMO-1000-42
PTMO-1000-40
PPO (TDI-MOCA)-1000-45
SBS-40

FIGURE 4

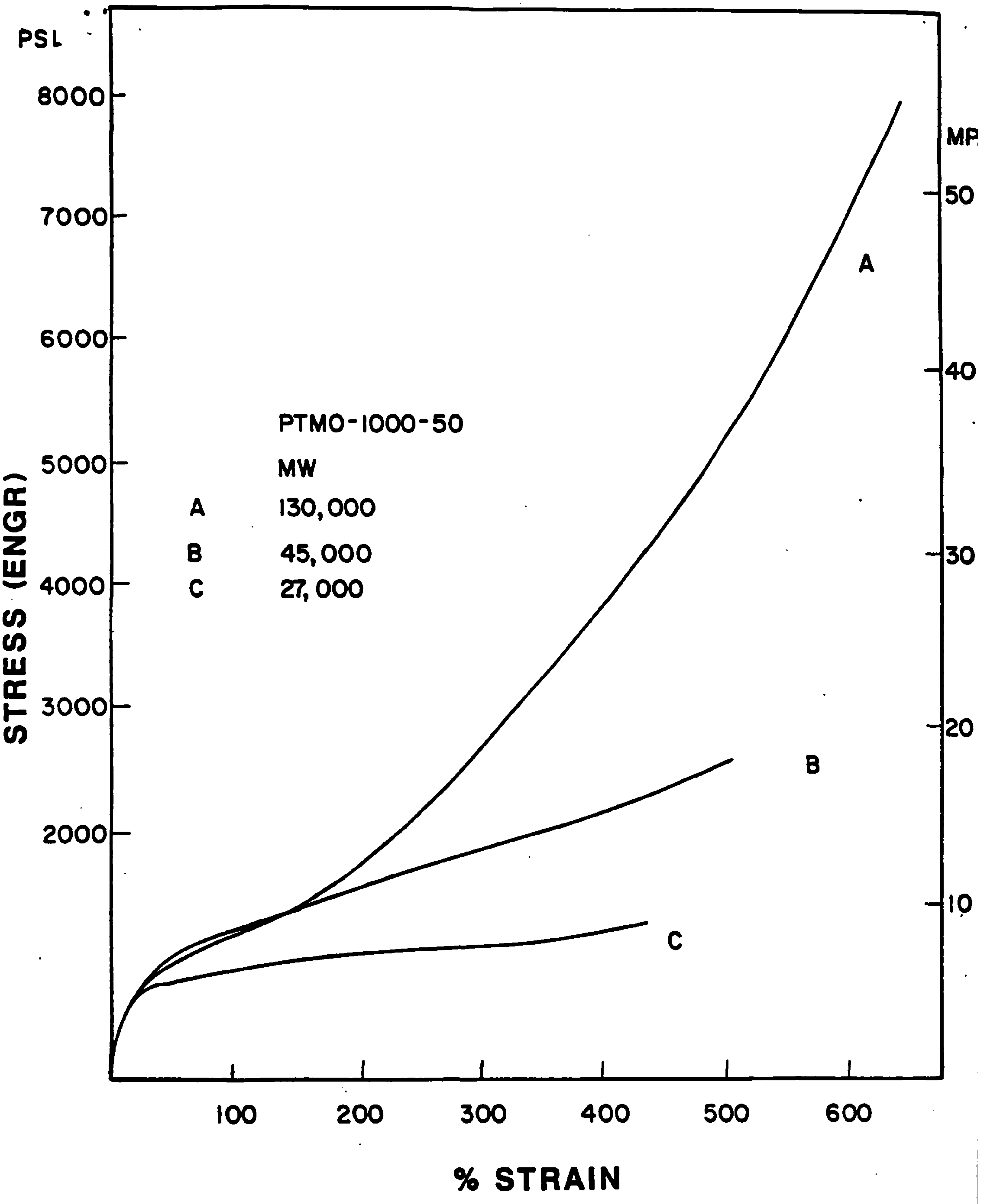
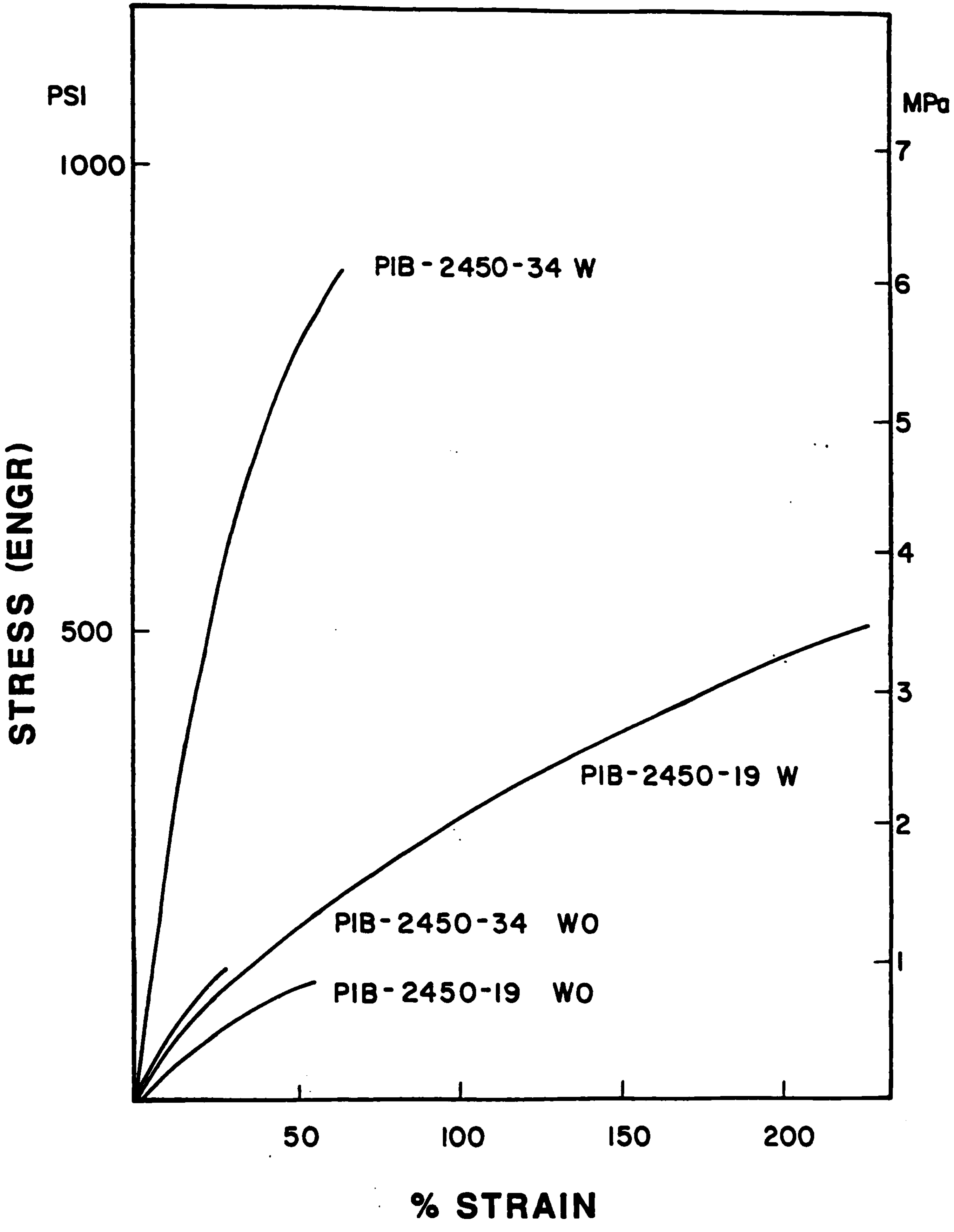

