

## Effects of Methyl Ethyl Ketone Peroxide on the Performance of Cast Polymers

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### Abstract

The effect of varying levels of Methyl Ethyl Ketone Peroxide cure initiator on the performance of cast polymer resins is investigated. Resin and initiator suppliers routinely recommend initiator levels of 0.75 – 2.5% based on resin. This recommendation may not always be followed due to shop temperatures that cause the resin to react too quickly or too slowly. This study investigates the effects of initiator level including those outside the recommended extremes. Physical properties, extent of cure, and degree of yellowing were measured on castings of a standard cultured marble resin cured with initiator levels ranging from 0.3% to 5.0%. The results clearly show the impact of deviating from the recommended range.

### Introduction

Unsaturated polyester manufacturers and peroxide manufacturers routinely recommend specific levels of peroxides for the cast polymer industry. The recommended levels are typically between 0.75 and 2.5 percent. This study investigates these levels of peroxide on the specific attributes of color change due to heat exposure and thermal shock as well as physical properties and completeness of cure. The literature discusses the effects of peroxide level (1-3) on unsaturated polyesters, however, the specific effects on color change due to heat exposure and thermal shock exposure could not be found. The major peroxide that is used in the cast polymer industry is methyl ethyl ketone peroxide (MEKP). This peroxide, however, is not one specific chemical but rather a mixture of monomer, dimer, and other components (4). For this reason we have limited our study to one particular MEKP which has a high monomer to dimer ratio and approximately 1 percent concentration of hydrogen peroxide. We prepared castings of resin without filler at various temperatures. We also prepared, at the same temperatures, cast polymer “marble matrix” on a gel-coated surface.

During the fabrication of cast polymer materials, the unsaturated polyesters copolymerize with styrene and form a cross-linked network. The process begins with the decomposition of the peroxide initiator forming free

radicals. The free radicals begin the process of polymerization which leads to the phase change from liquid to gel and eventually to a solid. Heat is evolved during the cure and the chemical changes taking place lead to an increase in glass transition temperature (T<sub>g</sub>). At low levels of peroxide the cross-linking resin will not release a sufficient amount of heat to maintain molecular motion. The cross-linking that does occur will lead to the increase in T<sub>g</sub> and this will essentially isolate the free radicals. This process is referred to vitrification (3). If excessive amounts of peroxide are used, chain transfer to initiator reactions may be excessive and a reduction in crosslink density may occur. This is expected to result in a weaker part. This study was carried out to provide specific data to the cast polymer industry for these generally accepted concepts.

### Experimental

Three types of castings were prepared. Resin castings that were made for physical properties, marble matrix castings for color change measurements and thermal shock testing, and can lid castings for measurements of degree of cure. The resin castings were cured at three ambient temperatures, 19.4, 25.0 and 30.6°C. The peroxide levels were 3.0 and 5.0 percent at 19.4°C, 1.5 percent at 25.0°C, and 0.5 and 1.5 percent at 30.6°C. The marble matrix castings were prepared at the same temperatures as the clear castings and at 25.0°C. The marble matrix castings were cured at the same temperatures as the clear castings prepared with the same peroxide levels. The marble matrix castings prepared at 25.0°C were cured with peroxide levels at 0.5, 1.5, 3.0 and 5.0 percent. The can lid castings were all prepared at 25.0°C cured with peroxide levels from 0.3% to 5.0%.

### Resin Castings

Unfilled resin castings approximately one-eighth inch thick were prepared at three different ambient temperatures from an orthophthalic marble resin. The resin was brought to temperature with a hot water bath or ice bucket. The castings were prepared by mixing approximately 300 grams of the resin with various levels of MEKP. The resin was mixed with the peroxide with a tongue depressor in a paper cup for approximately one minute. The mixture was poured between two glass-plates separated by an approximately one eighth inch thick polyvinylchloride spacer and allowed to cure at the specified ambient temperature. These castings were allowed to cure overnight before removal from the casting cells. After approximately one week, the cured resin castings were then subjected to physical testing. Tensile and flexural strength and modulus as well as glass transition temperature and residual styrene content were measured. All physical testing was performed according to ASTM standards. The glass transition temperature was determined through Dynamic Mechanical Analysis (DMA). Residual cure was

measured by differential scanning calorimetry (DSC).

### Marble Matrix Castings

Marble matrix castings were prepared by first drawing down a 23 mil wet catalyzed clear gel coat on a glass plate and allowing it to cure for 2 hours. The matrix consisted of 24% w/w catalyzed resin and 76% w/w of commercially available calcium carbonate filler. The matrix was brought to the desired temperature and poured into a PTFE frame clamped to the glass plate to a depth of approximately three-quarters of an inch and allowed to cure overnight before de-molding. The marble matrix castings were cut into four pieces approximately six inches square. One piece from each casting was placed into a laboratory drawer and stored as a control. A second piece was placed in a 65.6°C oven for two weeks. A third piece was subjected to the ANSI standard Z124.3 Section 6.3 "Water Resistance" testing for a total of 750 cycles. The fourth piece was kept in reserve. Exposed pieces were measured for color and compared to the color of the control pieces to determine color change, or Delta E

### Can Lid Castings

A third set of castings was prepared at 25.0°C using various levels of MEKP to determine the degree of cure. One hundred grams of unfilled resin were mixed with peroxide and poured into a one gallon paint can lid and allowed to cure overnight at room temperature. These specimens were tested by DSC and compared to the heat generated by a resin sample.

