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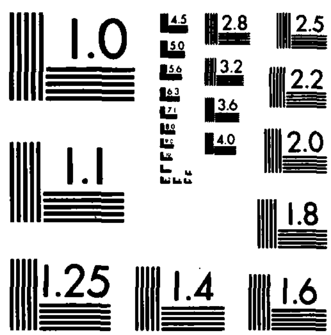

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EFFECT OF POST CURING PROCESS ON THE PROPERTIES OF GRAPHITE/EPOXY COMPOSITES

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14 June 1985

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19. Key Words Composite materials, graphite/epoxy, moisture absorption, glass transition temperature, post-cure, cross-linking, interlaminar shear strength.

20. Abstract

The objective of the study was to investigate the effect of post-cure on the moisture absorbtion and dynamic response of CFRP. The unidirectional materials were postcured in the range of 190-210°C for times up to 10 hrs. The dynamic response was measured by torsion pendulum technique and the interlaminar shear strength at room temperature and 120°C in short beam bending. The interlaminar shear strength and the glass transition temperature of the composite in wet condition was found to be governed by the amount of absorbed moisture. The different post-curing conditions did not cause a change in the mechanical behavior of the Fibredux 914C/T300 composite. The results are explained in terms of cross-linking density of the cured epoxy.

FORM 1473

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1. ABSTRACT

A study was made of the effect of post-cure on the moisture absorbtion and dynamic responce of CFRP. The unidirectional materials was postcured in the range of 190-210^{o}C for times upto 10 hrs. The dynamic responce was measured by torsion pendulum technique and the interlaminar shear strength at room temperature and 120^{o}C in short beam bending. The interlaminar shear strength and the glass transition temperature of the composite in wet condition was found to be governed by the amount of absorbed moisture. The different post-curing conditions did not couse a change in the mechanical behaviour of the Fibredux 914C/T300 composite. The results are explained in terms of cross-linking density of the cured epoxy.

2. PREFACE

This work has been prepared in cooperation with Messerschmitt Bölkow an Blohm GmbH. All the test specimens were prepared and machined in Germany and sent to METU for testing. The results of this work is to be submitted for publication in journal of Materials Science and Techonoly, UK.

EFFECT OF POST CURING PROCESS ON THE PROPERTIES OF GRAPHITE/EPOXY COMPOSITES

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This paper introduces a programme of work to investigate to what extend the mechanical properties are affected by post-cure procedures. In addition a number of tests to find the effect of degree of cross-linking on the moisture absorbtion characteristics were also investigated.

KEY WORDS : Composite materials, graphite/epoxy, moisture absorption, glass transition temperature, post-cure, cross-linking, interlaminar shear strength.

3. INTRODUCTION

In the modern aerospace community metals are designed to be used in their engineering limits for their structural applications. The search for higher performance materials, included the composite materials for primary structures. Although composite materials are used videly for secondary structures the move towards primary structures has been rather slow due to in sufficient data on the enviromental effects on the behaviour CFRP. These materials, in aeronautical and other structures, during the course of normal service life will often be exposed to on enviroment in which the temperature and humidity vary considerably with time. The variation may be on short time scale or over longer periods.

The CFRP structures with epoxy matrices, when exposed to humidity will readily absorb moisture from surrounding by a diffusion controlled process. The effect of moisture on the resin matrix of CFRP is to degrade some mechanical properties, especially at elevated temperatures. Thus serious consideration must be given to those mechanical properties of composites which are matrix controlled.

The way in which the CFRP absorb moisture although depends on many factors such as temperature, relative humidity, resin content surface conditions, it may be expected that the level of cross-link density may play some role.

This project was concerned with water absorption and degradation of mechanical properties of unidirectional carbon fibre/epoxy specimen 914C/T300. The first objective of the work was to determine the effect of post-cure conditions on water absorption process. The second was to asses the effectivenes of different post-cure cycles on the degree of degradation of mechanical properties at ambient and elevated temperatures in wet condition. Thus, in the paper the results of some experiments to study the effect of degree of cross-linking on moisture absorption as well as changes in interlaminar shear strength and glass-transition temperature due to the absorped moisture of 914C/T300 CFRP are presented.

4. EXPERIMENTAL

4.1. Materials

Carbon fiber reinforced epoxy laminates were fabricated from 914C/T300 prepregs in an autoclave at MBB. The unidirectional sheets produced by this method were 2mm in thickness. The curing cycle regarding the prepregs are given in the MBB specification FA 80-F-31-2930.

The sheet was tested for its carbon fiber content by matrix digestion using sulfuric acid.

The unidirectional sheets were machiened by cutting with a diamond whell to produce specimens for

- -Interlaminar shear strength determination ($16x10x2mm^3$)
- -Internal friction test in torsion pendulum apparatus ($60x10x2mm^3$)
- -Moisture pick-up tests (aging tests) ($100x100x2mm^3$)

4.2. Hyrothermal Exposure

4.2.1. Predrying

All the specimens to be moisture conditioned were first predried. CFRP specimens may contain some residual moisture after the curing process which may change during storage. This excess moisture was dried by predrying process to establish a zero moisture content datum.

The predrying of CFRP samples were carried out in a drying oven. To avoid irreversible damage to the laminate drying was accomplished in 3 stages at, 70^{o}C, 90^{o}C and finally at 110^{o}C.

The weight change measurements were made on traveller specimens which were removed from the oven at predetermined intervals, placed in the transient storage box to cool to ambient temperature and transported to weighing area. The specimens were weighed to the nearest 0.1 mg and replaced immediately to the transient box after weighing. The drying process was continued untill weight constancy was reached. After drying, the samples were stored in a vacuum desiccator until further testing.

4.2.2. Moisture uptake

The predried specimens were stored at 70^{0}C and 75% RH over saturated salt solution in desiccators until equilibrium values of moisture content were obtained. Traveller specimens were weighted in predetermined intervals to follow moisture uptake until saturation.

For weighing, the travellers were transferred from desiccators at 70^{0}C and 75% RH to another set of desiccators containing the same saturated salt solution but at room temperature.

After cooling for two hours in the wet enviroment, the specimens were removed surface wiped and weighed.

4.3. Mechanical Testing

The pre-dried samples were post-cured an stored in wet enviroment until saturation before 3-point bending method was utilized for the measurement of shear strength. Testing at elevated temperature were performed in on enviromental chamber using a 500 N capacity Instron Testing Machine. The interlaminar shear strength (ILS) samples were mounted to an alignment device which was mounted in turn to the ram of the testing machine.

All tests were done at a constant cross-head speed of 1mm/min.

4.4. Dynamic Testing

An inverted torsion pendalum testing technique has been used for material damping and shear modulus determination. All samples were tested at 2 Hz in a temperature range from room temperature to 150^{o}C.

The dynamic glass transition temperature were determined according to DIN 7224 at the maximum, damping tan δ value.

A new concept of softening point was also introduced to yield a better explanation of the effects of post-cure which is the begining of a drastic decrease in dynamic modulus of CFRP. This point has been taken as the temperature where a drop of 5% in elastic modulus occured.

4.5. Experimental Programme

The experimental programme was divided three segments. The first phase was on investigation of the moisture uptake of the composite subsequent to different levels of post-curing.

The second phase was the investigation of shear strength of composite as a function of post-curing. Thus upon completion of post-cure and moisture saturation of composites, the specimens were tested in three-point bending to failure at room temperature and 120^{o}C.

The last phase of the experimental programme examined the effect of degree of cross-linking on the glass transition temperature and softening point of the composite uniderectional laminate.

The experimental post-cure conditions studied were as follows

4 hours at 190^{o}C

4 hours at 190^{o}C 2x Bonding cycle

10 hours at 190^{o}C

4 hours at 210^{o}C

10 hours at 210^{o}C

Each bonding cycle consisted of heating to 175^{o}C at a rate of 1-3^{o}C/min and holding at 175^{o}C for 1 hour fallowed by cooling to 70^{o}C with a rate of 1^{o}C/min.

To study effects of post curing in wet samples, saturated specimens were post-cured according to above programme and after post-cure cycle they were returned to over saturated salt solutions to resaturate the samples to their equilibrium value. This necessary because samples were dried to certain extend during post curing process.

