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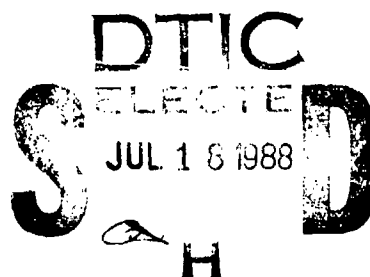
**CHEMICAL AGENT SIMULANTS
FOR TESTING TRANSPARENT MATERIALS**

by **Randall E. Lewis
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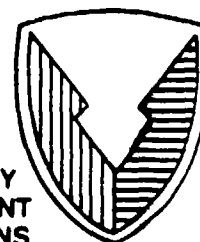
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May 1988



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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Chemical Warfare Transparent polymeric materials undergo physical changes when exposed to CW agents. The object of this task was to: 1) select candidate liquids to simulate GB, VX and HD effects (three each) and 2) perform three point bend tests to determine critical strain values for cracking/crazing for simulant/transparent polymer materials combinations. The critical strain tests were accomplished using ASTM method D790-80 for stress crazing. The method was modified and enhanced to detect stress crazing via changes in reflection/diffraction patterns produced with a helium-neon (He-Ne) laser. Four transparent polymer materials were tested; namely, as cast polymethyl methacrylate (PMMA), biaxially stretched PMMA, polycarbonate and polyurethane GAC-590. The critical strain values obtained for the simulant/polymer combinations are presented as a four by nine map that allows easy comparisons as a function of material or simulant. Comparison with actual agent data is possible using this four by nine map.					
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PREFACE

The work described in this report was authorized under Contract DAAA15-87-D-0007-0002. This work was started in September 1987 and completed in January 1988.

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CHEMICAL AGENT SIMULANTS FOR TESTING TRANSPARENT MATERIALS

1. INTRODUCTION

This study was conducted as part of an ongoing effort at the U.S. Army Chemical, Research, Development and Engineering Center (CRDEC) to evaluate the survivability of transparent polymeric materials in a chemical agent environment. Since chemical agents cannot be used without appropriate safety and surety procedures and apparatus for the laboratory or in the field, simulants must be selected and substituted for the chemical agents in these environments. Simulants employed in properly designed laboratory tests assist in evaluating the performance and behavior of challenged transparent polymeric materials. Subsequent modeling aids in predicting the performance of these polymeric materials under the realistic condition of chemical agent challenges. Using appropriate evaluation techniques, candidate chemicals can be selected to determine the best simulants to employ in a testing program. In particular, this program had the following tasks:

1. Conduct a literature search to identify and retrieve results from previous stress crazing tests and identify and recommend alternative methods of stress crazing testing and detection.
2. Select appropriate simulants for GB(Sarin), VX, and HD(mustard) for use in transparent polymer testing and evaluation.
3. Perform three point bend calibration and simulant/polymer tests for stress crazing. Four generic transparent polymeric materials were tested; namely, as cast PMMA, biaxially stretched PMMA, polycarbonate, and polyurethane, GAC-590.

Results obtained from Tasks 2 and 3 are discussed; namely simulant selection and three-point bend test results.

2. SIMULANT SELECTION

Simulants are substituted for actual chemical agents in these tests for a variety of reasons. The major reasons are the elimination of the need to use a surety facility with its accompanying rules, procedures, and associated costs, and the ability to develop test and evaluation procedures in a more benign chemical environment. Also, the testing of transparent polymeric materials with simulants for GB, VX, and HD could be conducted at the polymer manufacturer's own facilities under non-surety conditions prior to, if necessary, testing under the more stringent surety conditions.

The test simulants utilized in these studies were carefully selected by comparing important physical and chemical parameters of the simulants to the same characteristics of the agents. These parameters included molecular weight, solubility, viscosity, melting and boiling points, density, vapor pressure, and reactivity.^{1,2,3} The simulants were also selected not only for their chemical similarities to the agents but, also, for their molecular size similarities. Thus, we intend to develop or establish an envelope or region of comparable simulant

and agent absorption into the various polymers being tested, as well as, similar reaction/behavior between the simulant or agent and the polymer.

Simulants selected for isopropyl methylphosphonofluoridate(GB) were diisopropyl methylphosphonate(DIMP), diethyl ethylphosphonate(DEEP), and dimethyl hydrogen-phosphonate(DMHP). GB has a liquid density of 1.09 g/ml at 20°C, a vapor pressure of 2.9mm at 20°C, and a viscosity of 1.28 centistokes at 20°C. For comparison, DIMP has a liquid density of .976 g/ml at 25°C and, like GB contains, an isopropyl group(Table 1). DEEP allows for the simulation of the methylphosphorous group, while DMHP has a similar viscosity and vapor pressure.

Table 1. Selected Simulants for GB(Sarin)

	M.W.	Density (g/ml)	BP (deg. C)	Vapor Pressure (mm)	Viscosity (centistokes)	Solubility (g/l.)
GB	140.1	1.09 @20C	158	2.9 @ 20C	1.28 @ 20C	miscible
DIMP	180.2	.976 @ 25C	190 211	.274 @ 25C	---	1.5 @ 25C
DMHP	110.04	1.2 @ 25C	171	4.5 @ 25C	1.06 @ 25C	---
DEEP	166.12	---	---	.3814 @ 25C	---	---

The simulants used for 2,2'-dichloroethyl sulfide(HD) were 2-chloroethyl methyl sulfide(CEMS), 2-chloroethyl ethyl sulfide(CEES), and 1,5-dichloropentane(Table 2). CEES and CEMS have reactivities similar to mustard, namely all undergo hydrolysis, are alkylating agents and exhibit comparable solubilities, molecular weights, and liquid densities. 1,5-dichloropentane(1,5 DCP) was chosen because of its similar end group and structural configuration to HD, i.e. -CH₂CH₂Cl groups.

Table 2. Selected Simulants for HD(mustard)

	M.W.	Density (g/ml)	BP (deg. C)	Vapor Pressure (mm)	Viscosity (centistokes)	Solubility (g/l.)
Mustard	159.08	1.27 @25C	217	.11 @ 25C	3.95 @ 25C	.0092 @ 22C
CEES	124.63	1.07 @ 20C	157	3.3 @ 25C	---	.017 @ 25C
CEMS	110.60	1.12 @ 20C	140	---	1.06 @ 25C	---
1,5 di- dichloro pentane	140.05	1.106 @ 25C	182	---	---	---

VX(O-ethyl S-diisopropylaminoethyl methylphosphonothiolate) simulants used were O,S diethyl ethylphosphonothiolate(DEEPT), N,N-diisopropylethylamine, and diethyl(ethylthiomethyl) phosphonate(DEETMP).

N,N diisopropylethylamine was employed to examine the amine effect upon the polymers. DEEPT and DEETMP simulated various functional groups of VX aside from the physical characteristics, e.g. molecular weight, viscosity, and vapor pressure.

Table 3. Selected Simulants for VX

	M.W.	Density (g/ml)	BP (deg. C)	Vapor Pressure (mm)	Viscosity (centistokes)	Solubility (g/l.)
VX	276.40	1.008@25C	298	.0007@25C	8.98@25C	inverted solubility
DEEPT	182.18	—	—	.01@25C	—	—
DEETMP	212.25	1.097@25C	110	—	—	—
N,N diiso propyl ethylamine	129.25	.714@20C	127	—	—	—

3. EXPERIMENTAL METHOD

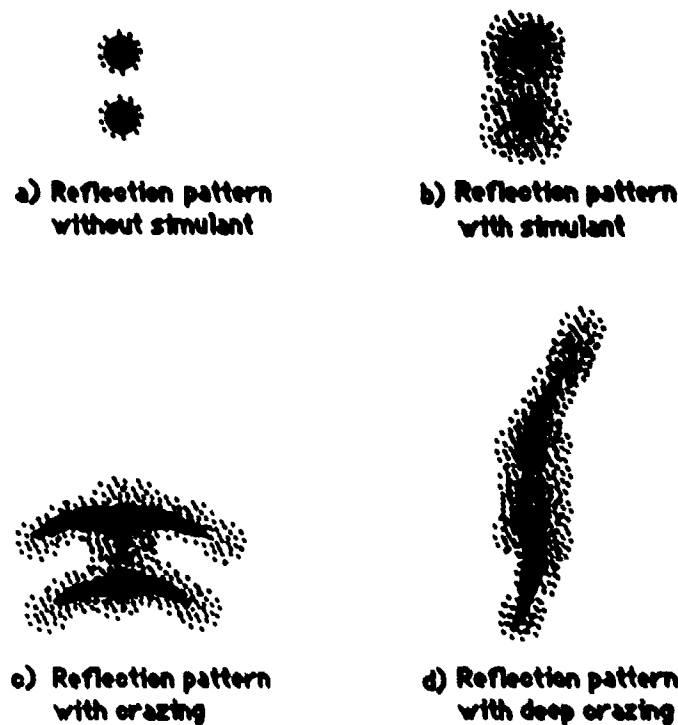
To determine stress crazing in transparent polymeric materials, American Society of Testing and Materials method ASTM D790-80 was employed. ASTM D 790-80 determines the flexural properties of plastics in the form of rectangular bars molded directly or cut from sheets, plates, or molded shapes.⁴ This ASTM procedure is generally applicable to rigid and semirigid materials but does not determine the flexural strength of materials that do not break or fail in their outer fibers.

The method employed for craze determination under load for this series of tests employs a three-point loading system that utilizes center loading on a simply supported beam (Figure B1). Normally, crazing is detected visually. However, the detection method employed for our tests was improved by employing a He-Ne laser to produce a diffraction pattern. By recording the diffraction patterns with a Sony U-Matic VCR and Sony Tricon color camera equipped with a macro-zoom lens (Figure B2), the determination of the time of crazing is easily accomplished. The determination of the onset of crazing by changes in the diffraction pattern is superior to the visual method because the diffraction pattern enables minute crazing to be detected which are generally not apparent to the unaided eye. Permanent records of the diffraction patterns produced were also photographed with a Pentax K1000 35mm SLR camera with close-up rings and a red transmission filter.

The use of a He-Ne laser in conjunction with the three-point bend apparatus allows increased sensitivity in detecting the onset of crazing. The He-Ne laser reflection pattern is observed to diffract at the onset of crazing.^{5,6} Patterns vary from horizontal lines to total diffusion of the reflection. Figure 1 illustrates the various patterns observed with employment of the He-Ne laser to detect the onset of crazing. Figure 1a represents the normal pattern observed with no simulant present. When the simulant is added, some diffusion is noted in the pattern (i.e., the degree of diffusion depends upon the optical characteristics of

the simulant)(figure 1b). As crazing occurs, a horizontal line appears at the edges of the pattern, the pattern changes from b) to c). However, with deep crazing, the pattern directly changes from b) to d).

Figure 1 **He-Ne Laser Diffraction Patterns of Transparent Material**



Strain in a polymer sample is calculated in the outer layers of the sample from the equation⁴:

$$r=6Dc/L^2 \quad (1)$$

where r =strain in outer layers; D =Displacement of sample in center; L =support span; d =thickness. Rearrangement of the equation for this series of experiments allows determination of the amount of displacement(D) for each sample via:

$$0.6667 \cdot (\%r/d)=D \quad (2)$$

where 0.6667 is $L^2/6$ ($L=2$ in.), $\%r$ represents a selected strain value divided by 100, and d is the thickness of the sample.

Calibration tests for each three-point bend apparatus were determined prior to data collection. The reference material used was polycarbonate and HPLC grade diethylenetriamine was employed as the chemical challenge.

Care must be taken in handling the sample because oils from the hands and moisture can induce crazing in the sample. A calibration sample(e.g., no. 2-37) is initially measured for thickness($d=0.1183$ in.) using a micrometer. The starting $\%r$ value to be used was selected as 0.00579. Using equation 2, the

starting strain and thickness are inserted to give the displacement value of 0.00326 in.

Once the deflection has been induced on the sample, the three point bend apparatus with sample is placed in a Plexiglass container with a white background. The He-Ne laser is oriented so that the beam reflects from the center of the sample and knife edge onto the white background. The video recording equipment is then aligned to record the reflection pattern appearing on the white background.

A 1.0 microliter drop of simulant is added at the center of the sample, where the laser beam intercepts the sample. The timer is started at the time of the addition and the reflection is recorded. The reflection pattern is carefully monitored. If the pattern begins to diffuse, develop horizontal lines, or the two initial points separate, crazing is occurring and the time is recorded. Extreme care is needed in determining the onset of crazing because evaporation of the simulant can distort the reflected pattern.

If crazing occurs at the %r initially selected, this %r value is divided by a factor of 1.2 and the new %r value is used in the next test. If crazing does not occur within thirty minutes, the %r value initially selected is multiplied by a factor of 1.2 and this new %r value used for the next sample. Since the sample used as an example did not craze within thirty minutes, the %r value 0.00479 is multiplied by 1.2 and the new %r value 0.00575 is used for the next test. This process is repeated until a critical strain value is produced.