### DMA Testing

Individual test specimens were machined to a size of 48 mm x 13 mm x sample thickness. They were evaluated in a 3 point bending mode in a Rheometrics Solid Analyzer RSA II under the following conditions: temperature range of 30.0°C to 150°C, stepwise by 3.0°C increments with a 60 second dwell time at each temperature. The samples were subjected to a static load of 300g cycling at a rate of 6.28 rad/sec.

### DSC Testing

A standard resin sample was prepared by mixing 100.0 grams of liquid resin with 1.0 grams of t-butyl perbenzoate, (TBPB). Approximately 6 mg of resin mixed with TBPB was weighed into an aluminum sample pan and the lid is crimped on. The test resin sample consisted of approximately 7 mg of cured resin also sealed in a crimped aluminum sample pan. These samples were then each placed into a Perkin Elmer DSC7 test instrument and analyzed from 10°C to 190°C with a heat up rate of 10°C per minute. The % residual cure is defined as the ratio of the heat released per unit mass of the test sample to the standard sample.

### Solvent Extraction Gas Chromatography

Casting samples were fractured into particles using standard testing sieves greater than 1.18mm and less than 2.8mm. Approximately  $5 \pm 0.05$ grams of these particles were weighed into a 200ml bottle. Methylene chloride (75ml) was added and sealed. The soaking samples were allowed to stand for 24 hours at ambient temperature. This mixture was then filtered through Whatman #4 filter paper into a 100 ml. beaker. The extracted liquid was then added into a 100 ml volumetric flask and 1.0ml of a standard solution was added. Methylene chloride was added to fill the volumetric flask. The standard solution was made with 1.000 gm octane in 100 ml methylene chloride. A methylene chloride calibration standard was also prepared by mixing 0.04g styrene with 1.000 gm of the internal standard in a 100 ml volumetric flask.

### Results and Observations

The physical properties of the unfilled resin castings are summarized in Table 1. The flexural strength and modulus are not significantly affected by changing the amount of peroxide from 3 to 5 percent at 19.4°C. The change in peroxide from 0.5 percent to 1.5 percent for castings prepared at 30.6°C leads to a slightly lower flexural strength and flexural modulus. The tensile strength is not significantly affected by the cure conditions however the tensile modulus is greatest for the casting cured at the high temperature, 30.6°C with 1.5% peroxide and lowest for the casting prepared at 30.6°C with 0.5 percent peroxide.

The temperature at which the resin castings were cured seems to have a major effect on the glass transition temperature (Tg) of the polymer. Castings cured at 19.4°C have a Tg about 12°C lower than castings cured at 30.6°C even though higher MEKP levels were used. As expected, the degree of cure as measured by DSC increases as the MEKP level increases. (see Fig. 1 and Fig. 2 through 8).

Table 1  
*Physical Data of Unfilled Resin Castings of Marble Resin Cured at Different Temperatures and MEKP Levels\**

Cure Temp, °C / MEKP Level	ID# 043-171-	Flex Strength, psi	Flex Modulus, kpsi
19.4 / 3.0	A	18,000 (1428)	676 (8)
19.4 / 3.0	B	16,700 (390)	473 (9)
19.4 / 5.0	C	17,000 (978)	479 (7)

25.0 / 1.5	D	15,000 (1131)	490 (14)
30.6 / 0.5	E	17,100 (510)	490 (14)
30.6 / 0.5	F	16,600 (891)	470 (13)
30.6 / 1.5	G	14,900 (492)	380 (25)

\* Numbers in parentheses are standard deviation

Cure Temp, °C / MEKP Level	ID# 043-171-	Tensile Strength, psi	Tensile Modulus, kpsi
19.4 / 3.0	A	8700 (308)	480 (11)
19.4 / 3.0	B	8600 (171)	500 (10)
19.4 / 5.0	C	8300 (448)	495 (9)
25.0 / 1.5	D	7000 (1561)	470 (13)
30.6 / 0.5	E	8500 (507)	450 (24)
30.6 / 0.5	F	8500 (108)	427 (8)
30.6 / 1.5	G	7,500 (615)	530 (3)

Cure Temp, °C / MEKP Level	ID# 043-171-	Tensile Elongation	Tg, °C	% Cure by DSC
19.4 / 3.0	A	2.30 (0.10)	81	93
19.4 / 3.0	B	2.20 (0.12)	81	93
19.4 / 5.0	C	2.00 (0.19)	80	94
25.0 / 1.5	D	2.00 (0.71)	89	90
30.6 / 0.5	E	3.60 (0.91)	93	88
30.6 / 0.5	F	3.80 (0.38)	92	88
30.6 / 1.5	G	1.60 (0.17)	93	90