5. RESULTS

5.1. Moisture take up

Moisture pick-up in the specimen in un-post-cured condition as a function of time is given in fig 1 and fig 2. which provide moisture contents that are normalized to 60 fibre volume basis. The formula for normalizing was

$$\text{Moisture (normalized)} \; \frac{\text{Laminate resincontent for 60 fibre volume}}{\text{measured laminate resin content}} \times \text{Measured moisture content}$$

This normalization has been carried out to facilitate comparisons of laminates with slightly different resin contents. It is known that the absorption of moisture by graphite fibers is negligible, the resin phase is assumed to contain all the moisture absorbed by the CFRP laminate.

The desorption values obtained during predrying stage is given in fig.3 and these values are normalized to the same basis of 60% fibre volume content.

The observations made concerning the water absorption at 70^{o}C and 75 % RH appears to conform with Fickian behaviour. The diffusion coefficients for moisture in the unidirectional carbon fiber composite calculated from the initial slope of the graph shown in fig 2 was 2×10^{-7} mm^{2}/s for the samples exposed to 70^{o}C and 75% RH. It has been found that this value did not change significantly by any type of post-curing cycle applied to the laminate.

The maximum amount of moisture absorbed was about 2% by weight after 38 days. These results are in accordance with Fickian diffusion theory, that is the rate of absorption was mainly a function of temperature and the amount of moisture absorbed would be a function of relative humidity.

The equilibrium amount of moisture absorbed did not seemed to change by the post-cure conditions in 914C/T300 system.

It is of interest to note the implications suggested by the absorption results that the network and free volume changes after post-curing at 190^{o}C and 210^{o}C in 914C/T300 is not in accordance with absorption findings of many other epoxy systems.

5.2. Interlaminar shear strength

5.2.1. Non-post cured samples

The results of the short bean 3-point bending tests performed at room temperature and 120°C in dry and wet state are given in table 1.

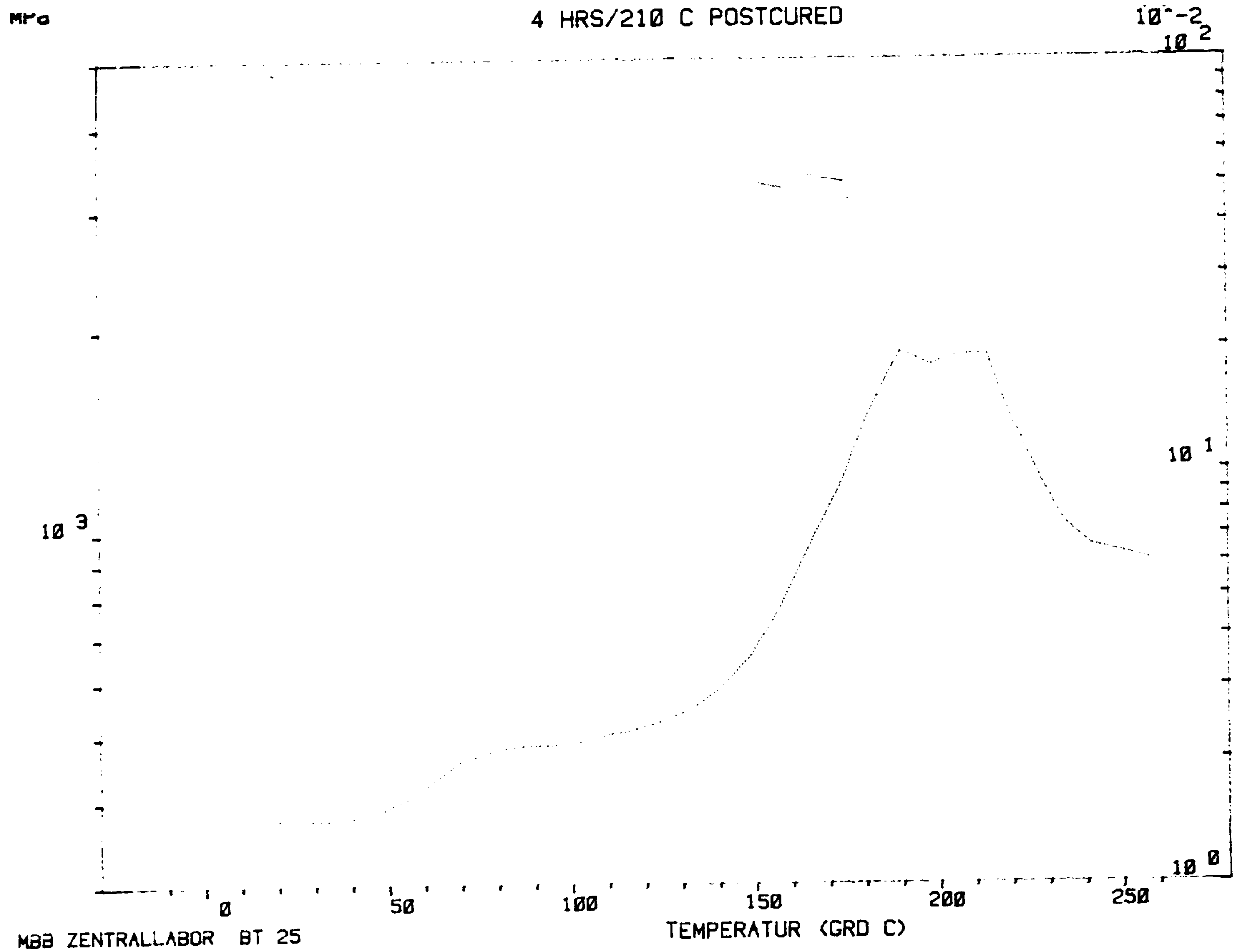
TABLE 1. Interlaminar shear properties of 914C/T300. (Not-Postcured)

	Interlaminar shear strength N/mm^2	
Specimen	Room temperature	120°C
DRY	100	60
WET	95	45

The interlaminar shear strength of wet laminates drop rather drastically at elevated temperature. The difference in strength between dry and wet samples at room temperature is not significant.

5.2.2. Post cured samples

The interlaminar shear strength of post-cured laminate is given in table 2. The wet samples were reaged for moisture saturation after post-cure treatment.