From a plot of the %r values versus the specific times for crazing to occur, a critical strain value(%r_c) is determined where the critical strain is defined as the percent strain value where a discontinuity occurs in the plot of time versus percent strain. A table of critical strain values is constructed by collecting data from each simulant and transparent material combination.

Figure 2 shows the behavior of the calibration solution diethylenetriamine on polycarbonate samples. Crazing did not occur. Only the more diffuse diffraction pattern of b in Figure 1, was observed. This more diffuse diffraction pattern is due to hazing of the transparent material. Figure 3 represents typical strain behavior for a simulant and transparent material. The critical strain is observed to occur at %r_c=0.00479 where the time for crazing to occur shifts from >1800 seconds to 26 seconds. Note how the behavior of triethylenediamine on polycarbonate(Figure 2) differs from the behavior of CEES on polycarbonate(Figure 3).

The samples were initially examined under polarized light. By utilizing polarized light, the defects and strains within the individual samples can be examined. Strain induced during sample preparation, thickness discontinuity within the sample, and fragment displacement become apparent.

Fig. 2 Calibration Plot of Polycarbonate and Diethylenetriamine

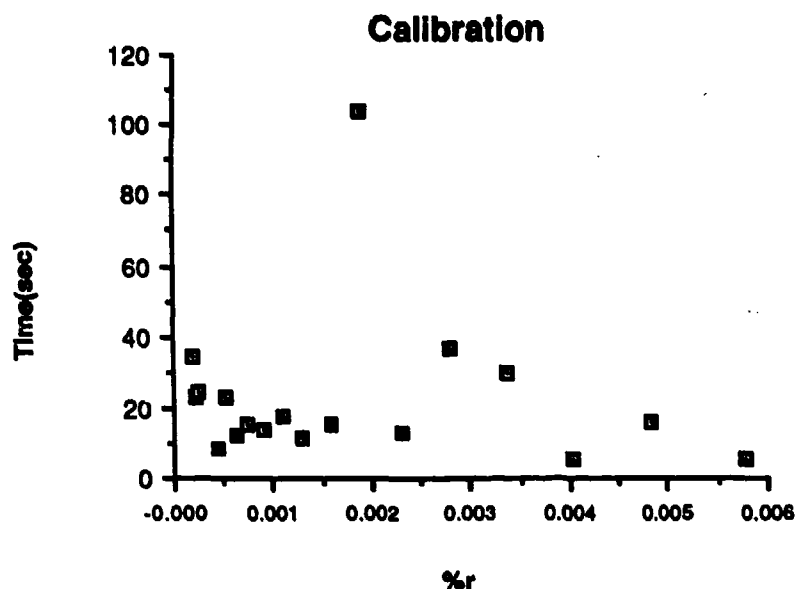
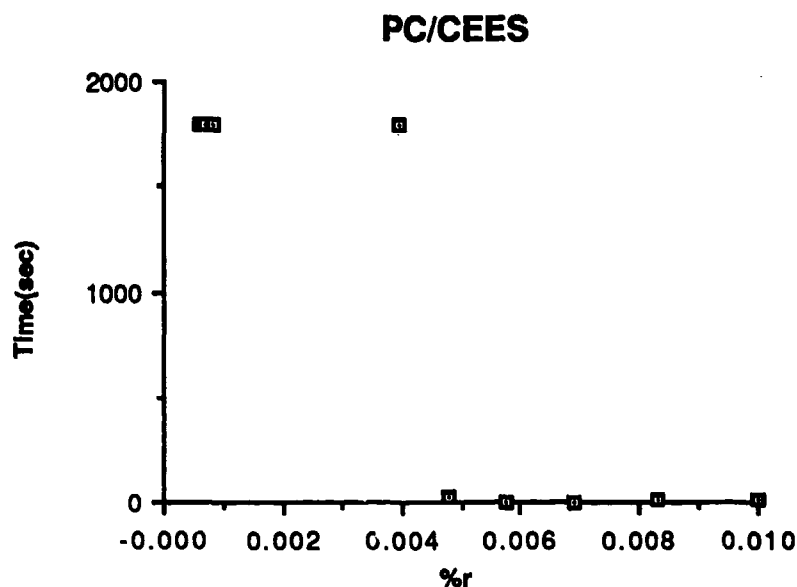


Fig. 3 Critical Strain Curve of Polycarbonate and CEES



4. RESULTS AND DISCUSSION

Critical strain values($\%r_c$) have been determined for four transparent polymer materials challenged with nine different simulants. The strain versus time data used to produce the appropriate critical strain values are given in Appendix C. In this section, we shall discuss the effect of the simulants on each

of the classes of materials that were tested. Finally, all of the critical strain data will be compared in a single matrix.

4.1 POLYCARBONATE

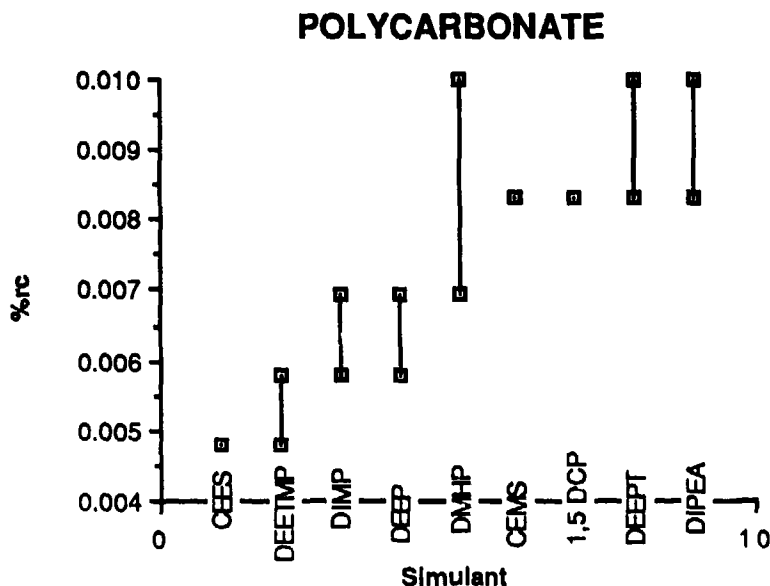
Under examination by polarized light, the polycarbonates exhibited a "ripple" effect and the stress induced by sample preparation could be detected. The "ripple" effect apparently is introduced during the extrusion of the polymer during processing which produces varying polymer thickness in the samples.

The polycarbonate samples crazed under stress with each simulant. The GB simulants, DIMP, DEEP, and DMHP produced crazing between $\%r_c=0.00579$ and $\%r_c=0.00999$ (Fig. 4). DMHP crazed between $\%r_c=0.00695$ - 0.00999 , while DEEP and DIMP had critical strain ranges of $\%r_c=0.00579$ - 0.00695 .

CEES produced the lowest critical strain value for the polycarbonates at $\%r_c=0.00479$. The critical strain values for CEMS and 1,5 DCP were the same at $\%r_c=0.00833$.

The VX simulants DEEPT and DIPEA induced crazing at $\%r_c=0.00833$ - 0.00999 . DEETMP substantially decreased the critical strain value for the polycarbonates to $\%r_c=0.00483$ - 0.00578 .

Fig. 4 Polycarbonate Critical Strain as a Function of Simulant



4.2 CAST PMMA

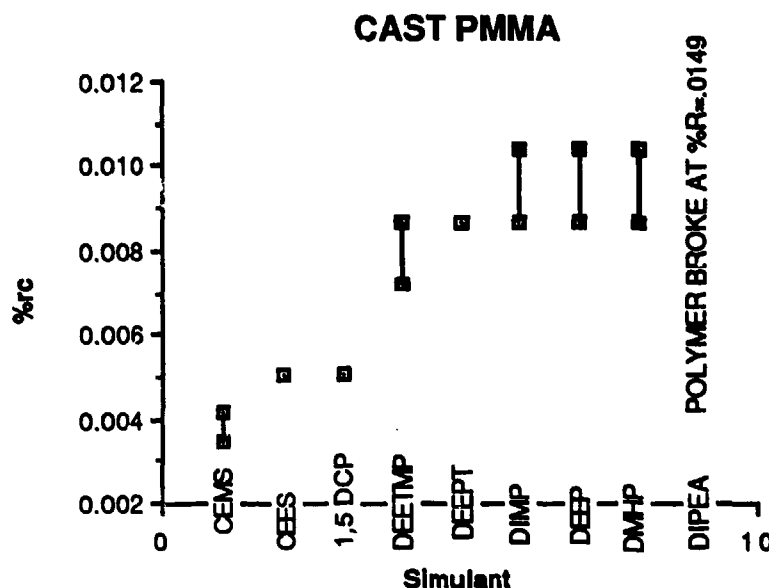
Cast PMMA showed very little strain under examination by polarized light. The strain that could be detected was structural damage along the edges of the

sample that had been caused by sample preparation, i.e. cutting the sample with a saw.

The GB simulants (Fig. 5), DIMP, DEEP, and DMHP, remained consistent in the cast PMMA samples, all producing critical strain values of $\%r_c=0.00867-0.0104$. The mustard simulants decreased the $\%r_c$ value considerably. CEES and 1,5 DCP induced crazing at $\%r_c=0.00503$, while CEMS lowered the $\%r_c$ value to 0.00349-0.00419. DEETMP crazed at $\%r_c=0.00870$, DEEMPT crazed at $\%r_c=0.0725-0.00867$ and DIPEA did not induce crazing (i.e., the polymer sample broke at $\%r_c=0.0149$).

Fig. 5

Cast PMMA Critical Strain as a Function of Simulant



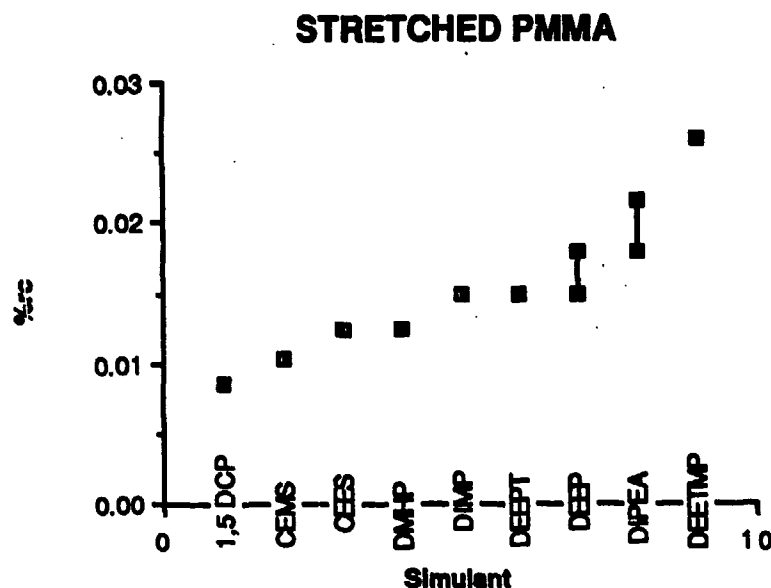
4.3 STRETCHED PMMA

Stretched PMMA showed little distortion under examination by polarized light. The fragment displacement along the edges of the samples was present, induced by the sample preparation method.

The GB simulants caused the polymer samples to craze at $\%r_c$ values of 0.0125-0.0180. DMHP caused the samples to craze at $\%r_c=0.0125$, DIMP at $\%r_c=0.0150$, and DEEP between $\%r_c=0.0150$ and 0.0180. CEMS induced crazing at $\%r_c=0.0104$. 1,5 DCP resulted in the lowest $\%r_c$ value for the stretched PMMA ($\%r_c=0.00867$), while the $\%r_c$ value for CEES was 0.0125 (Fig. 6).

Simulants for VX had a smaller effect on the crazing of stretched PMMA than did the simulants for GB and mustard. DEETMP induced crazing in the samples at $\%r_c=0.0259$. DEEPT had a $\%r_c$ value of 0.0150 and DIPEA ranged from 0.0180 to 0.0216.

Fig. 6 **Stretched PMMA Critical Strain as a Function of Simulant**



4.4 POLYURETHANE

Polyurethane demonstrated the most resistance to simulant induced crazing of all the transparent materials tested. Most of the simulants did not induce crazing at the maximum $\%r_c$ values ($\%r_c=0.0311$) that could be attained with the equipment used (Fig. 7). Under examination by polarized light, no anomalies were noted within the samples.

Polyurethane challenged by DIMP crazed at $\%r_c=0.0216$, but DEEP and DMHP did not induce crazing in the samples. The mustard simulants, CEMS and CEES, caused the samples to craze at values of $\%r_c=0.0216$ and 0.0259 respectively, whereas, 1,5 DCP did not induce crazing. Only one of the VX simulants, DEETMP caused the polymer to fail, $\%r_c=0.0259$. DEEPT and DIPEA did not induce crazing at the strain values that could be attained.