In Table 2 the glass transition temperatures, percent cure based upon DSC, and residual styrene levels (solvent extraction gas chromatography) are listed for unfilled resin castings prepared at 25.0°C. We see that the Tg is lowest for the lowest amount of peroxide reaching about 80°C from the range of 0.6 to 1.5 percent peroxide and reaching a maximum of 98°C at 2.5 percent peroxide. The Tg then decreases at higher levels of peroxide. In examining the different DMA graphs we see that as the peroxide level increases the Tan Delta peaks become sharper and more defined. The broader Tan Delta peaks are indicative of the polymer continuing

to cure during the test. For the lowest levels of peroxide there is also a peak in the loss modulus at approximately 50°C. This peak shifts to higher temperatures as the amount of peroxide increases. This peak is an indicator of movement within the polymer matrix.

Table 2

*Glass Transition Temperature and Degree of Cure vs. Methyl Ethyl Ketone Peroxide (DDM-9) Level for Can Lid Castings of Unfilled Marble Resin.*

MEKP Level	Tg, °C	% Cure by DSC	% Residual Styrene
0.3	72	91	3.7
0.6	77	90	3.3
0.9	79	92	3.0
1.2	82	92	2.8
1.2	79	90	2.7
1.5	80	91	2.5
2.5	98	>98	0.38
3.0	96	>98	0.36
4.0	92	>98	0.17
5.0	84	>98	0.08

Castings cured at 25.0°C

The percent cure is essentially constant at approximately 90 percent from 0.3 to 1.5 percent peroxide. At levels of 2.5 to 5.0 the percent cure is greater than 98%. As can be seen in the DSC curves, the maximum exothermic heat occurs at higher temperatures for the lower levels of peroxide. For example the peak is approximately 127°C for 0.3% peroxide and is approximately 108°C for 1.5% peroxide. This indicates that higher temperatures are required to complete the cure for castings made with the lowest levels of peroxide. At 0.3 percent peroxide there doesn't appear to be sufficient peroxide to complete the cure and vitrification apparently results. As expected, the residual styrene measurements correlate with the DSC data. The residual styrene measurements provide a greater sensitivity for the castings with greater than 98% cure based on DSC (See Fig. 9-19).

Table 3 lists the Tg and percent residual styrene for the resin matrix castings. We see the same trends here that we saw in the unfilled resin castings including the broad Tan Delta peaks in the DMA scans (See Figs. 20 through 32). Very high levels of MEKP yield very low residual styrene but the Tg of the cured matrix is lower. Resins that use very low levels of MEKP, on the other hand, show some further curing. The percent residual styrene levels were essentially the same for the marble matrix castings compared to the unfilled resin castings when the resin content was taken into account. In fact when tested for percent cure by DSC all matrix samples measured between 93% and 96% cure.

Table 3.

*Glass Transition Temperature and % Residual Styrene of Resin Matrix Castings*

ID# 043-177-	Cure Temp. °C	MEKP Level	Tg, °C	% Residual Styrene (on resin content)
A	19.4	3.0	91	1.33
B	19.4	5.0	87	0.17
C	25.0	0.5	94	3.88
D	25.0	1.5	96	2.71
E	25.0	3.0	90	1.46
F	25.0	5.0	86	0.42
G	25.0	0.5	91	3.75
H	25.0	3.0	89	1.46
I	30.6	0.5	93	3.96
J	30.6	1.5	95	2.92
K	30.6	0.5	93	3.92
L	19.4	3.0	89	1.38
M	19.4	5.0	84	0.25

Table 4 lists the changes in color for marble matrix castings that were subjected to heat in a 65.6°C oven for two weeks, and marble matrix castings that were subjected to 750 cycles of thermal shock (ANSI testing). The lower the levels of peroxide used, the lower are the color changes for the heat-exposed samples. Surprisingly, there is no significant affect of cure temperature on color change. The samples where the peroxide levels were the same but curing temperatures varied essentially had the same Delta E values. The changes in color of marble matrix castings when subjected to thermal shock were greatest for the marble matrix castings prepared at the lowest temperature 19.4°C. The marble matrix castings cured at 25.0°C and 30.6°C were similar, however the lowest amount of peroxide marble matrix castings has a slightly lower Delta E than the marble matrix castings cured at higher levels of peroxide.

Table 4

*Color Change (Delta E) of Matrix Cured at Different Temperatures and MEKP Levels by Exposure Type. (CIE D65 Illuminant, 10° Observer)*

Temperature, °C	MEKP Level	Delta E, 2 wks @ 66°C	Delta E, 750 cycles thermal shock
19.4	3.0	6.56	6.15
19.4	5.0	6.80	4.19
25.0	0.5	3.80	1.95
25.0	1.5	5.90	2.86
25.0	3.0	6.08	2.84
25.0	5.0	6.82	2.60
30.6	0.5	3.50	2.45
30.6	1.5	6.13	3.82

In Table 5 the gel characteristics of the resin used in this study are listed. The change from 3 to 5 percent peroxide at 19.4°C only reduced the gel time by 0.2 minutes. At 25.0°C the gel times varied from 22.7 minutes for 0.5% to 5.5 minutes for 5% peroxide. At 30.6°C the gel time was 14.2 minutes for 0.5% peroxide and 5.5 minutes at 1.5%. The exotherm peaks were similar for all levels above 0.5% with the 0.5% at 25.0°C being the lowest at 96.7°C.