MPa
4 HRS/210 C POSTCURED
10^-2
10 2
10 1
10 3
10 0
0
50
100
150
200
250
TEMPERATUR (GRD C)
MBB ZENTRALLABOR BT 25

Fig. 7

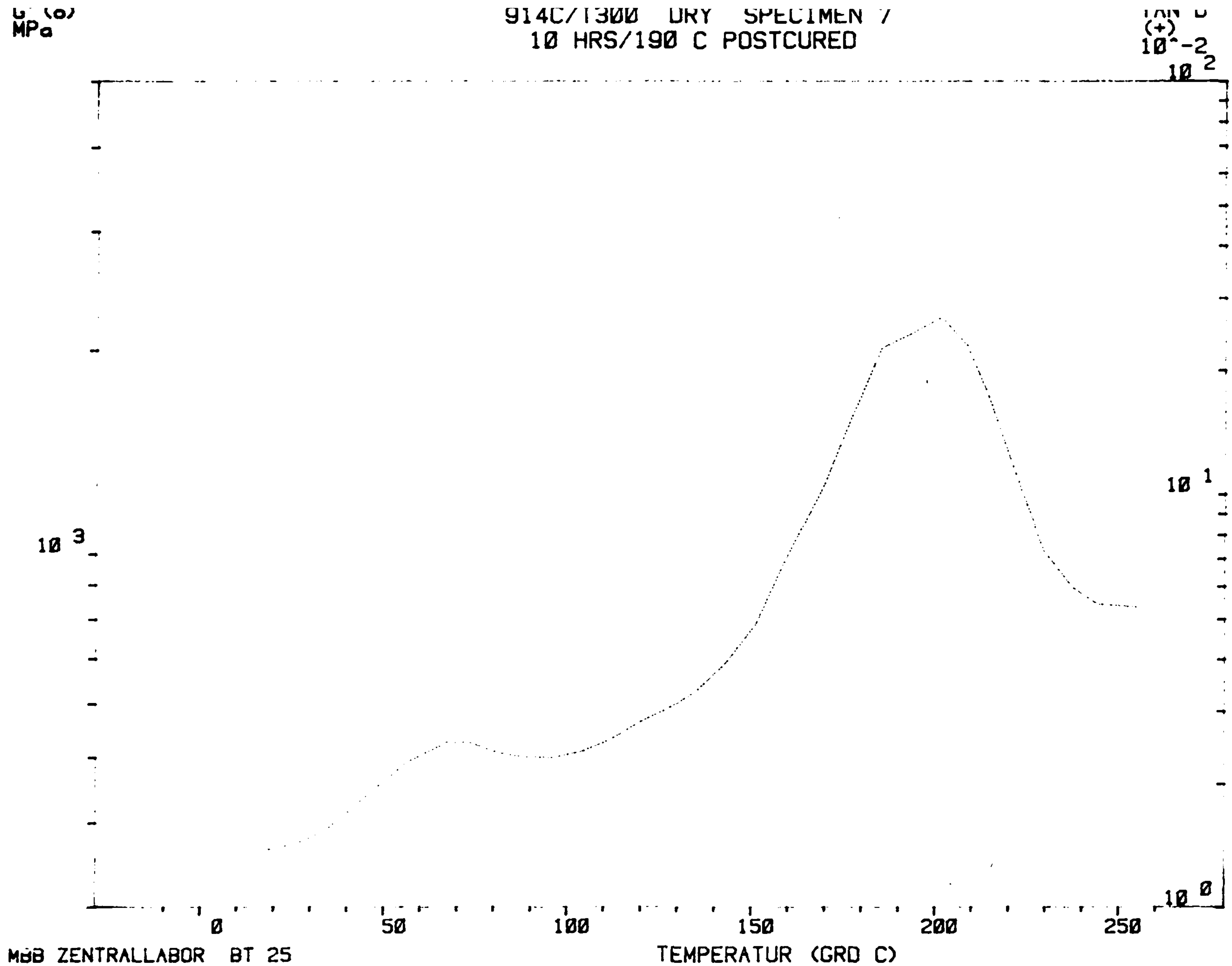

G' (o)
MPa
914C/T300 DRY SPECIMEN 7
10 HRS/190 C POSTCURED
TAN D
(+)
10^-2
10 2
10 1
10 0
10 3
0
50
100
150
200
250
TEMPERATUR (GRD C)
MBB ZENTRALLABOR BT 25

Fig. 6

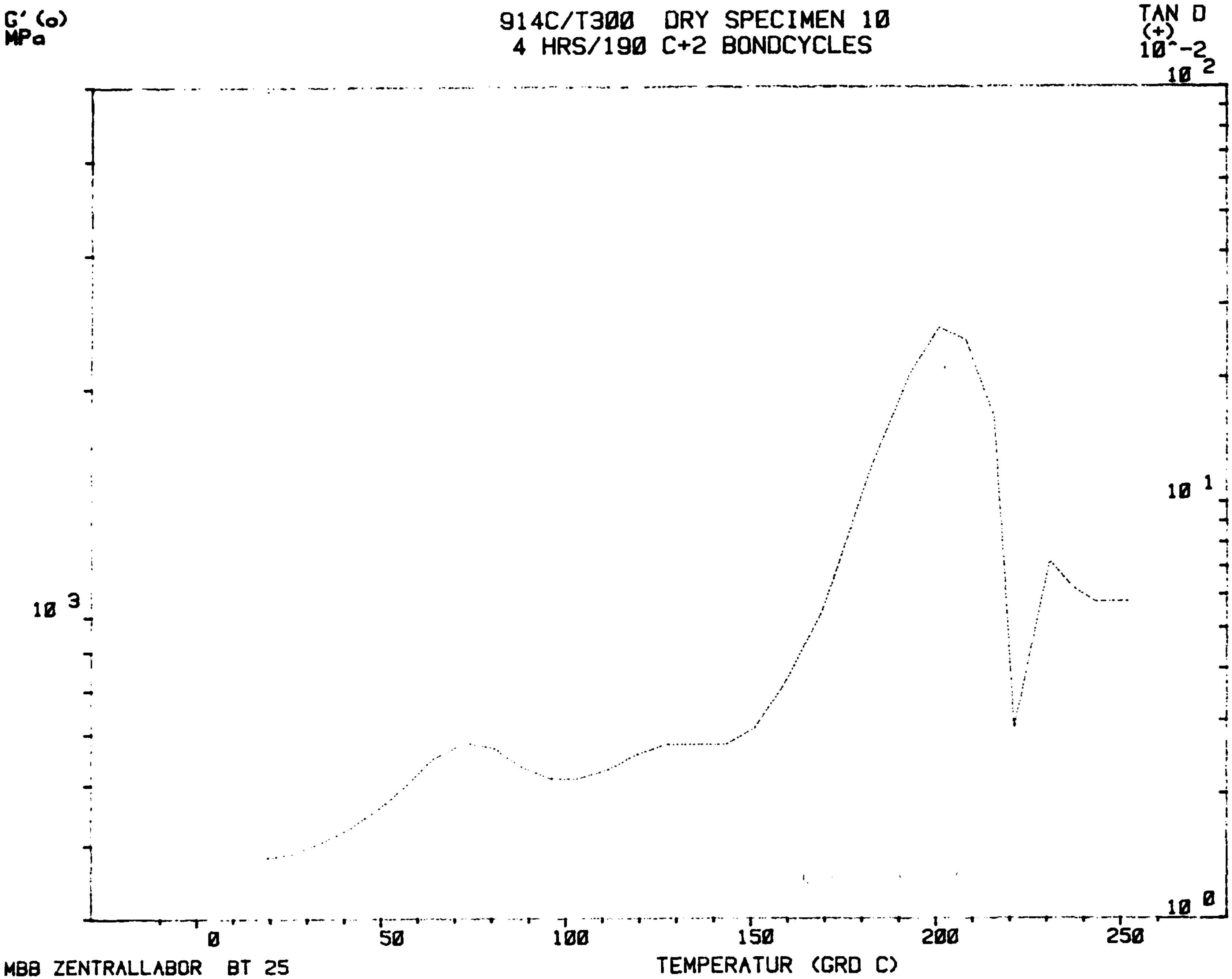

G' (o)
MPa
914C/T300 DRY SPECIMEN 10
4 HRS/190 C+2 BONDCYCLES
TAN D
(+)
10^-2
10 2
10 1
10 0
10 3
0
50
100
150
200
250
TEMPERATUR (GRD C)
MBB ZENTRALLABOR BT 25