Fig. 7

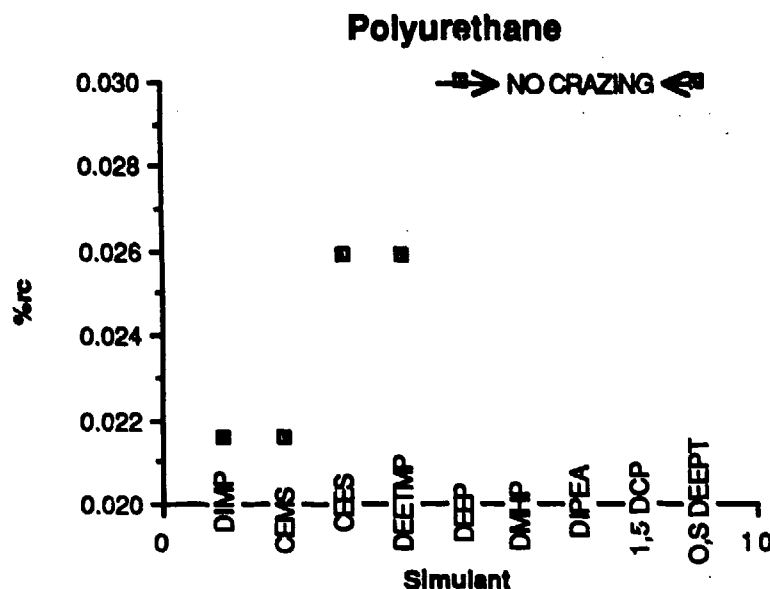
Polyurethane Critical Strain as a Function of Simulant

Table 4 represents a tabular matrix that summarizes the critical strain values that were determined for the tested materials and simulants. As an example, the material polycarbonate(PC) and the simulant CEES(Figure 3), produced $\%r_c$ values in region 2(0.00349-0.00483). The other three materials tested with CEES produced critical strain values that were greater; namely 0.00484-0.00604 for cast PMMA, 0.01000-0.01500 for stretched PMMA, and 0.02160-0.02590 for polyurethane. Table 4 allows the results of our testing to be evaluated at a glance. Again, note that the simulants exerted the least crazing effects on the polyurethane samples.

Table 4**Critical Strain Values Determined as a Function of Material/Simulant Combination**

		PC	CP	SP	PU
GB	DMHP	4-5	6-7	7	10
	DEEP	3-4	6-7	7	10
	DIMP	3-4	6-7	7	8
HD	CEES	2	3	7	9
	CFMS	5	2	7	8
	1,5 DCP	5	3	5	10
VX	DEEPT	6	6	7	10
	DEETMP	2-3	4-6	9	9
	DIPEA	5-6	5-6	8	10

Region	Critical Strain ($\%r_0$)
1	<.00349
2	.00349-.00483
3	.00484-.00604
4	.00605-.00725
5	.00726-.00867
6	.00868-.00999
7	.01000-.01500
8	.01510-.02160
9	.02160-.02590
10	>.02590

PC=polycarbonate
 CP=cast PMMA
 SP=stretched PMMA
 PU=polyurethane

5. COMMENTS

In this section, some of the complications and limits of the procedures used in the sample preparation and detection of the onset of crazing are presented.

1. The methods used to prepare the individual transparent samples induced thermal strain and structural damage in each sample. The induced thermal strain and structural damage were detected using polarized light. The ranges of the strain behavior observed may be due to induced structural damage/fragment displacement along sample edges.

2. Another anomaly detected with polarized light was the "ripple" phenomenon found in the polycarbonate samples. This phenomenon is apparently introduced during the extrusion process. The ripple causes the thickness of the sample to vary where the ripple is perpendicular to the length of the sample. In some polycarbonate samples, the ripple is parallel to the length of the sample, possibly strengthening these samples, while weakening those samples where the ripple is perpendicular.

3. The visual techniques using the unaided eye cannot detect the onset of minute crazing that occurs in some transparent materials. Laser diffraction allows the detection of such crazing and provides a more real-time monitoring of the degradation process.

4. The introduction of simulant poses some problems, in that, the simulant can roll off the transparent material or evaporate at a non-uniform rate. Roll-off and evaporation need to be explored further to determine how they affect the observed results.

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Appendix A

Glossary of Terms

1. CEES- 2-chloroethyl ethyl sulfide
2. CEMS- 2-chloroethyl methyl sulfide
3. CP- cast PMMA
4. % r_c -critical strain- the percent strain value where a discontinuity occurs in the plot of the time versus percent strain
5. 1,5 DCP- 1,5 dichloropentane
6. DEEP- diethyl ethylphosphonate
7. DEEPT- O,S diethyl ethylphosphonothiolate
8. DEETMP- diethyl (ethylthiomethyl)phosphonate
9. DIMP- diisopropyl methylphosphonate
10. DIPEA-N,N diisopropylethylamine
10. DMHP- dimethyl hydrogen-phosphonate
11. % r -percent strain in the outer layers of a polymer sample measured by the equation:

$$r=6Dd/L^2$$

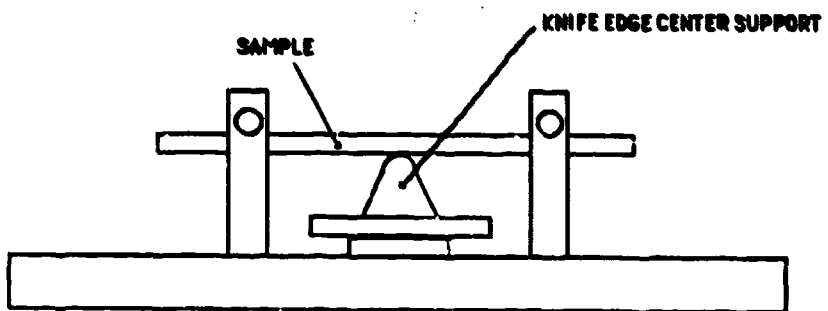
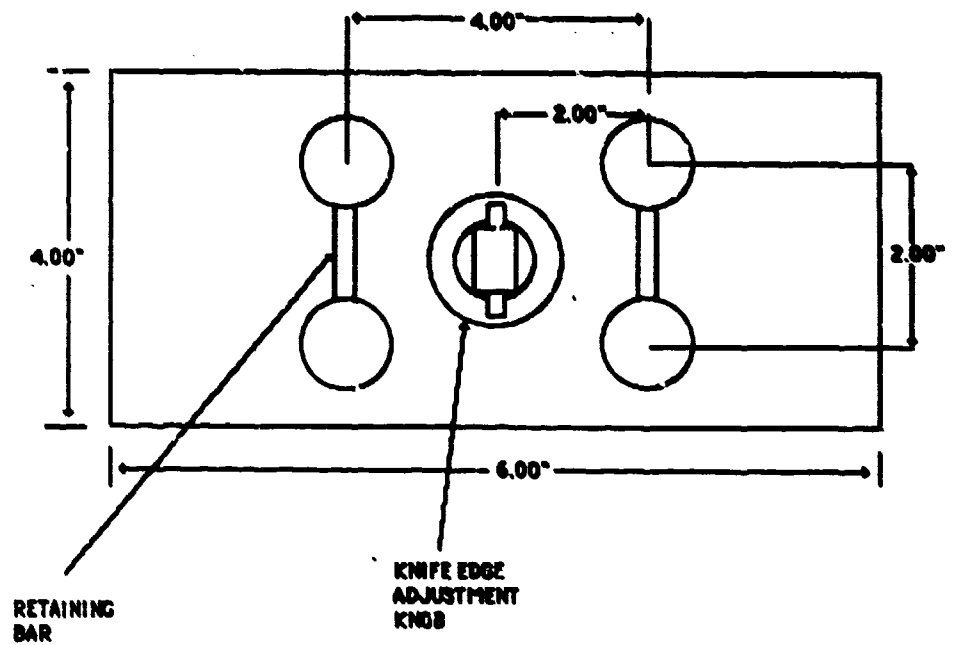
where D=displacement of the sample in the center, d=thickness, and L=support span

12. PC- polycarbonate
13. PU- polyurethane
14. SP- biaxially stretched PMMA

Blank

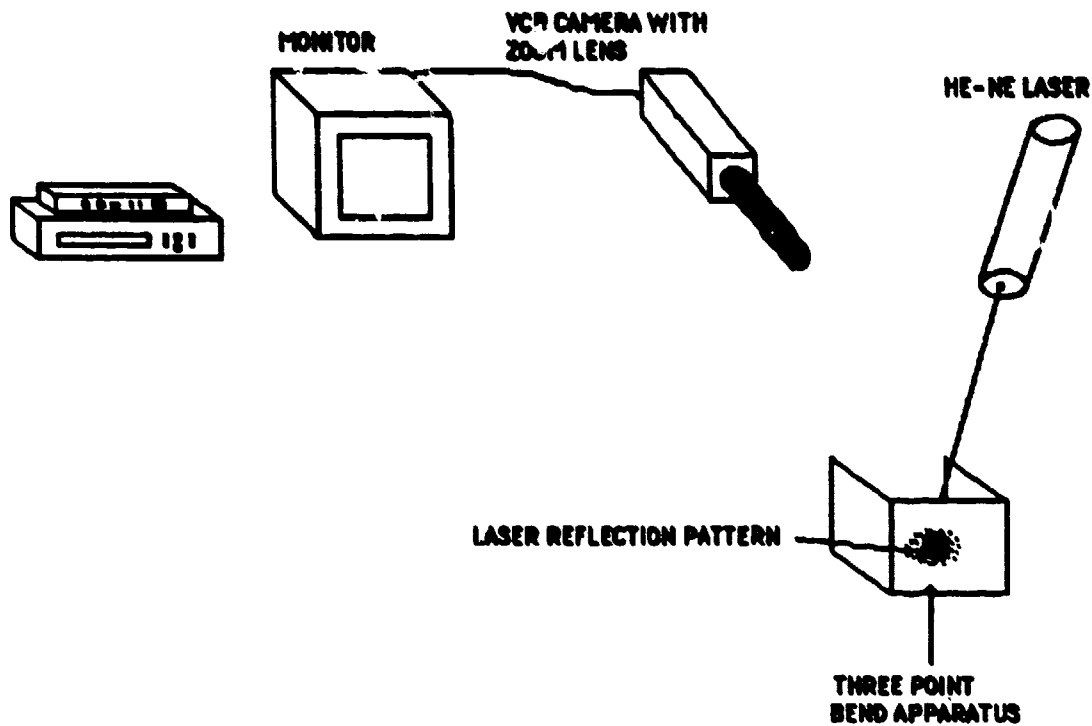
Appendix B
Diagrams of Experimental Apparatus