Table 5

*Room Temperature Cure Data on Neat Resin*

Temp, °C	MEKP Level	RT Gel, minutes	Gel to Peak, minutes	Peak Exo, °C
19.4	3.0	9.0	7.8	149.4
19.4	5.0	8.4	7.3	155.0
25.0	0.5	22.4	33.5	96.7
25.0	1.5	8.7	9.3	141.7
25.0	3.0	6.0	6.4	150.0
25.0	5.0	5.5	5.3	159.4
30.6	0.5	13.2	19.8	112.2
30.6	1.5	5.5	6.5	138.9

**Conclusions:**

At very high levels of peroxide, i.e. greater than 3.0%, the Tg is reduced, color changes with heat exposure or thermal shock increase, and a reduction in physical properties result. These changes may result from increased content of residual peroxide solvent or the higher concentration of initiator leading to the greater tendency for the free radicals to react with each other or chain transfer reactions, resulting in a lower cross-link density. This demonstrates that increasing the peroxide to achieve a proper gel time may be detrimental to the resulting cast polymer part. For example, raising the peroxide level from 0.5 to 1.5% raises the Delta E from 3.8 to 5.9 for the heat exposed marble matrix.

At low levels of peroxide there is evidence of vitrification that limits the cross-linking. At 0.3 % peroxide, the residual unreacted components are not able to cross-link until the part temperature is raised to approximately 120°C. The exotherm temperatures, as listed in Table 5, also confirm this conclusion. If the ambient temperature is higher then the exotherm is higher and less amount of peroxide may be used to achieve acceptable cure. This study indicates that the recommended level of peroxide from 0.75 to 2.5% is a valid recommendation. Further studies should be carried out to determine the optimum peroxide mixtures.

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**Acknowledgement**

Larry Anderson provided significant assistance in interpreting the DSC and DMA data.