Fig. 5

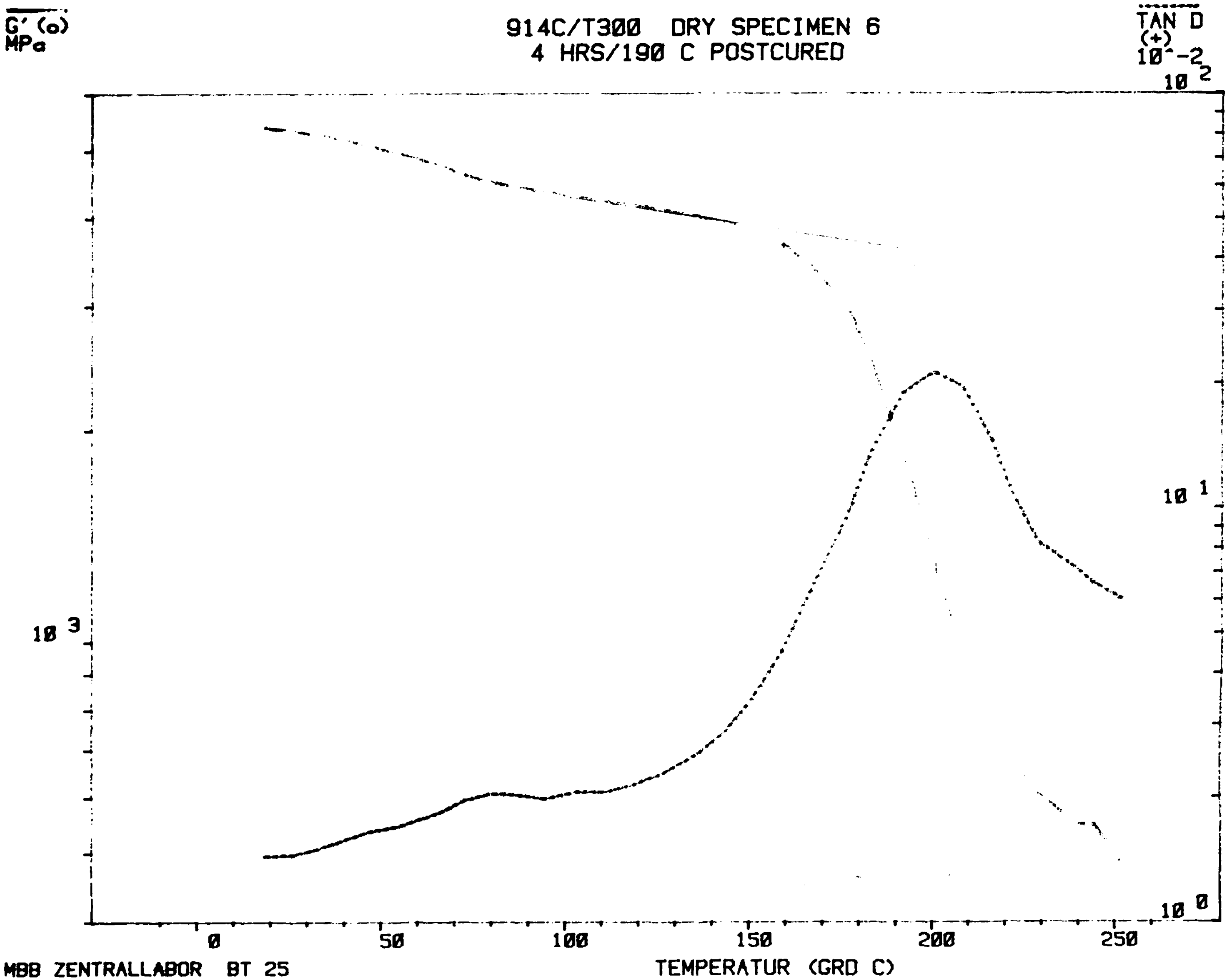

G' (o)
MPa
914C/T300 DRY SPECIMEN 6
4 HRS/190 C POSTCURED
TAN D
(+)
10^-2
10 2
10 1
10 0
10 3
0
50
100
150
200
250
MBB ZENTRALLABOR BT 25
TEMPERATUR (GRD C)