Figure B1



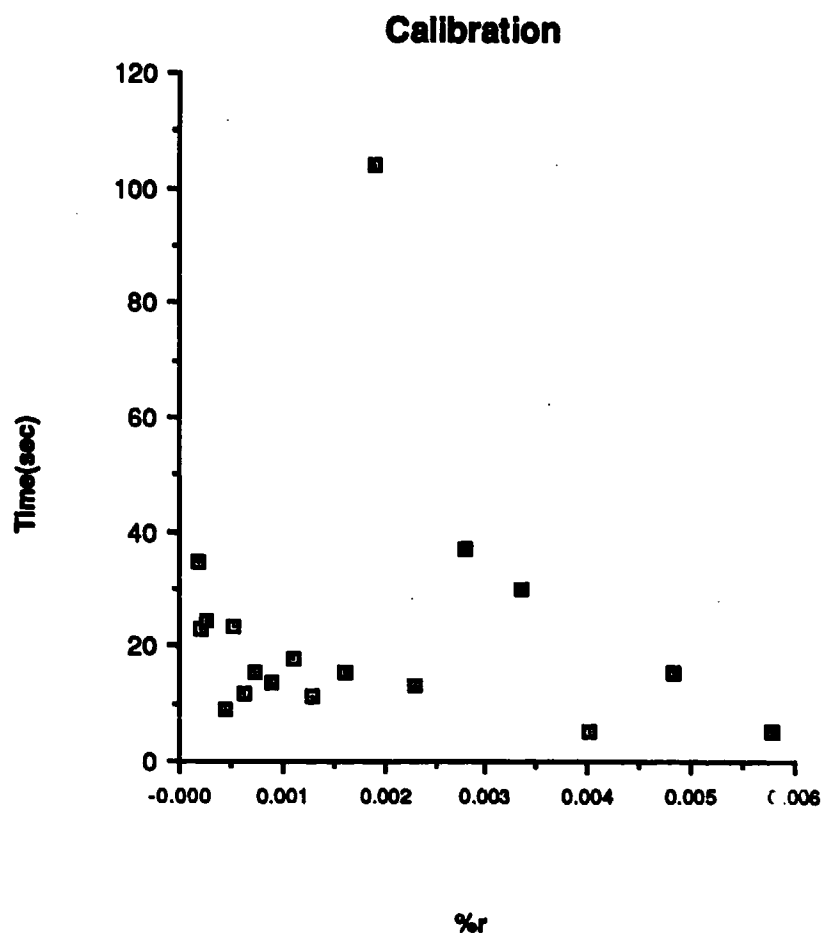
THREE POINT BEND TEST APPARATUS

FIGURE B2

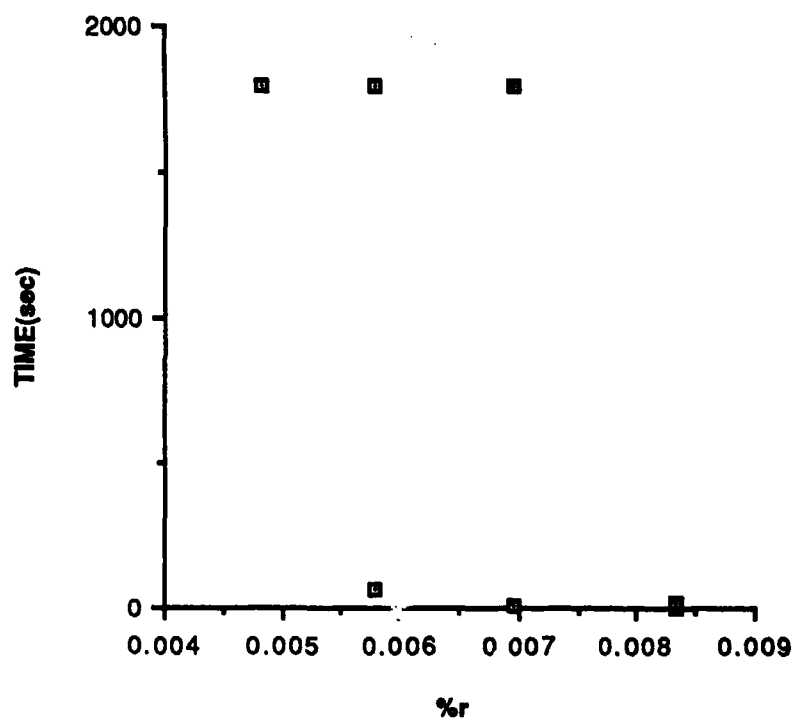


**SCHEMATIC OF THE SYSTEM USED TO
DETECT THE ONSET OF CRAZING**

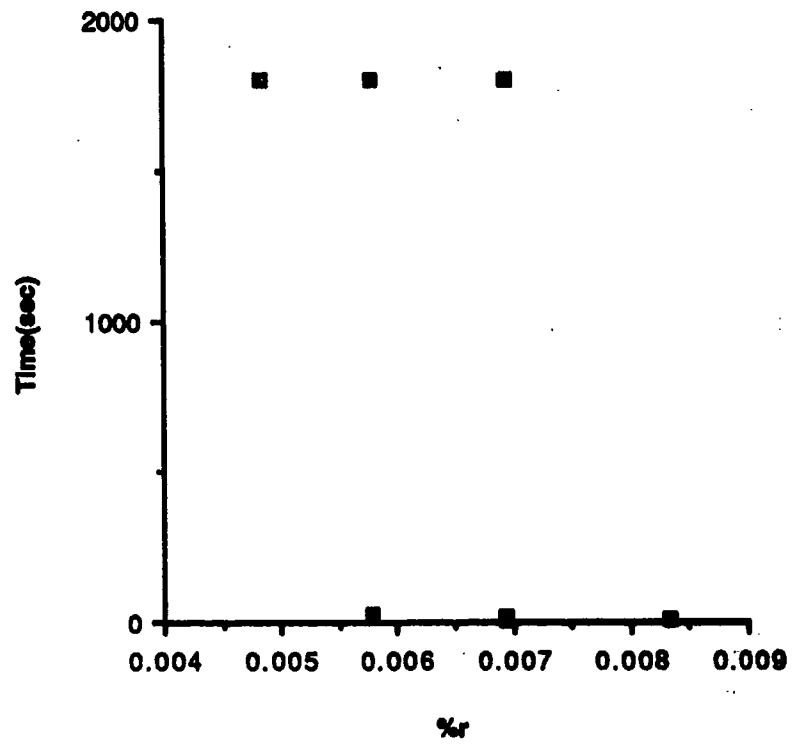
Appendix C
Experimental Results

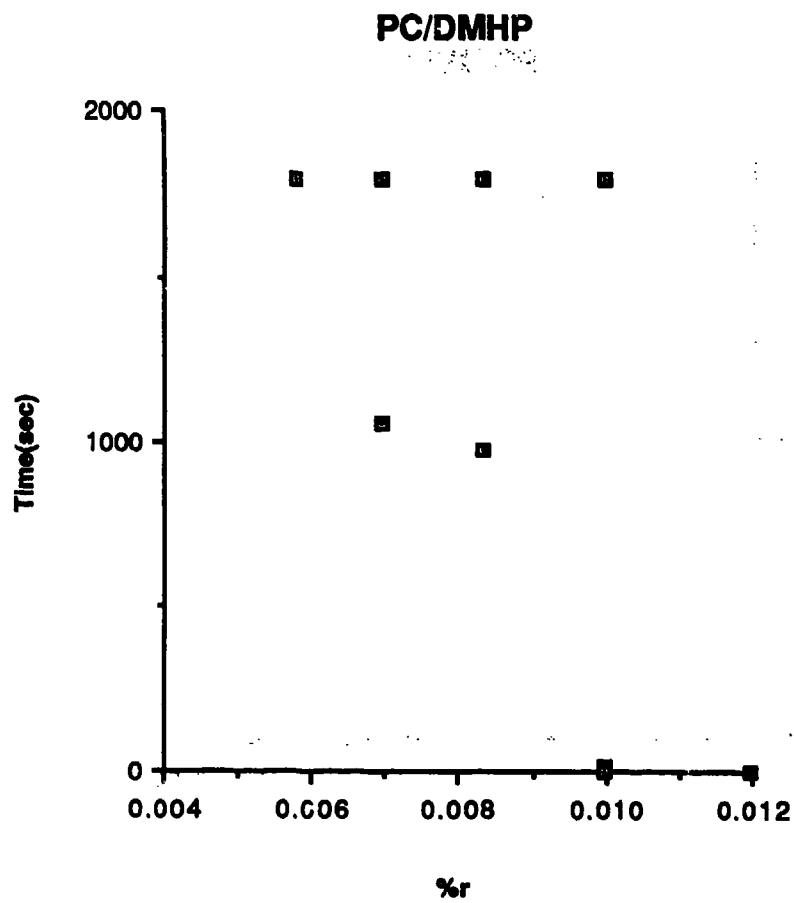


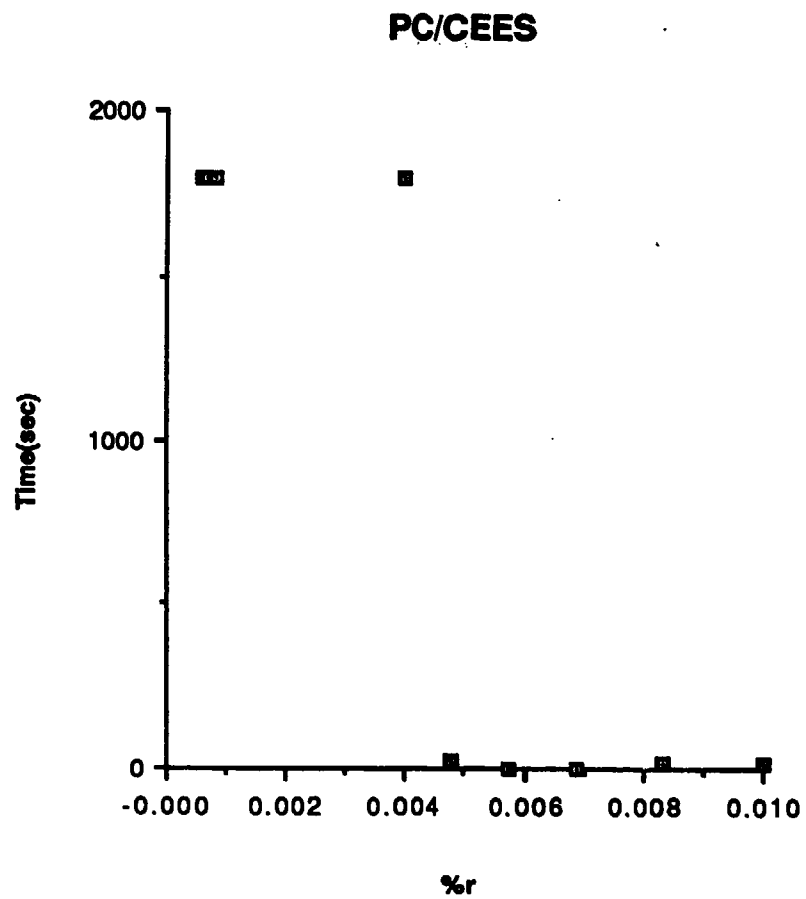
PC/DIMP



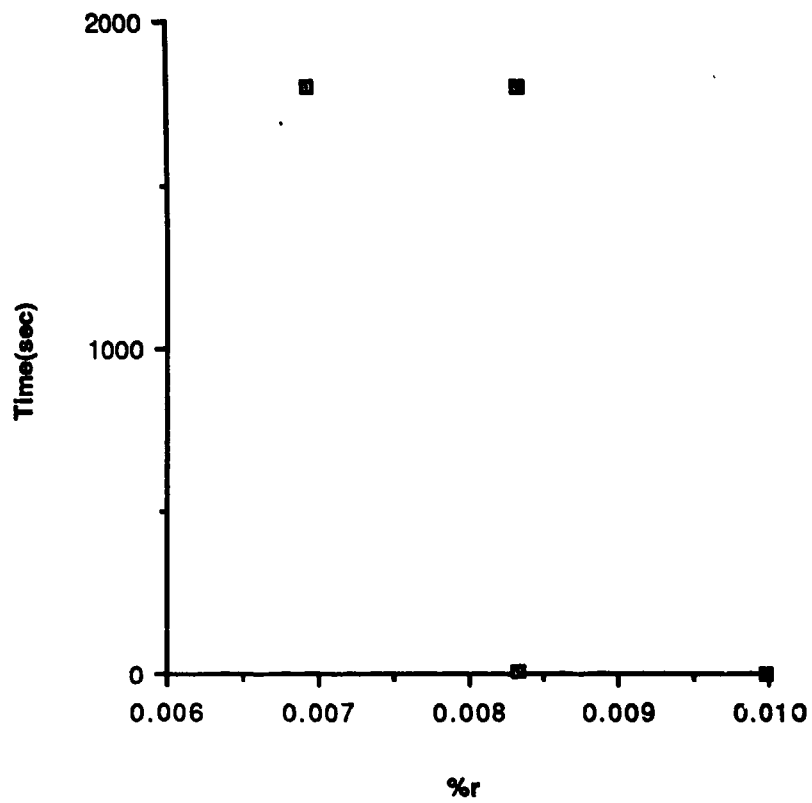
PC/DEEP



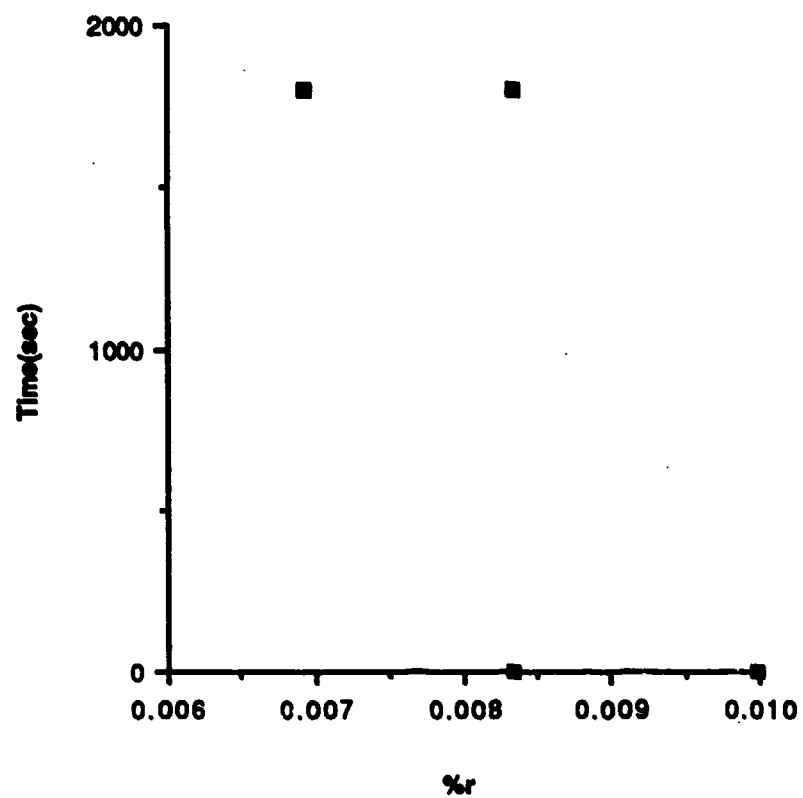




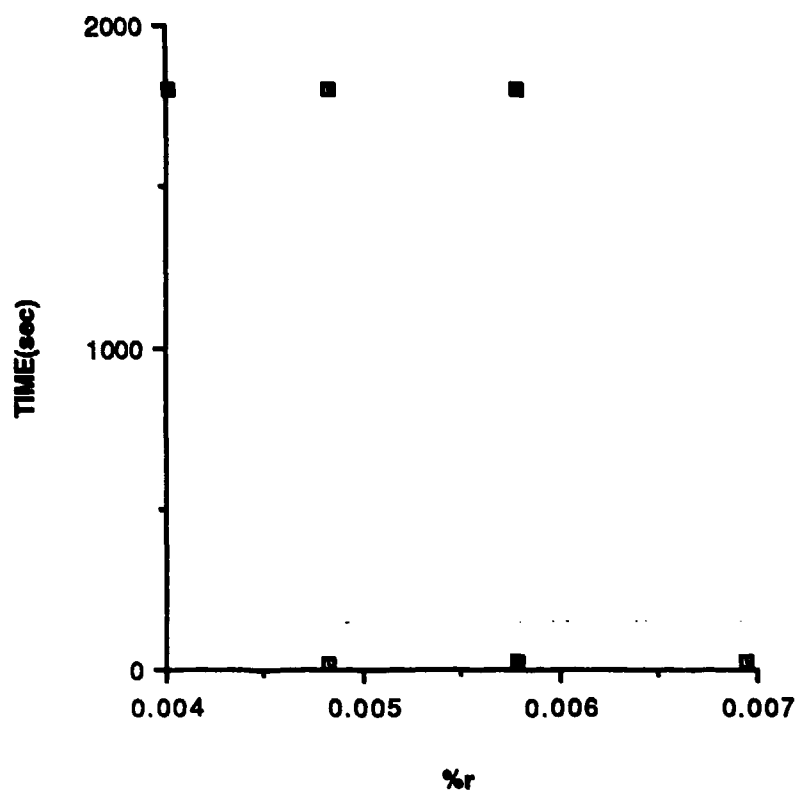
PC/CEMS



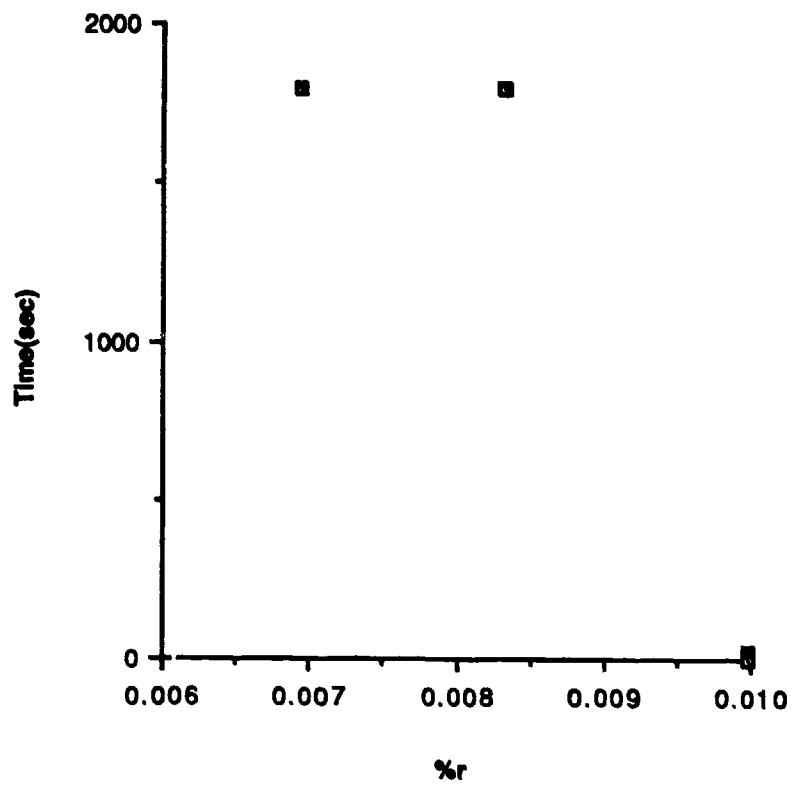
PC/ 1,5 DICHLOROPENTANE