**DSC Graph of Residual Heat for Table 1**

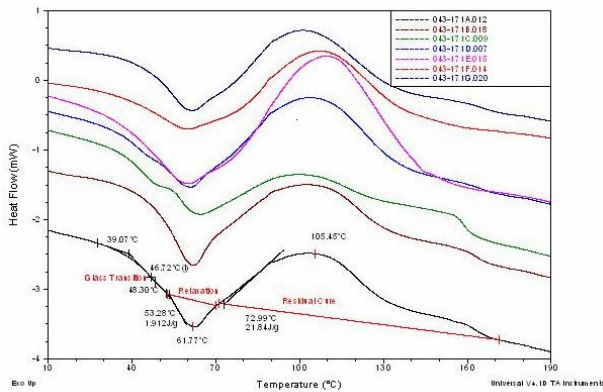


Fig. 1

**DMA Graphs (Tg) for Table 1**

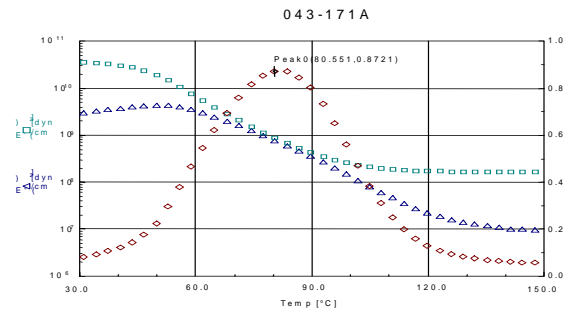


Fig. 2

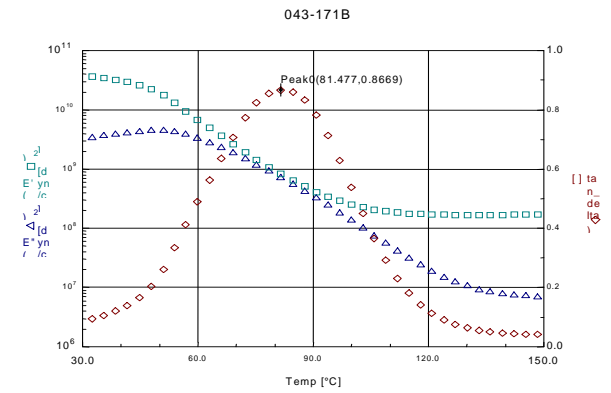


Fig 3

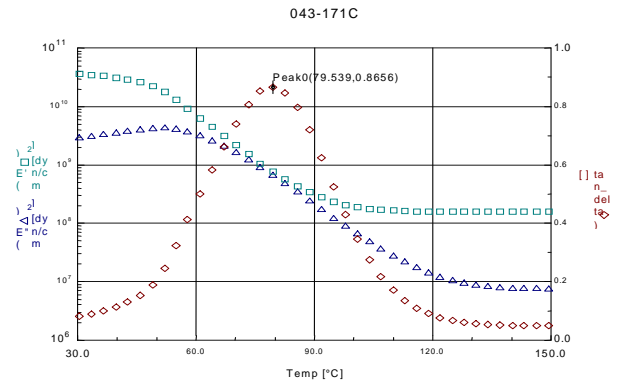


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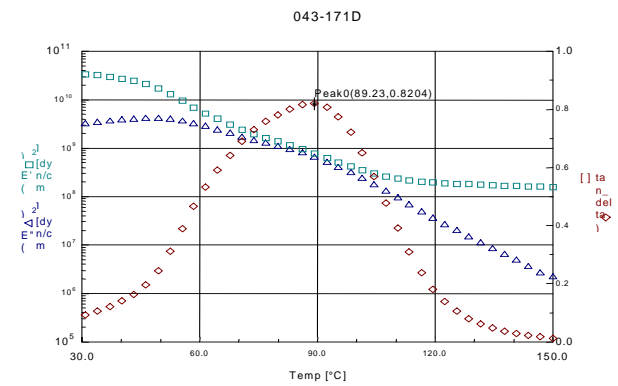


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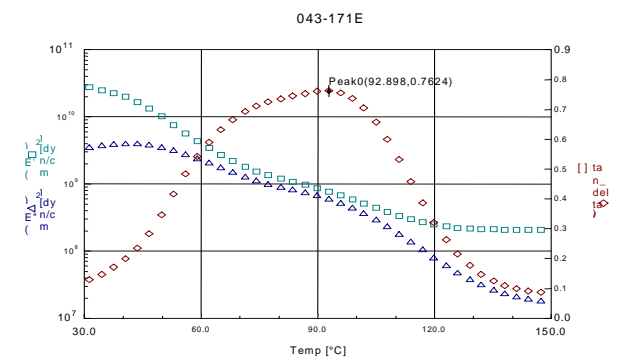