Fig. 4

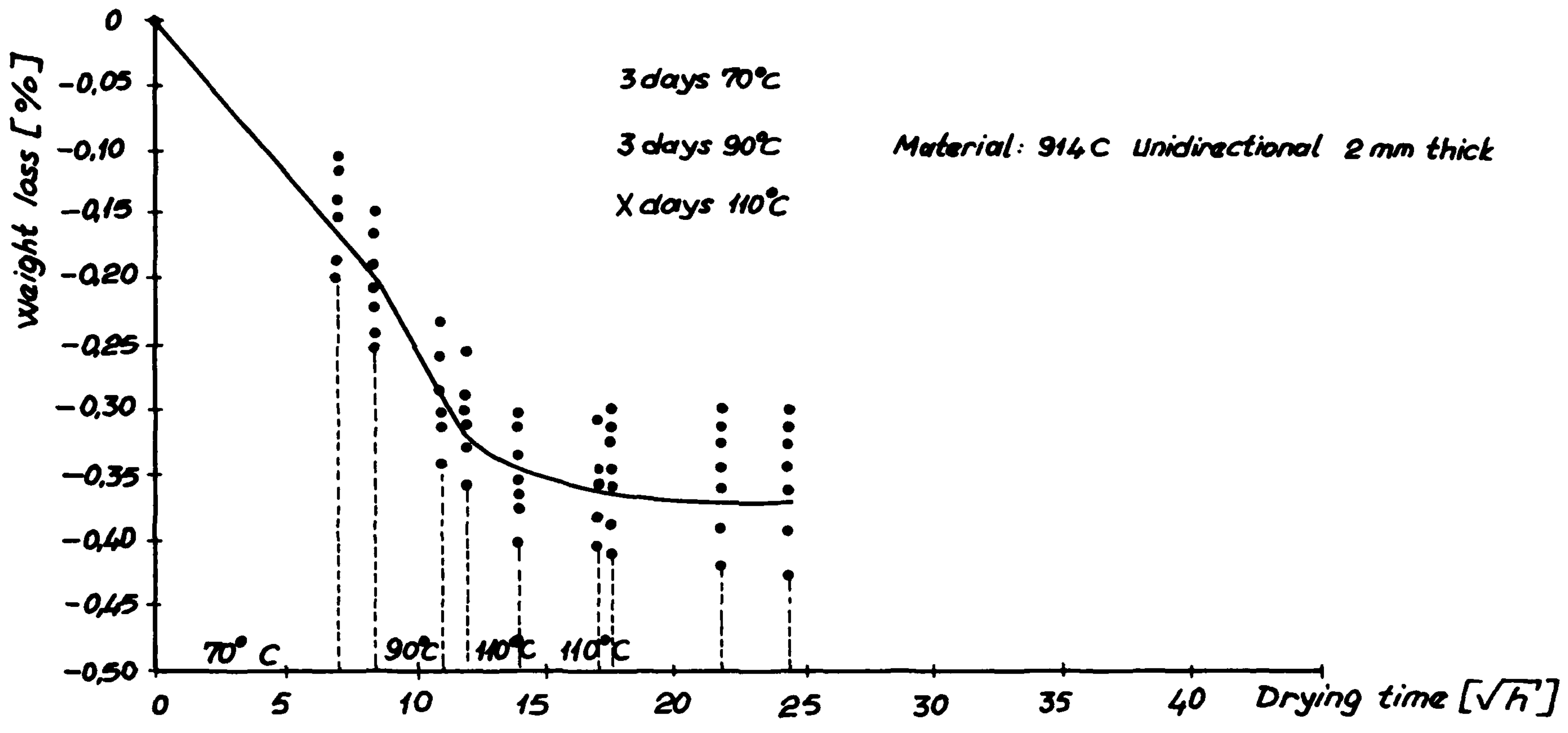


Fig. 3 WEIGHT LOSS DURING PREDRYING

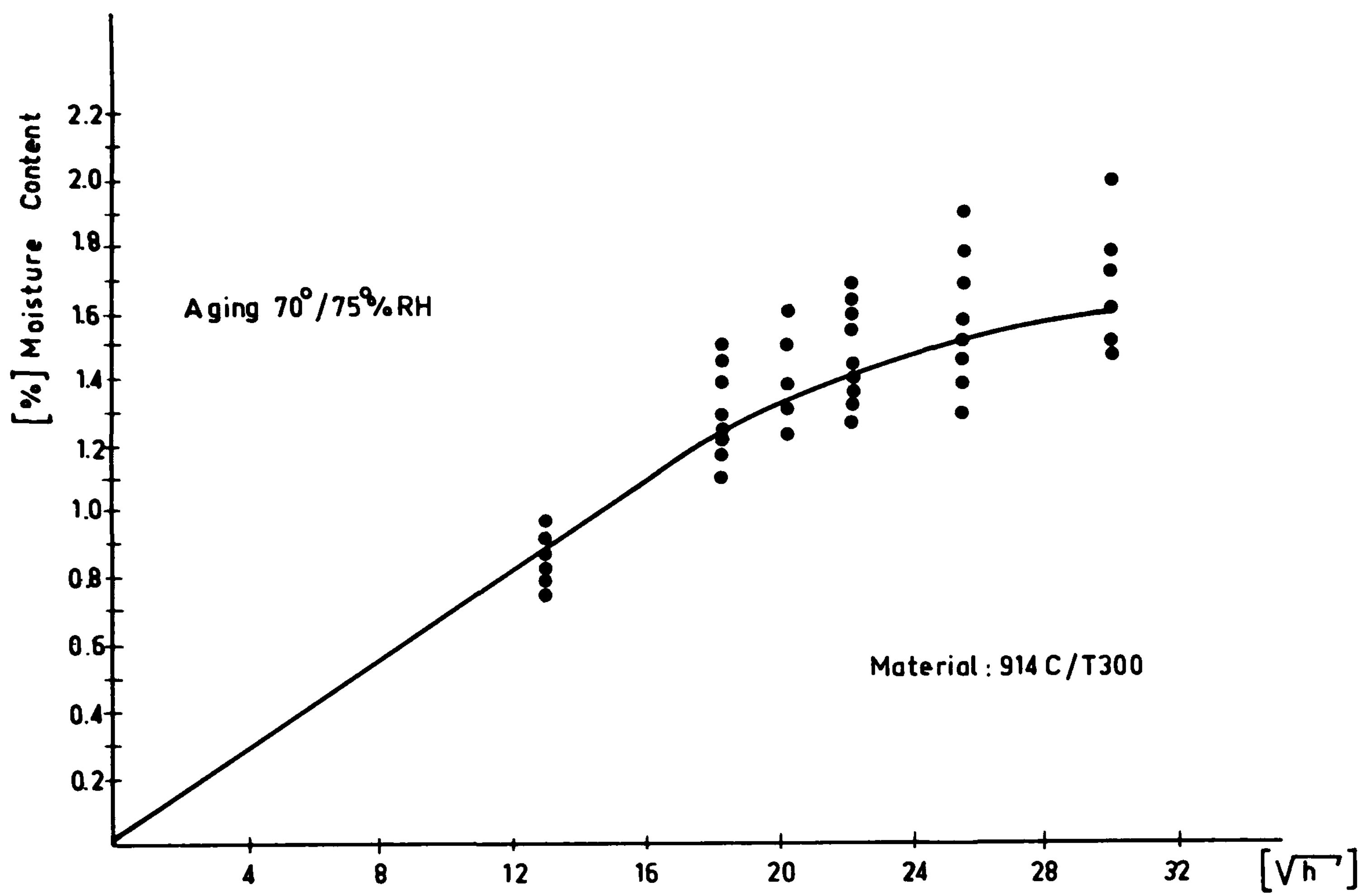


Fig. 2 MOISTURE ABSORPTION IN POST CURED SAMPLES (10 hrs at 190°C)

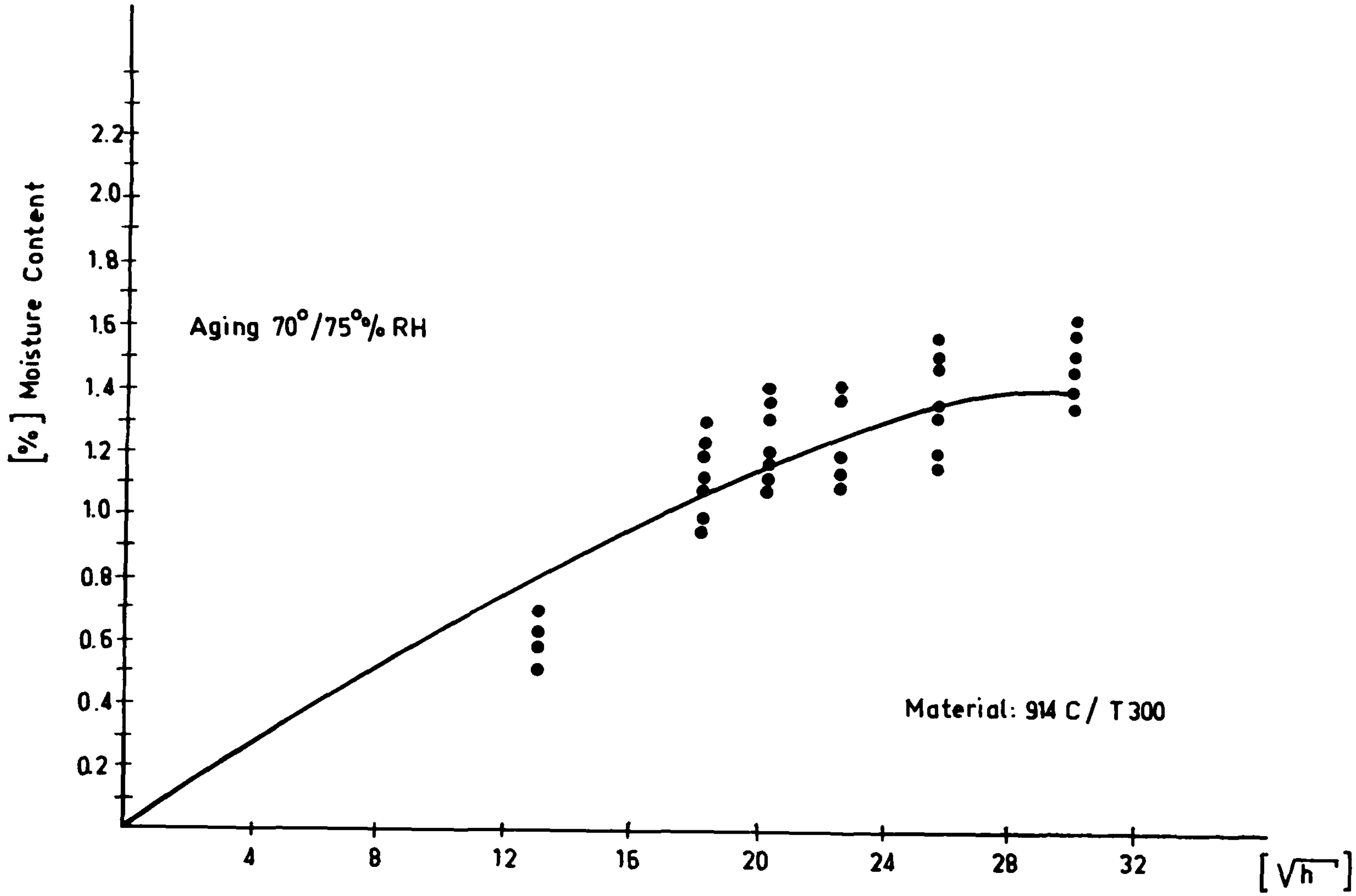


Fig. 1 MOISTURE ABSORPTION IN SAMPLES NOT POST CURED

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8. ACKNOWLEDGEMENTS

This research is carried out jointly at MBB and METU. The specimens were manufactured and shipped to METU for post-cure, aging and mechanical testing. The dynamic behaviour were determined at central laboratories of MBB. The research was sponsored by air force office of scientific research, Air Force Systems Commond USAF. Under the grant number AFOSR 83-0284. The US goverment is authorized to reproduce and distribute reprints for govermental purposes not with standing any copyright notation there on.

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6.3.2. Wet samples

The softening temperature Ts of wet samples were not effected by post-curing. Measurement of glass transition temperature was not possible due to the broadening of damping peak aroung Tg. The average measured Ts value of wet samples were about 105°C and was indcpendant of cross-link density. It is possible that moisture weakend the resin or the resin-fiber interface bond of the laminate, so that the increased intermolecular motion may be responsible to the observed softening. It is therefore not surprising that the results obtained for Ts temperature for different post-curing in wet condition would be simular.

It may well be speculated that in the 914°C resin the normal cure cycle may produce a high level of cross-link density. With further post-curing treatment only a very small additional cross-linking occured in the resin, and this may not change the behaviour of laminate.

7. CONCLUSIONS

The influence of cross-link density on the behaviour of 914C/T300 composites has been investigated experimentally and some interpretations of the effect have been presented.

The interlaminar shear strength and the softening temperature of unidirectional CFRP in wet condition is mainly governed by the amount of water absorbed by the resin matrix. The level of post-curing did not exibit any change in behaviour. It is believed that even after cure cycle a high level of cross-linking density is obtained and a further post-cure would thus have a very minor effect.

It may be possible that the amount of moisture absorbed by the carbon-fiber/epoxy laminate may cause the resin matrix to swell and modify the stresses in the laminate. If this dominates the changes arising from different cross-link densities it would be obvious to see no effect of post-cure cycles.

The situation was simular for dry samples for 914C/T300 system. So it may be speculated that different post-cure treatments yielding different cross-link densities may not alter the free volume content of the resin to affect the mechanical behaviour of the laminate.