PSI
8000
7000
6000
5000
4000
3000
2000
STRESS (ENGR)
MP
50
40
30
20
10
A
B
C
PTMO-1000-50
MW
A 130,000
B 45,000
C 27,000
100
200
300
400
500
600
% STRAIN

FIGURE 5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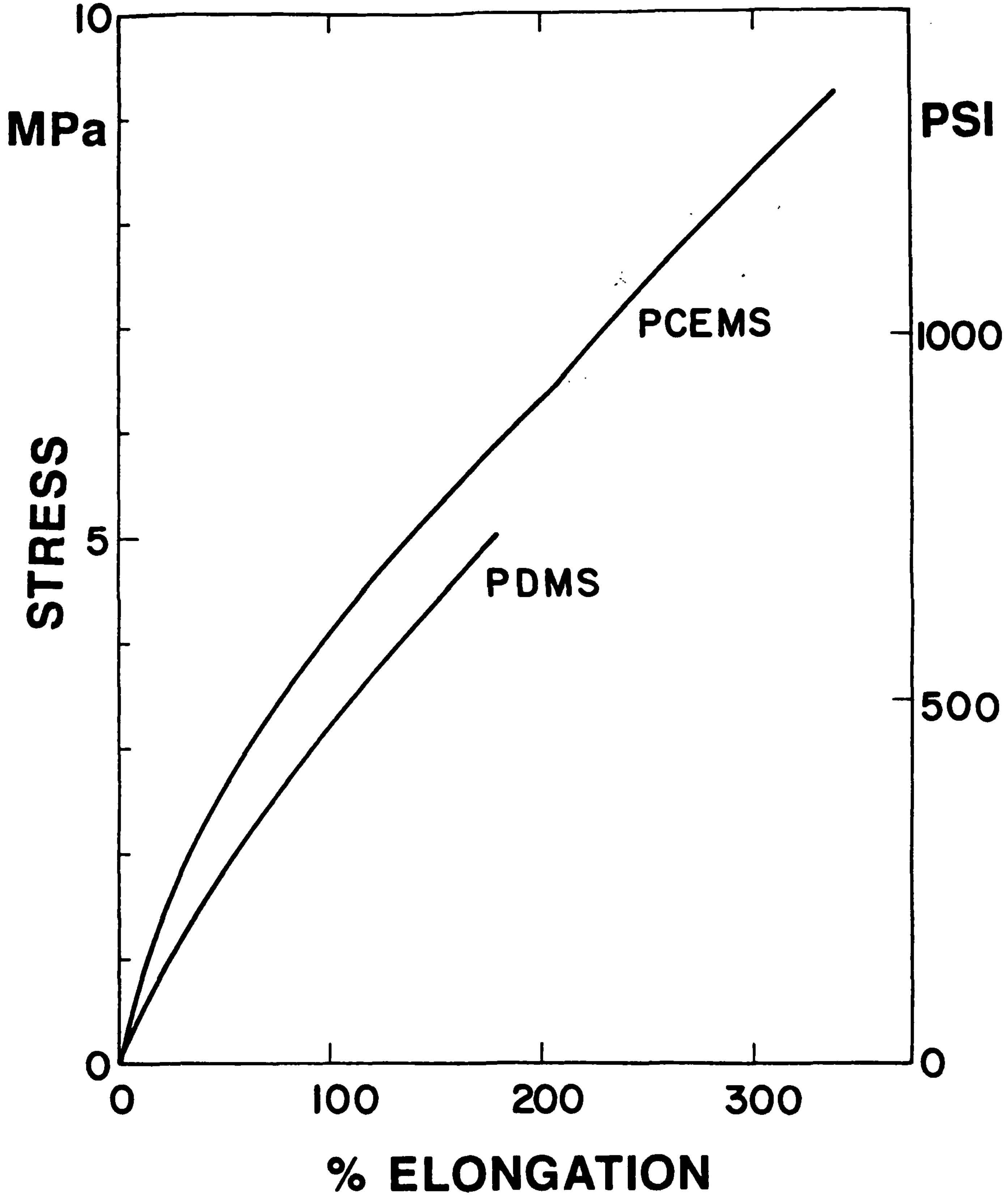
MPa
1000
500
7
6
5
4
3
2
1
PIB-2450-34 W
PIB-2450-19 W
PIB-2450-34 WO
PIB-2450-19 WO
STRESS (ENGR)
50
100
150
200
% STRAIN

FIGURE 6

Fig 7 1121CC-3



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