Fig.6

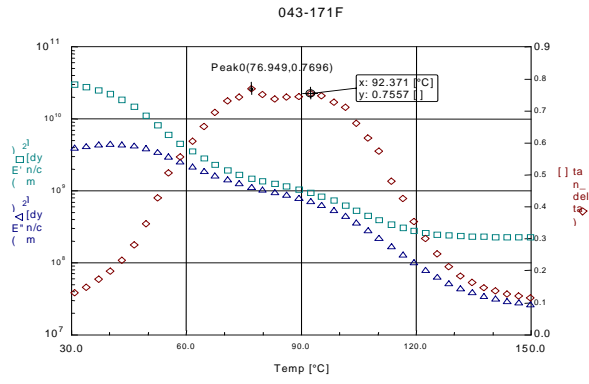


Fig. 7

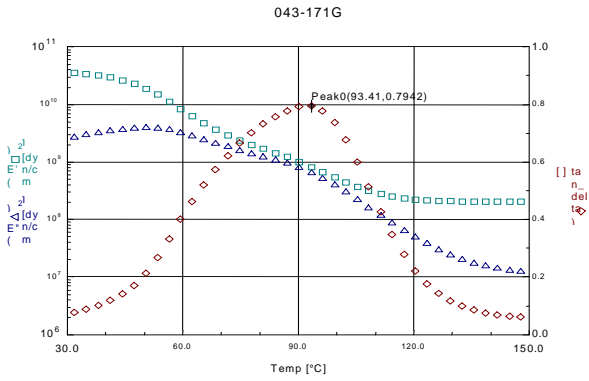


Fig. 8

DSC Graph (% Residual Cure) for Table 2

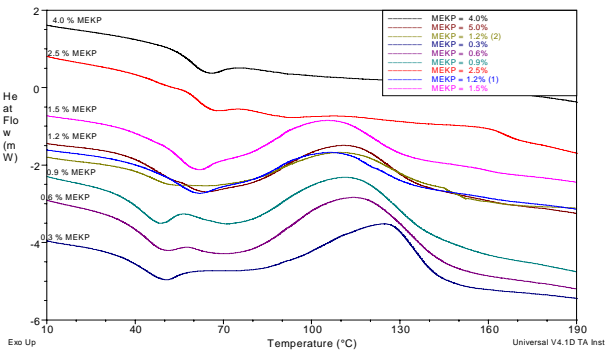


Fig. 9

DMA Graphs (T<sub>g</sub>) for Table 2

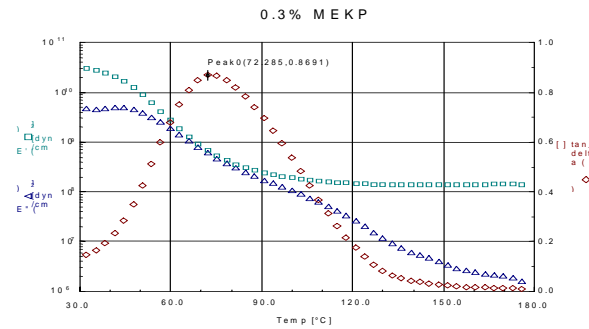


Fig. 10

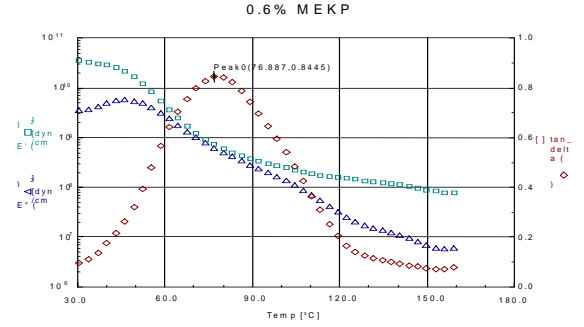


Fig. 11

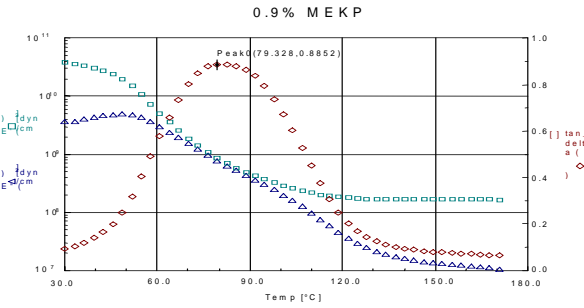


Fig. 12

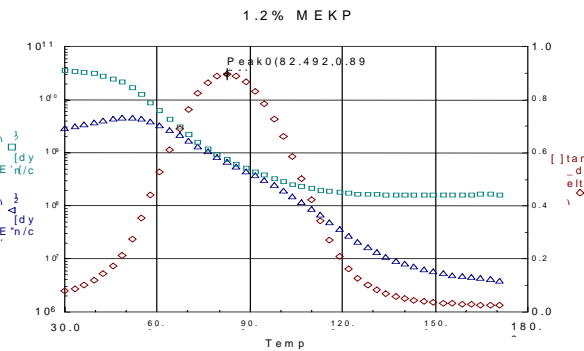


Fig. 13

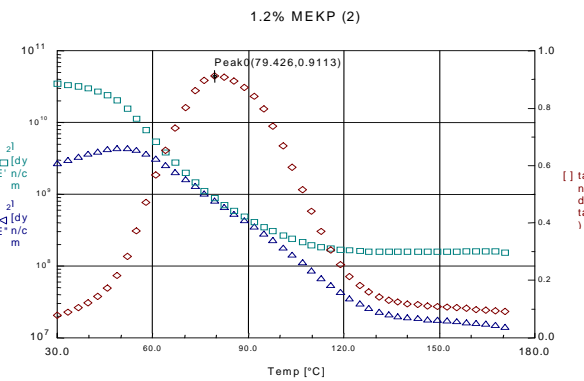


Fig. 14