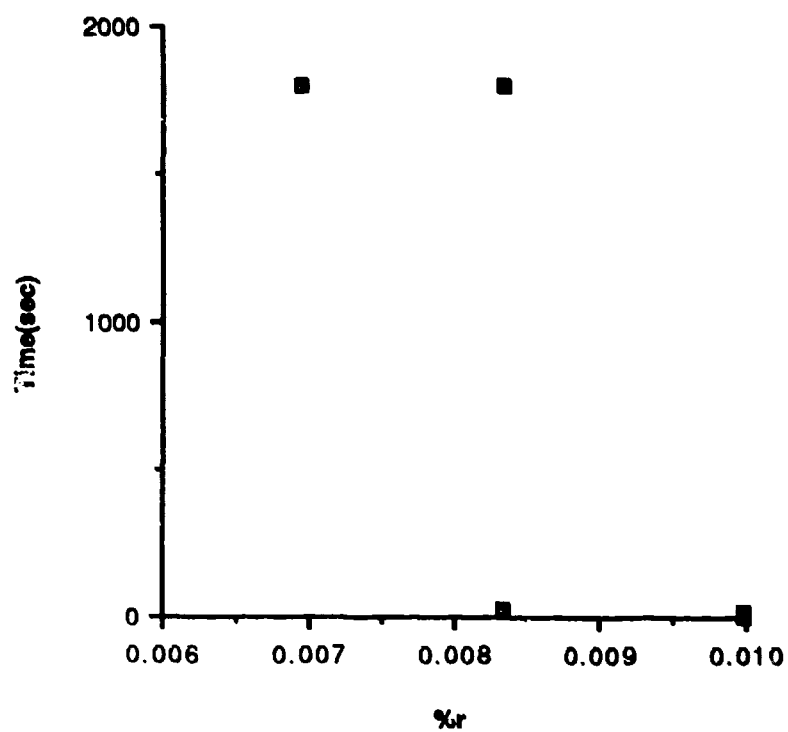
PC/DEETMP



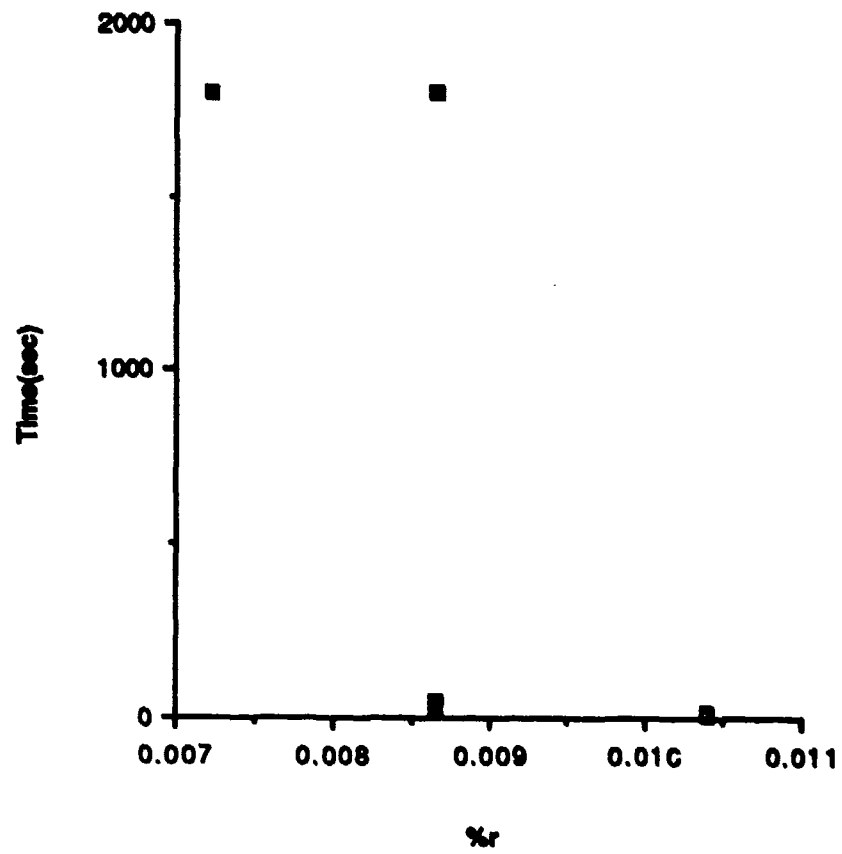
PC/DEEPT



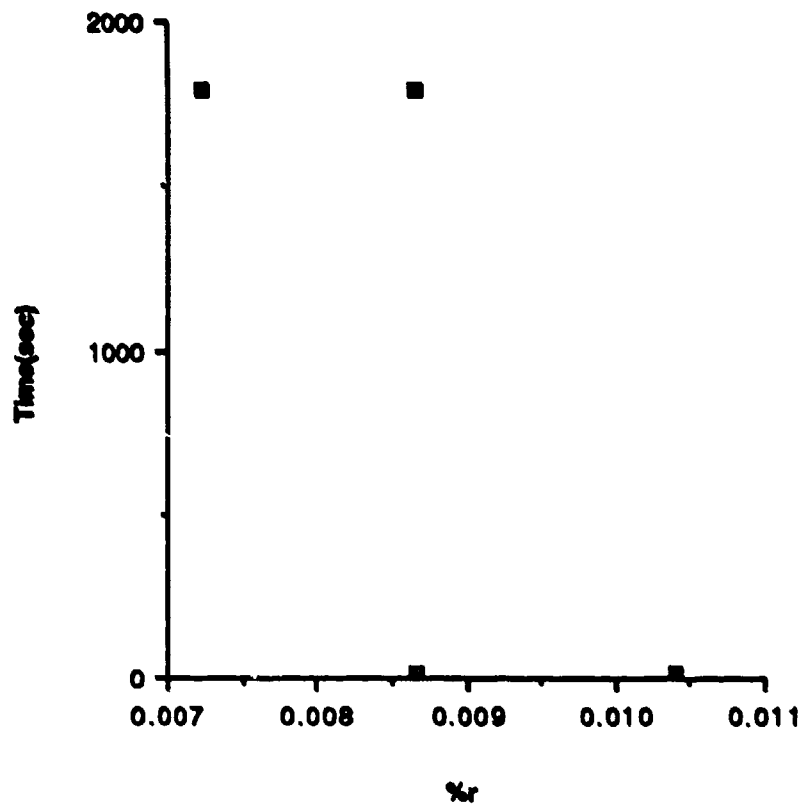
PC/N,N DIISOPROPYLETHYLAMINE



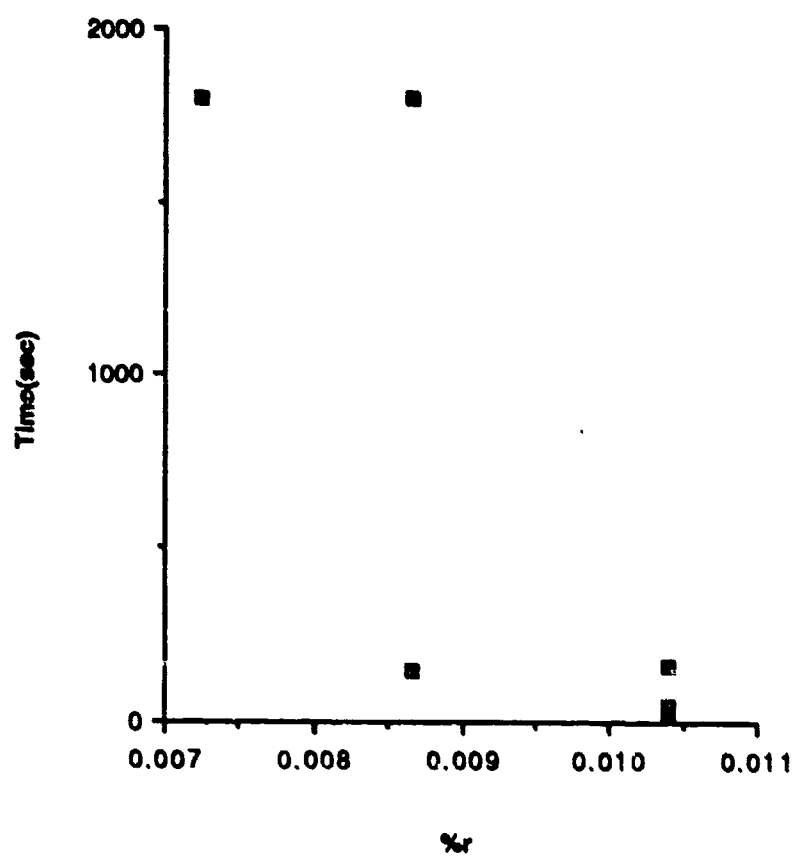
CP/DIMP



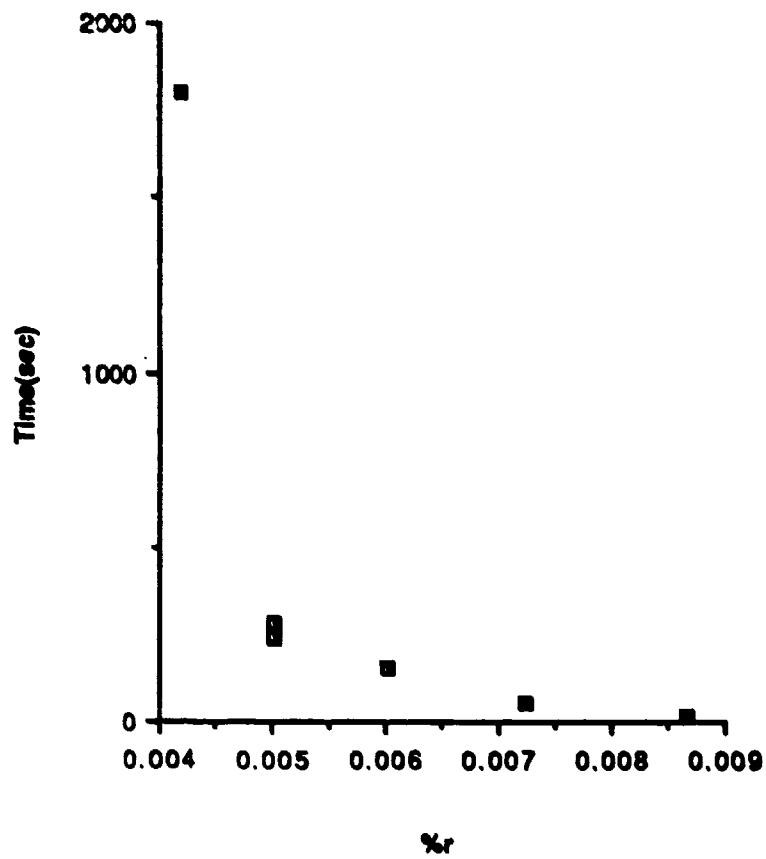
CAST PMMA/DEEP



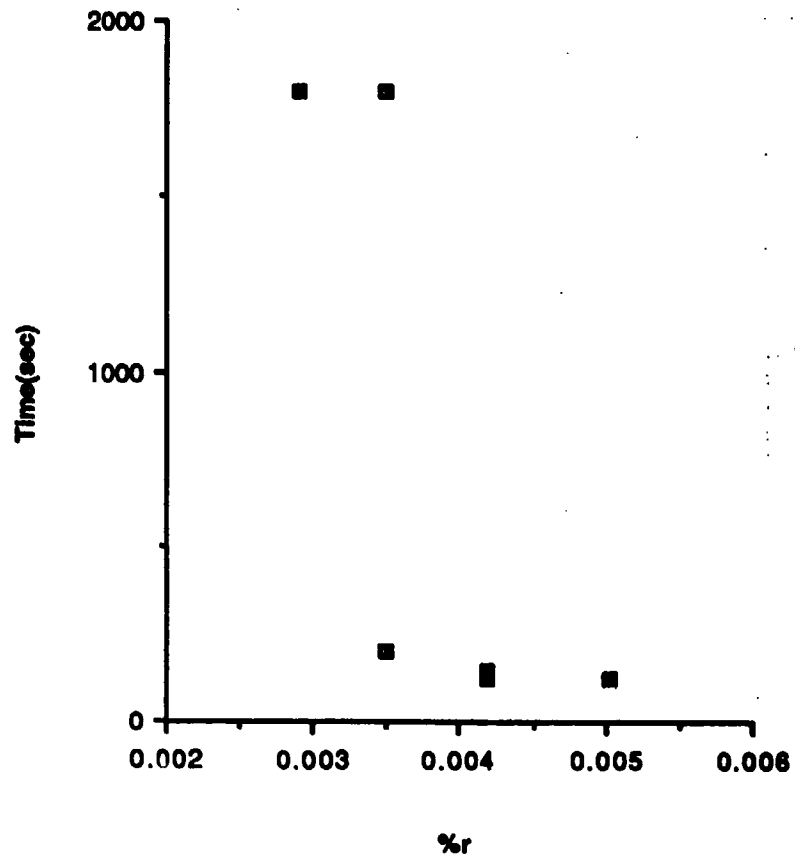
CP/DMHP



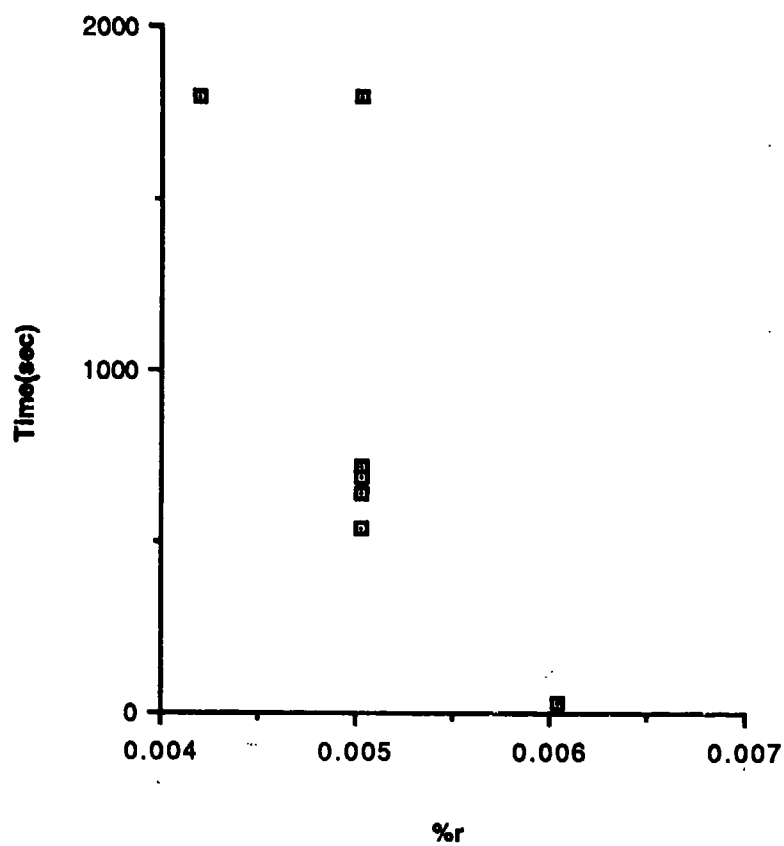
Cast PMMA/CEES



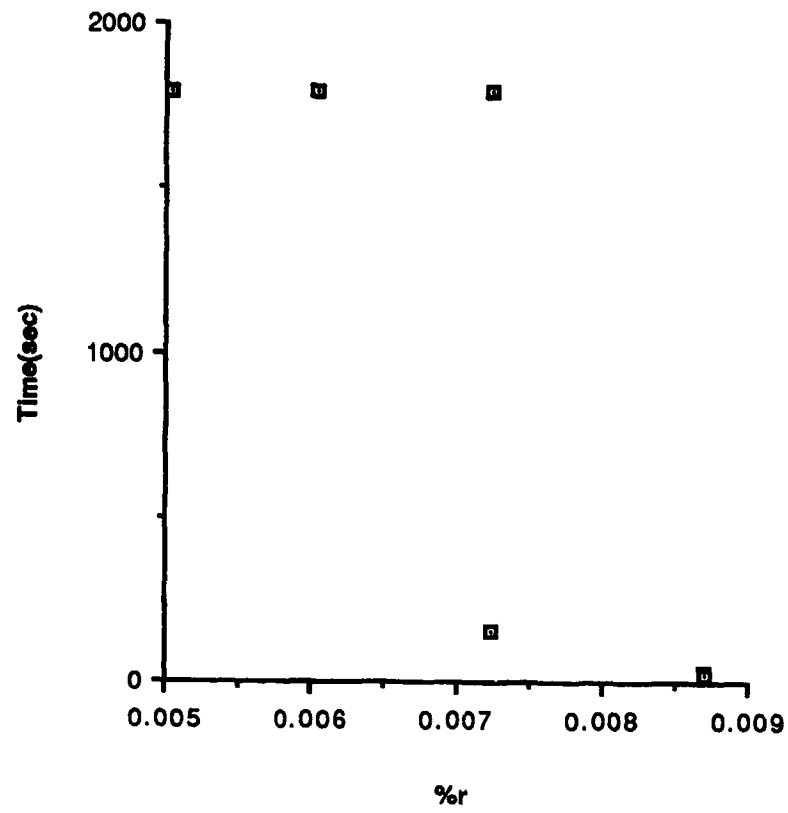
CP/CEMS



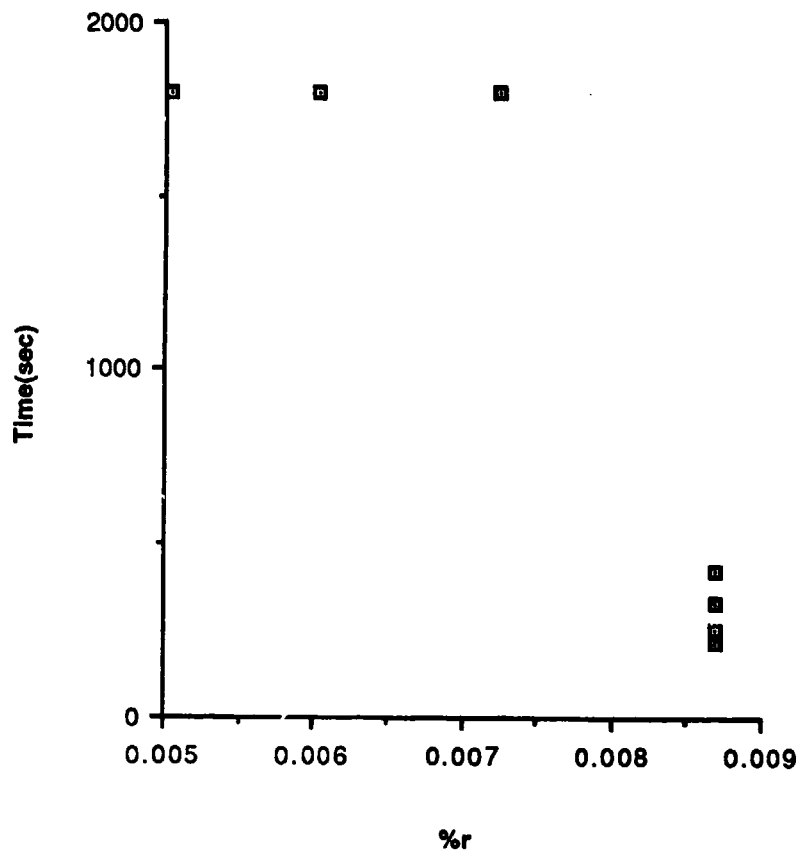
CP/1,5 DICHLOROPENTANE



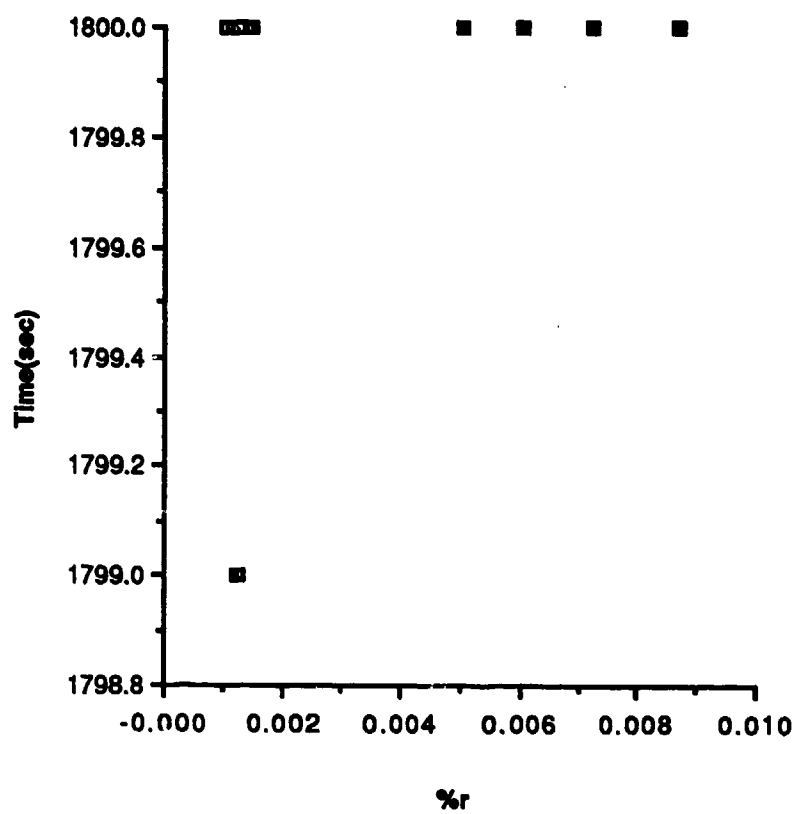
CAST PMMA/DEETMP



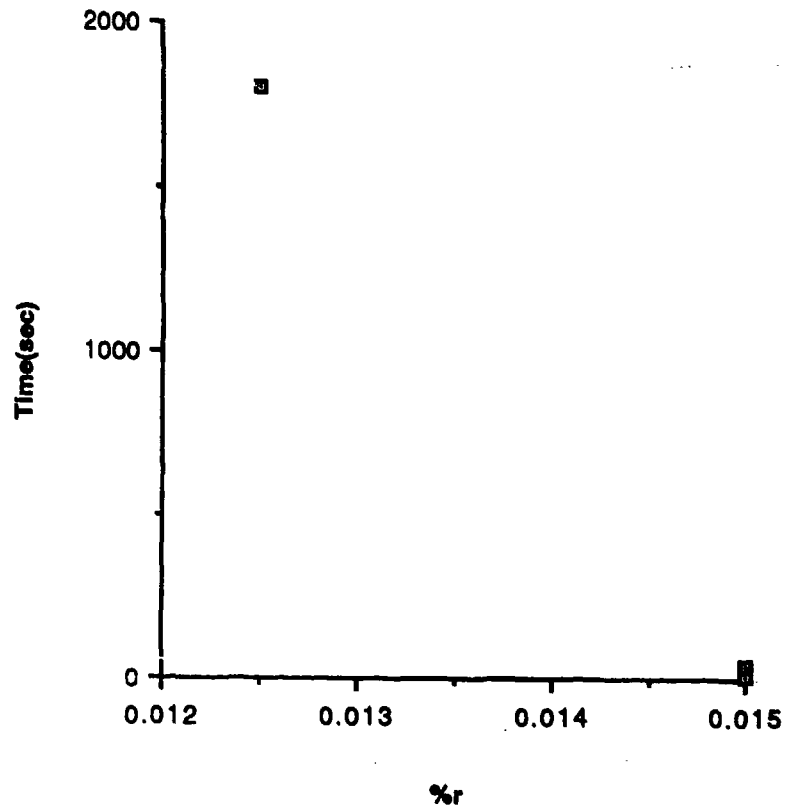