6.3. Dynamic Stiffness and Damping

6.3.1. *Dry specimens*

Torsion pendulum experiments were conducted on the filemantary composites to determine the vibration response of the laminate as a function of post-curing treatments. For the carbon fibre epoxy resin composite studied, the Ts and Tg showed only a trend to increase with increase in the amount of post-cure time. All the observed data were within the experimental scatter so it is impossible to reach an exact conclusion. As post-cure time was increased, the increase in cross-link density, sharpened the damping peak that appeared at Tg temperature.With low cross-link densities the peaks were smeared over a larger temperature range. With 10 hours of aging a second peak appeared at around 70^{o}C on the damping curves.

square root of time for 914C/T300 is given. The isothermal absorption curve shows that the initial absorption is diffusion controlled and as specimen begins to be filled up with water the absorption rate decreases. Near equilibrium moisture content the rate becomes exteremely slow, so actual equilibrium may not have been reached in 38 days and may require years.

It is interesting to note that the degree of cross-linking in 914C/T300 composites has no effect on absorption kinetics. The rate and amount of moisture absorbed seems to be dependant on temperature and relative humudity and independant on degree of cross-linking.

The test data indicated that no prefferred diffusion pathsnor a significant change in free volume results from the exzersized post-curing treatments. The calculated diffusion coefficients were independant on the level of cross-linking, having almost a constant value of $2 \times 10^{-7} mm^2/s$. based on Fickion diffusion with constant absorption properties.

The saturated moisture content of the laminate was predicted using the following equation[13]

$$M_\alpha = 1.4 \times 10^{-3} (RH)^{1.6}$$

to be equal to 1.4% This is the actual measured value of 1.4%.

6.2. Interlaminar shear strength

The ILS coupons were chosen for their sensitivity under 3-point bending to resin shear properties. Although so there was no effect of post-curing on shear strength.

TABLE 3. Glass transition and softening points

Post-Cure treatment	DRY SAMPLE		WET SAMPLE	
	Ts	Tg	Ts	Tg
4 hrs at 190^oC	152	198	108	
10 hrs at 190^oC	158	201	105	
4 hrs at 190^oC 2xBond cycle	159	202	106	
4 hrs at 210^oC			106	
10 hrs at 210^oC	161	199	107	

The dynamic measurements did not reveal any significant difference between samples post-cured to different levels. In dry samples the T_S value ranged from 152 to 161^oC and highest value was obtained for post-cure of 210^oC for 10 hours. However all data was within the experimental scatter so that it was difficult to reach a firm conclusion from the trend.

The dynamic behaviour of post-cured wet samples did not exibit any measurable changes with different post-curing treatments. When compared with dry samples the observed Ts values were about 50^oC lower than the dry samples. This result is important since it shows that any post-curing treatment would not alter the wet properties of the laminate.

6. DISCUSSION

6.1. Isothermal water absorption

The mathematical theory of water absorption in a resin has been treated in several works[1-12]. In fig 2 the plot of % weight gain versus

TABLE 2. Interlaminar shear strength of 914C/T300 Post-Cured

Post-cure cycle	Interlaminar shear strength N/mm^2			
	DRY		WET	
	room temp.	120°C	room temp	120°C
4 hrs at 190°C	102	59	95	45
10 hrs at 190°C	106	65	97	46
4 hrs at 190 2x Bond cycle	98	61	96	46
4 hrs at 210°C	104	63	95	45
10 hrs at 210°C	102	61	92	42

The studies showed that the observed values of shear strength are not affected by the post-cure treatment. Laminates subjected to post-cure treatment for 10 hrs at 190°C seemed to yield the highest strength value. Although this is the observed tendency all the results are within experimental scatter.

5.3. Dynamic properties

The thermomechanical behaviour of the laminate in dry and wet condition has been tested for dynamic shear modulus and damping tan δ as a function of temperature as given in figs 4 to 14.

From the dynamic modulus curves the softening points has been calculated by employing the 5% drop method. The Tg and Ts (softening point) values are given in table 3.

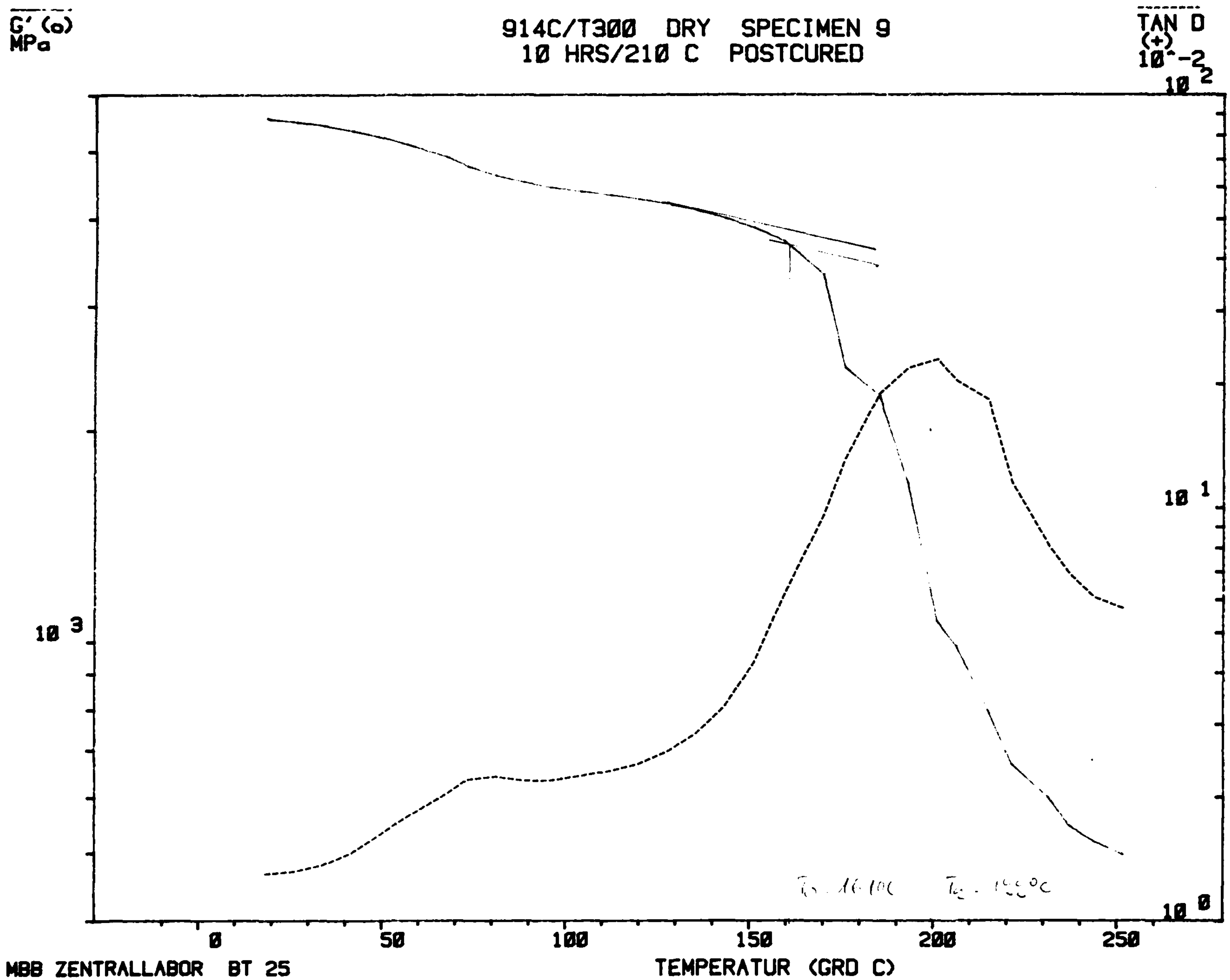

914C/T300 DRY SPECIMEN 9
10 HRS/210 C POSTCURED
G' (o)
MPa
TAN D
(+)
10^-2
10 2
10 1
10 0
10 3
0
50
100
150
200
250
TEMPERATUR (GRD C)
MBB ZENTRALLABOR BT 25