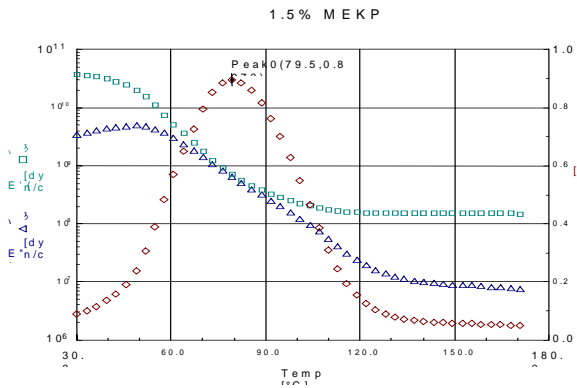


Fig. 15

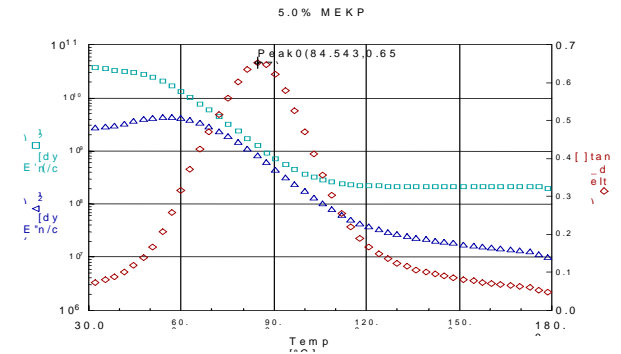


Fig. 19

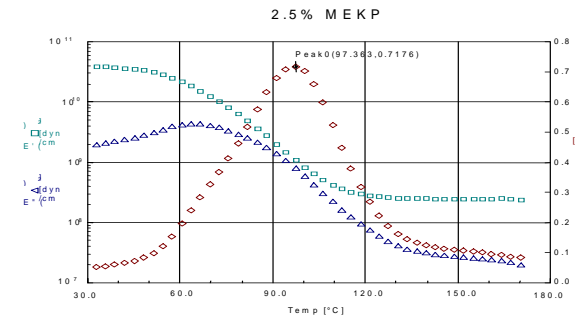


Fig. 16

DMA Graphs (Tg) for Table 3

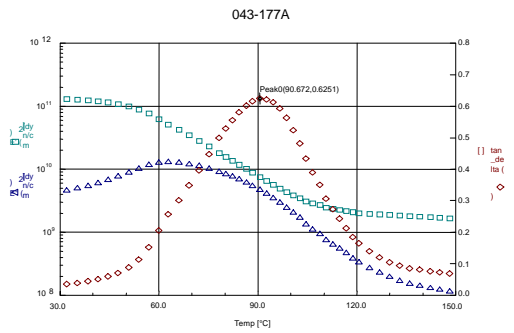


Fig. 20

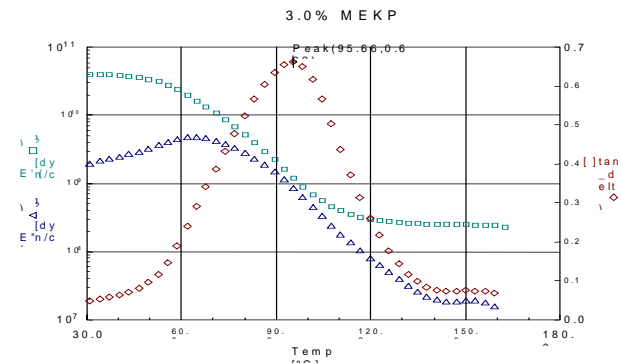


Fig. 17

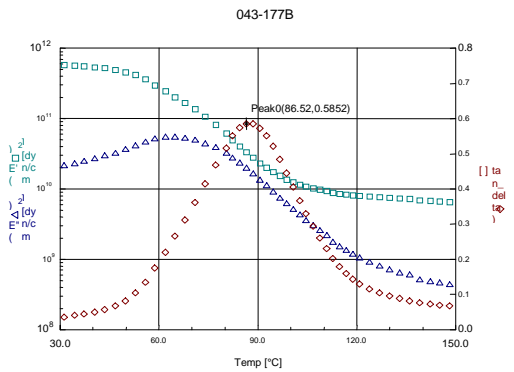


Fig. 21

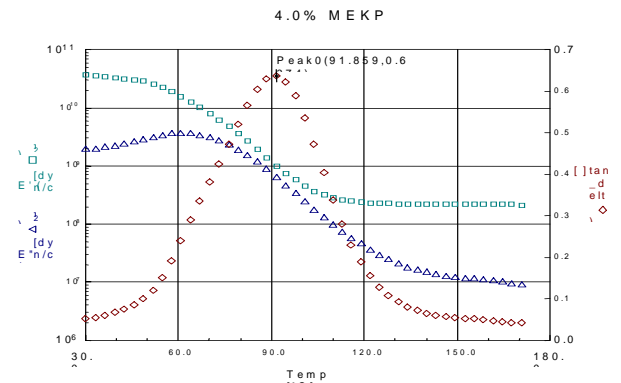


Fig. 18

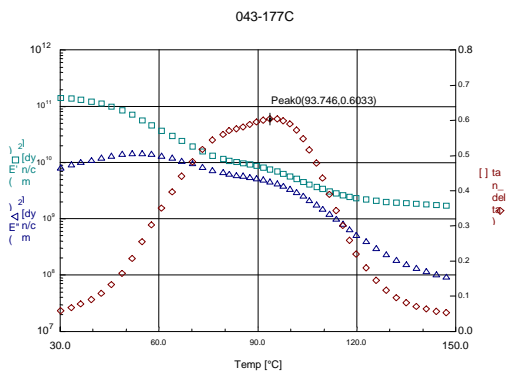


Fig. 22

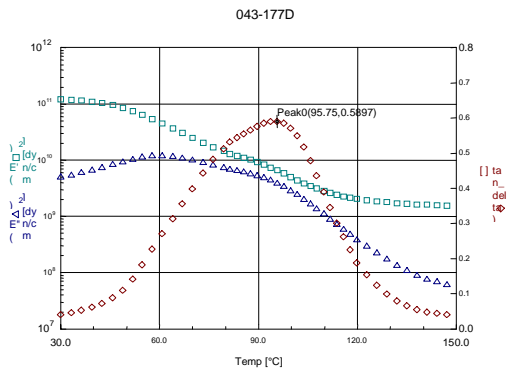


Fig. 23