CP/DEEPT



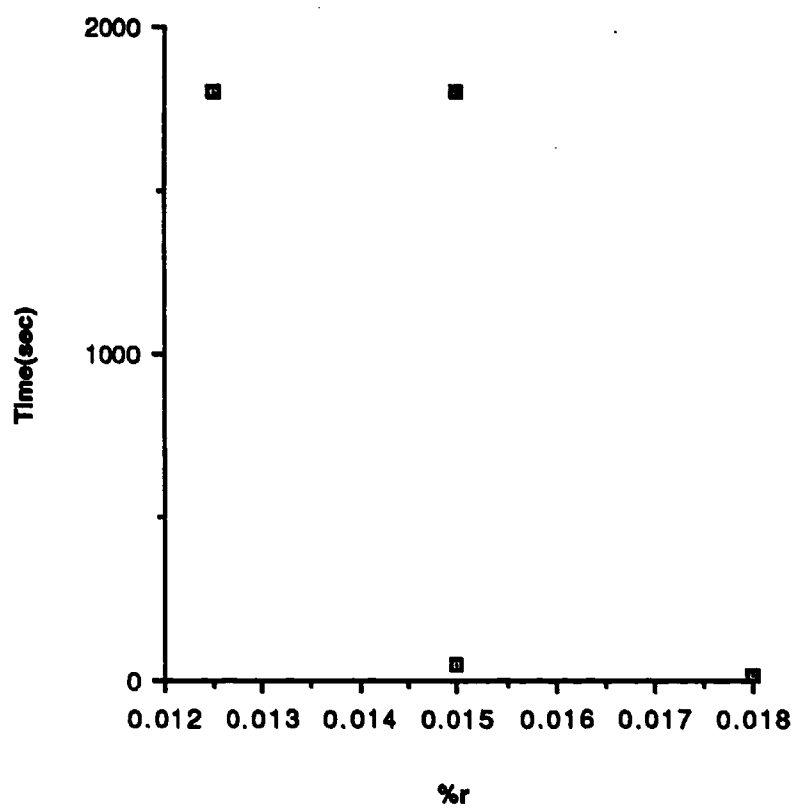
CAST PMMA/ DIPEA



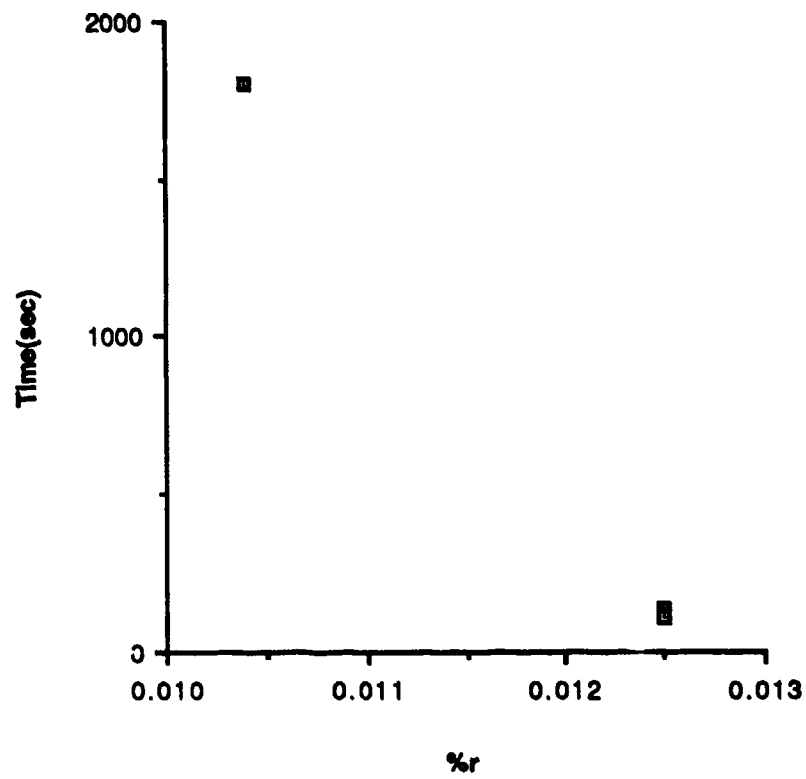
STRETCHED PMMA/DIMP



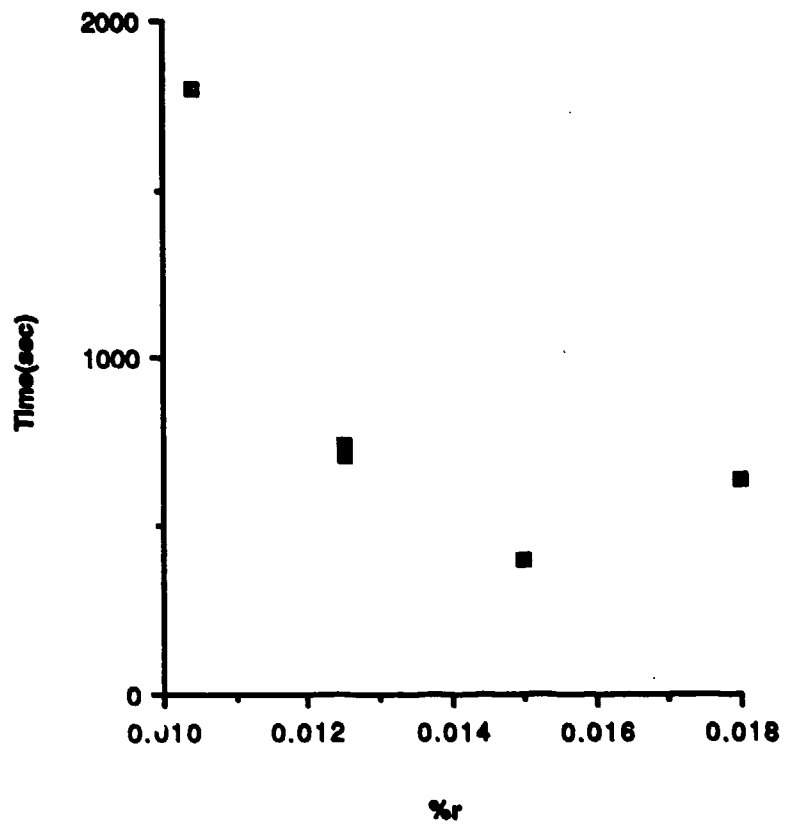
STRETCHED PMMA/DEEP



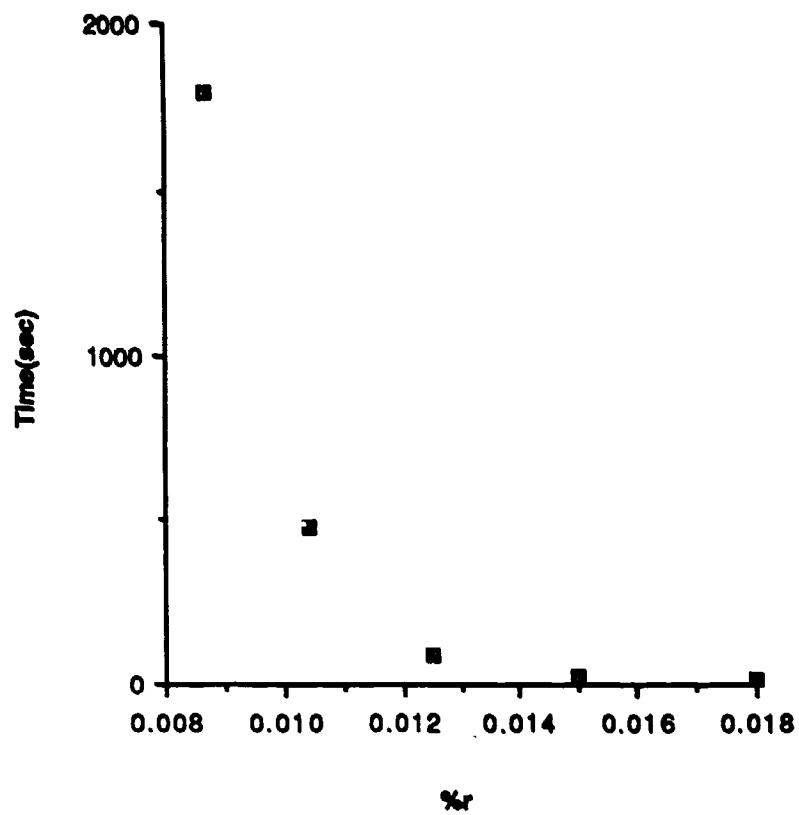
STRETCHED PMMA/DMHP



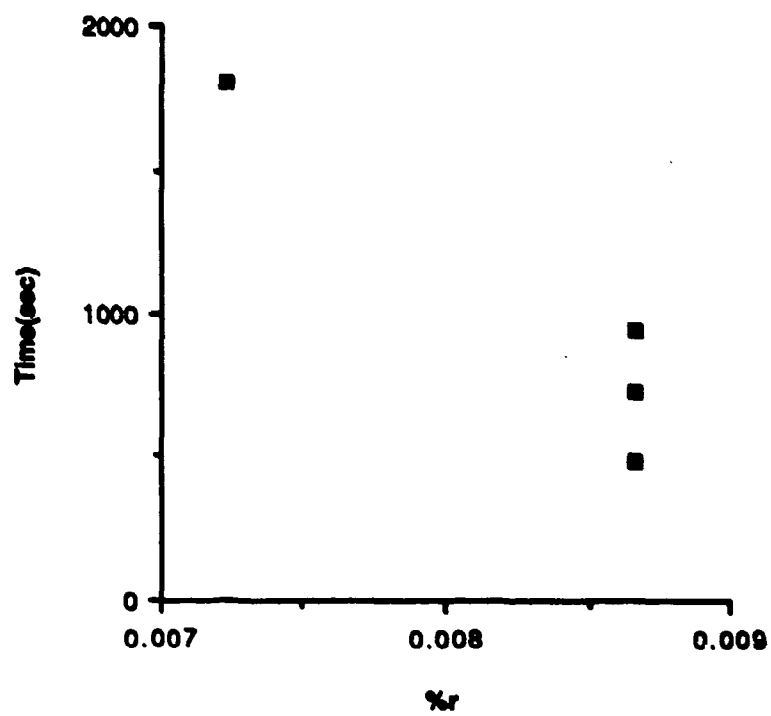
STRETCHED PMMA/CEES



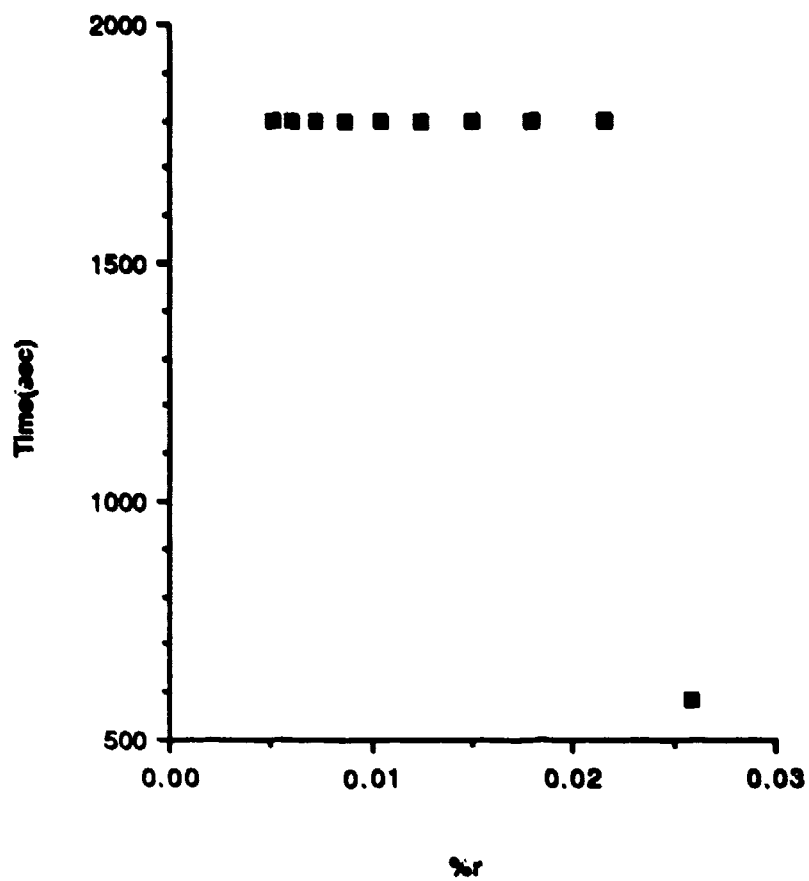
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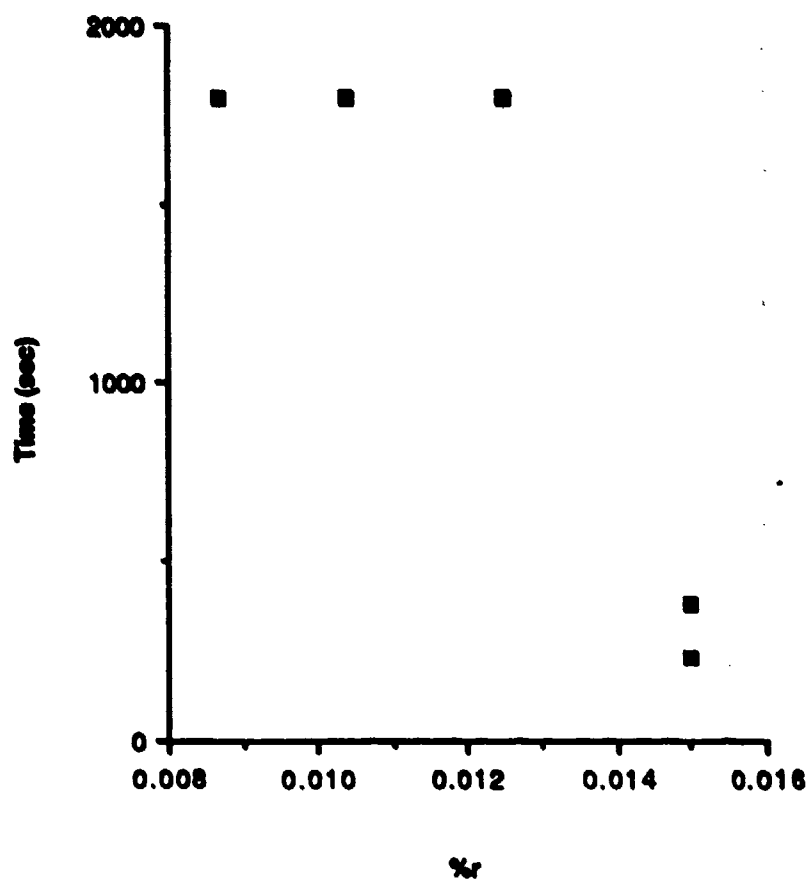
STRETCHED PMMA/ 1,5 DICHLOROPENTANE



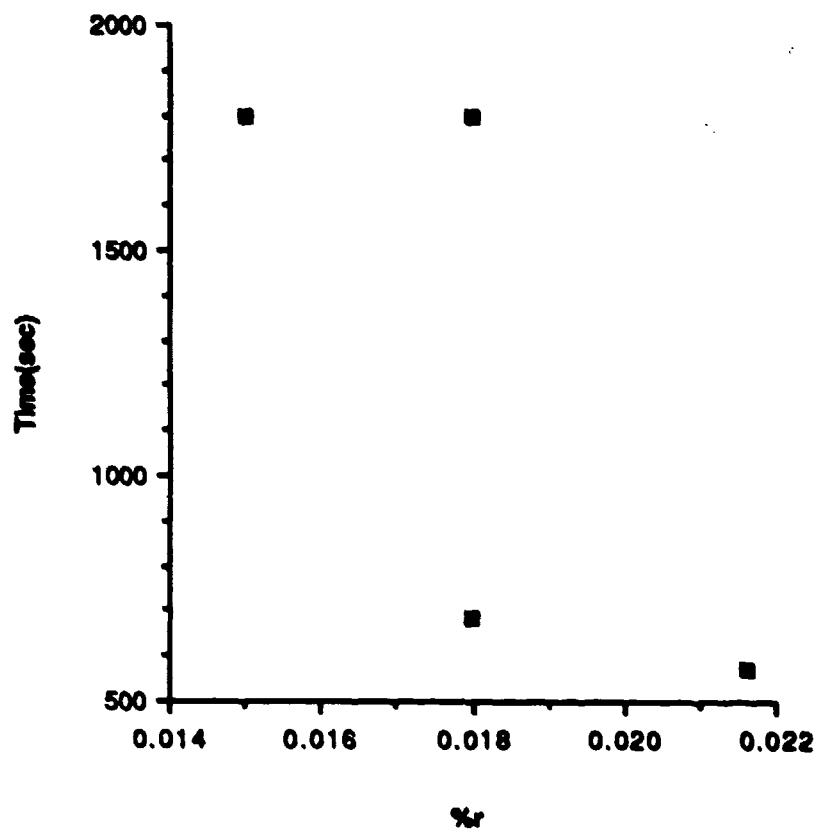
STRETCHED PMMA/DEETMP