Fig. 8

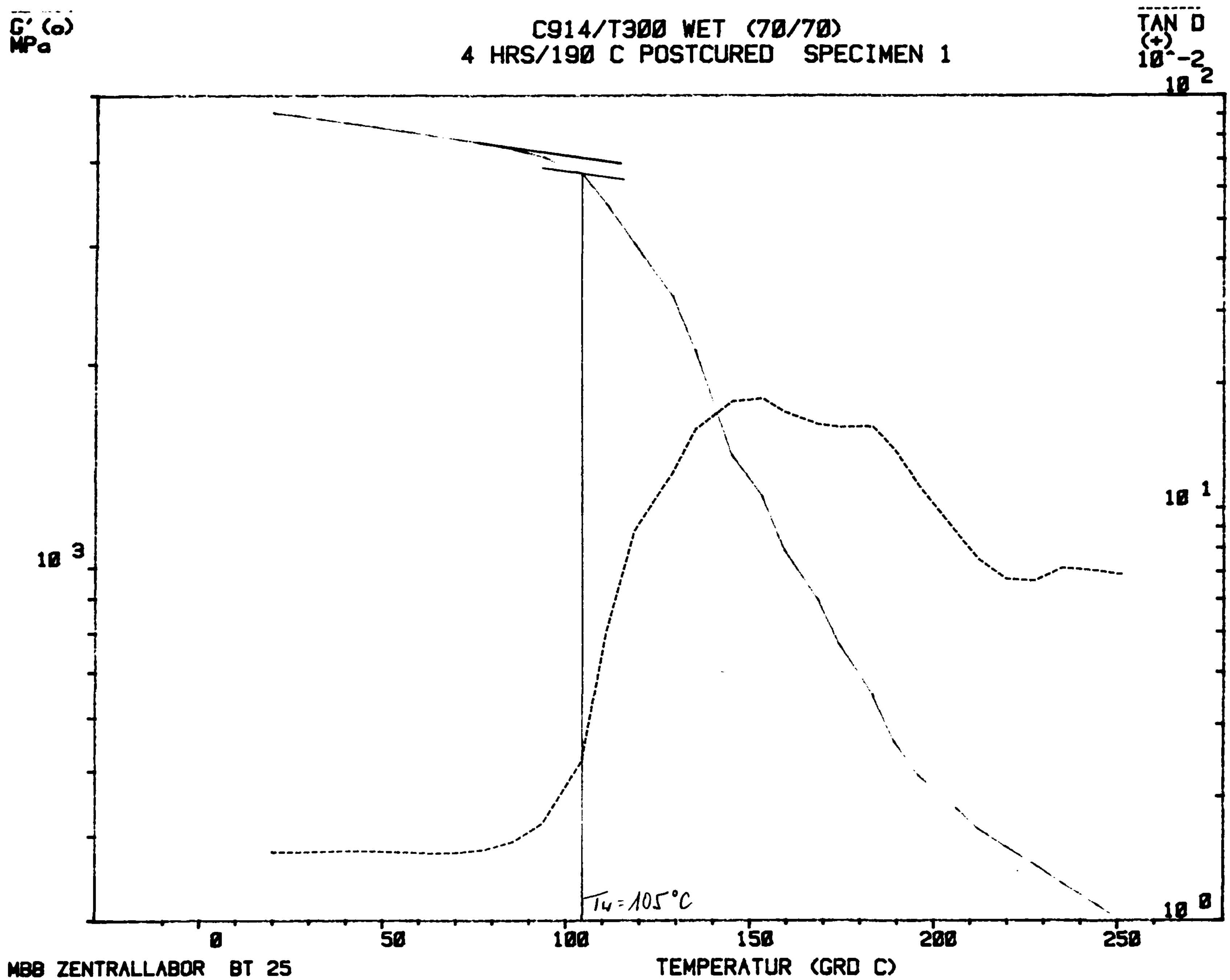
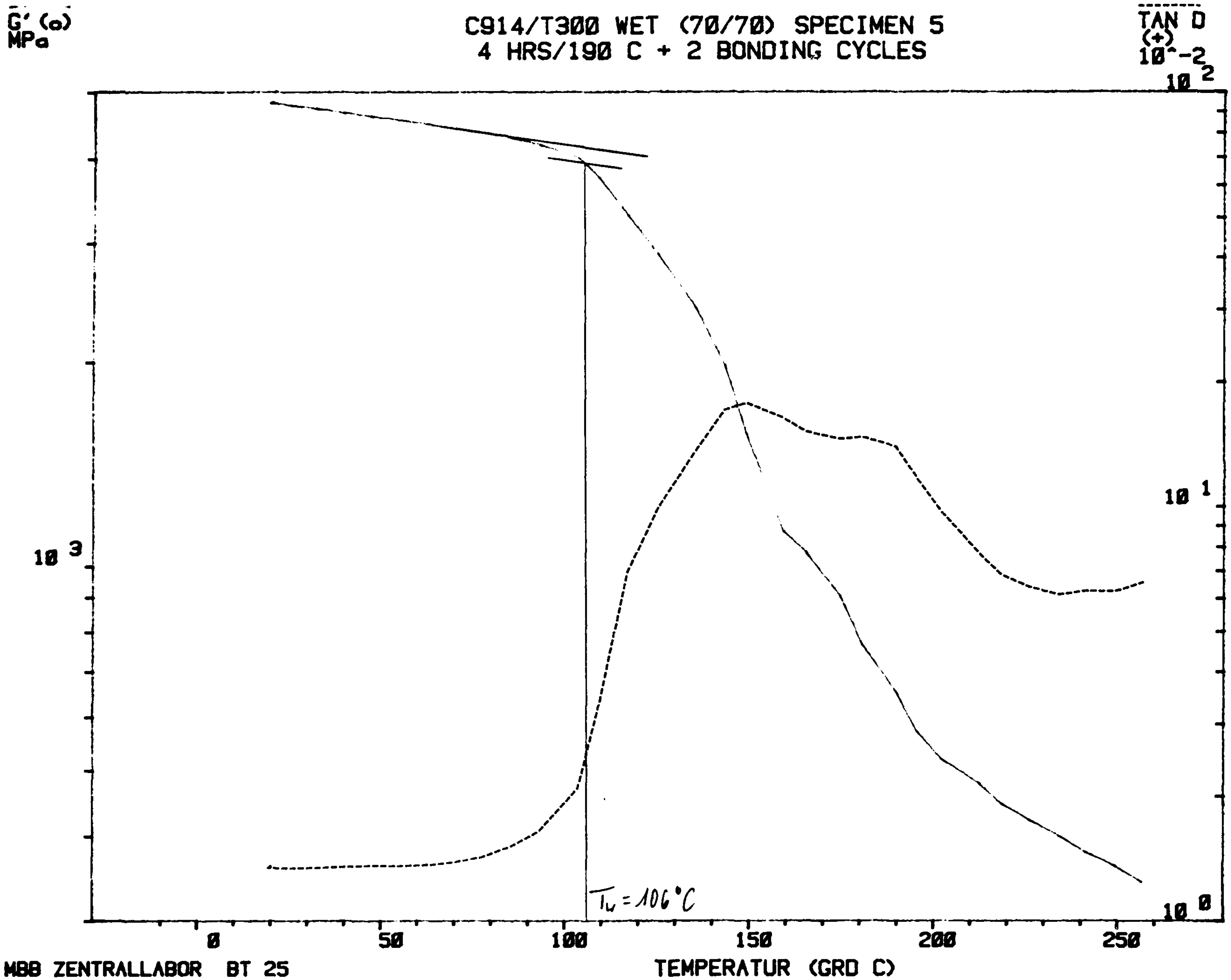

C914/T300 WET (70/70)
4 HRS/190 C POSTCURED SPECIMEN 1
G' (o)
MPa
TAN D
(+)
10^-2
10 2
10 1
10 0
10 3
0
50
100
150
200
250
TEMPERATUR (GRD C)
MBB ZENTRALLABOR BT 25
Tu = 105°C

Fig. 9



G' (o)
MPa
C914/T300 WET (70/70) SPECIMEN 5
4 HRS/190 C + 2 BONDING CYCLES
TAN D
(+)
10^-2
10 2
10 1
10 0
10 3
$T_w = 106°C$
0
50
100
150
200
250
TEMPERATUR (GRD C)
MBB ZENTRALLABOR BT 25