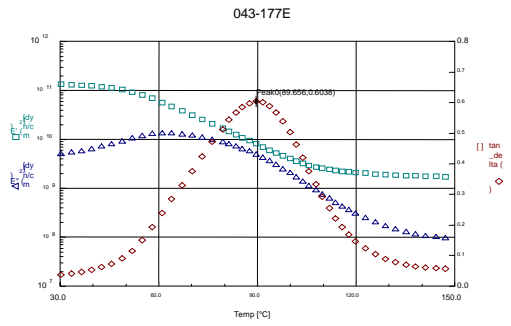


Fig. 24

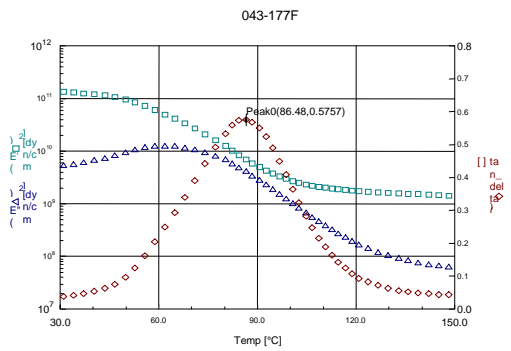


Fig. 25

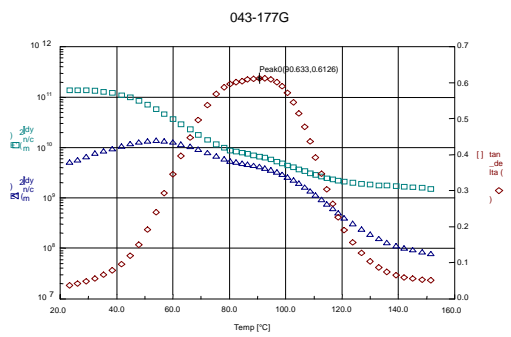


Fig. 26

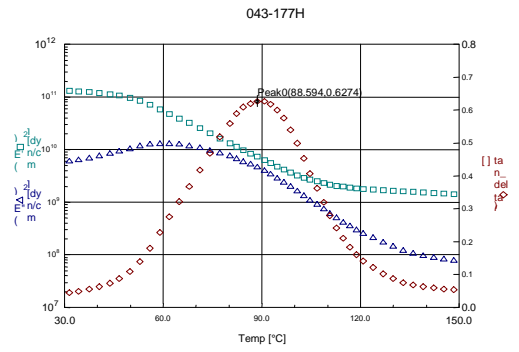


Fig. 27

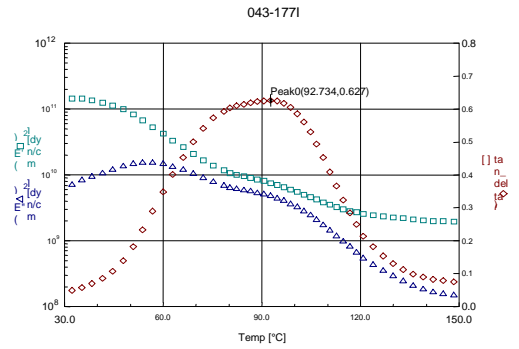


Fig. 28

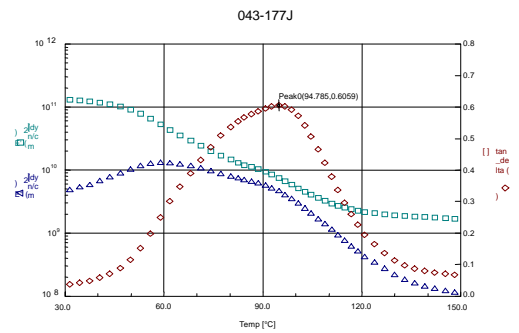


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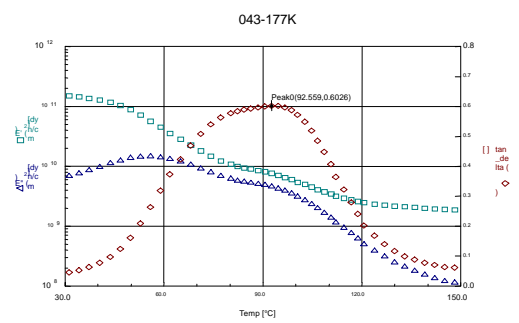


Fig. 30

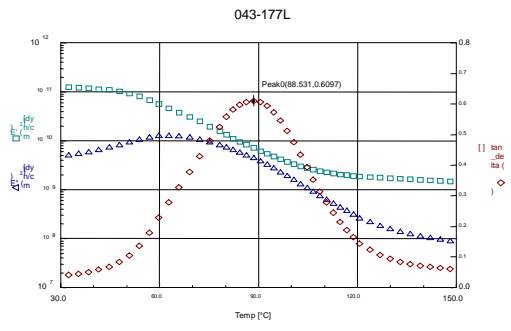


Fig. 31

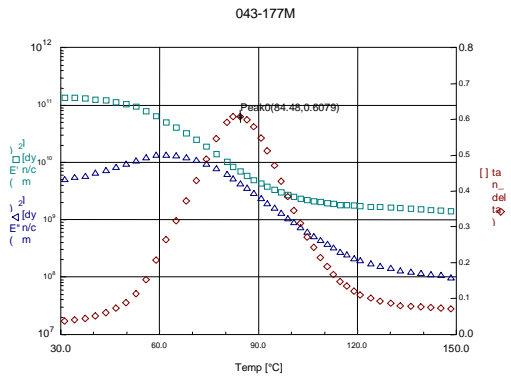


Fig. 32