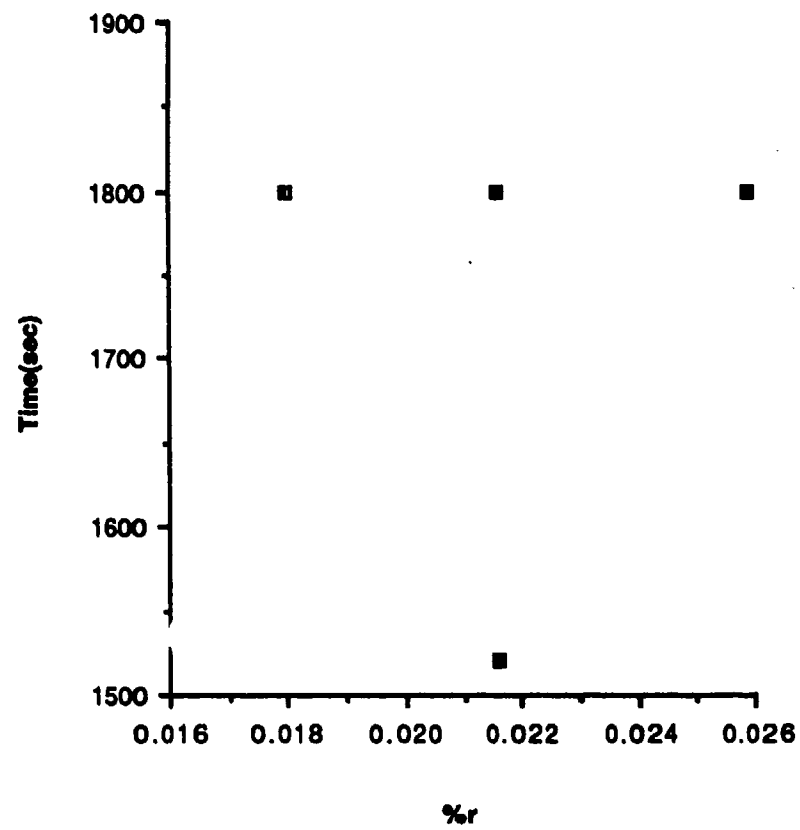
STRETCHED PMMA/ O,S DEEPT



STRETCHED PMMA/DIPEA



POLYURETHANE/DIMP



PU/DMHP DATA

<u>Time(sec)</u>	<u>%r</u>
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1800	.0259
1800	.0259*

* Apparatus at maximum allowable %r.

PU/DMHP DATA

<u>Time(sec)</u>	<u>%r</u>
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1800	.0259
1800	.0259*

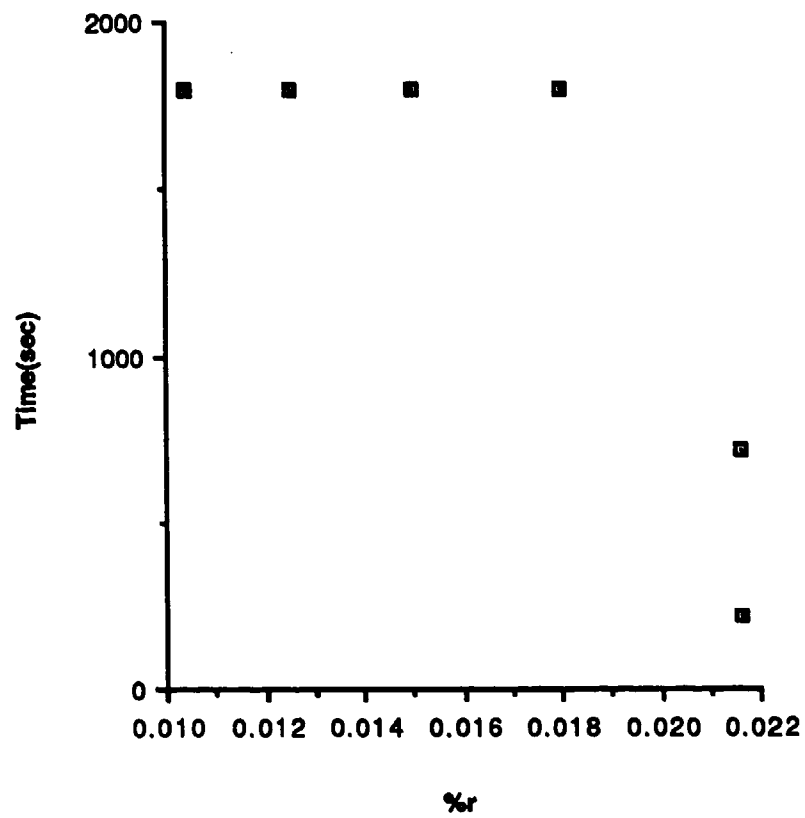
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PU/CEES DATA

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1800	.0259
1164	.0259*

* Apparatus at maximum allowable %r.

POLYURETHANE/CEMS



PU/DCP DATA

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1800	.0259*

* Apparatus at maximum allowable %r.

PU/DEEPT DATA

<u>Time(sec)</u>	<u>%r</u>
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1800	.0259
1800	.0259*

* Apparatus at maximum allowable %r.

PU/DEETMP DATA

<u>Time(sec)</u>	<u>%r</u>
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1800	.0259
968.4	.0259*
1800	.0216

* Apparatus at maximum allowable %r.

PU/DIPEA DATA

<u>Time(sec)</u>	<u>%r</u>
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1800	.0259*

* Apparatus at maximum allowable %r.