Fig . 10

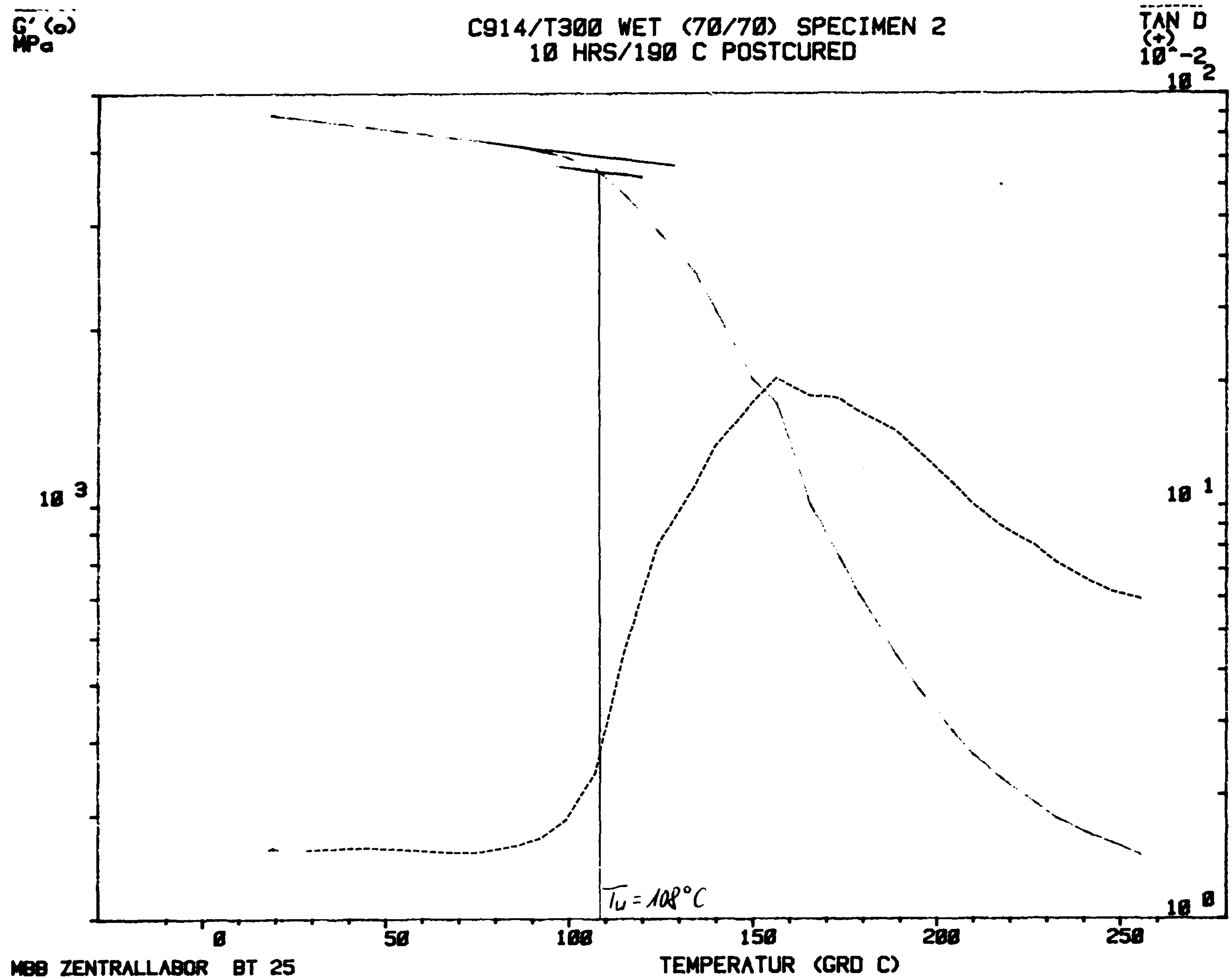
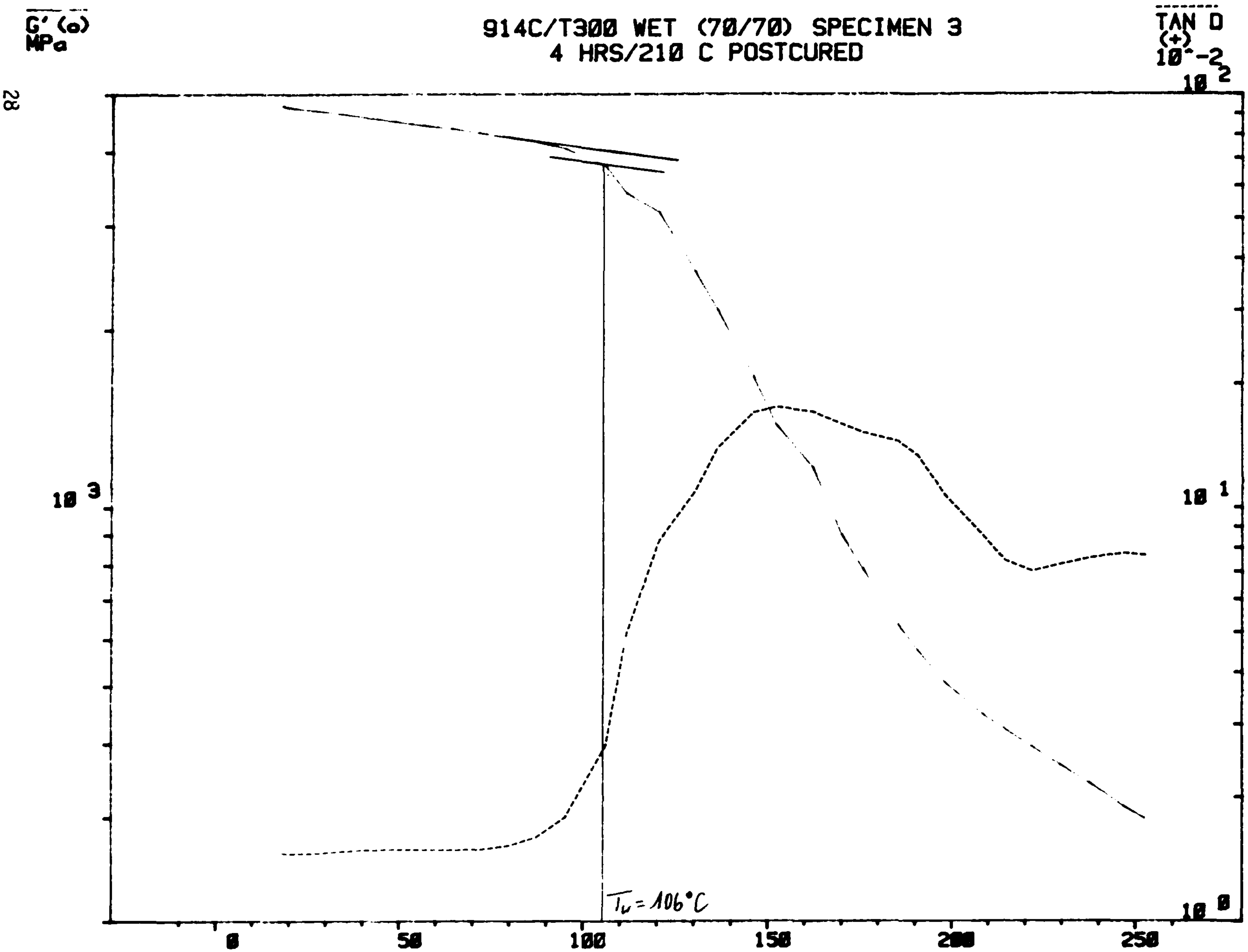

C914/T300 WET (70/70) SPECIMEN 2
10 HRS/190 C POSTCURED
G' (o)
MPa
TAN D
(+)
10^-2
10 2
10 3
10 1
10 0
0
50
100
150
200
250
TEMPERATUR (GRD C)
MBB ZENTRALLABOR BT 25
Tu = 108°C

Fig. 11



MBB ZENTRALLABOR BT 25

Fig.12

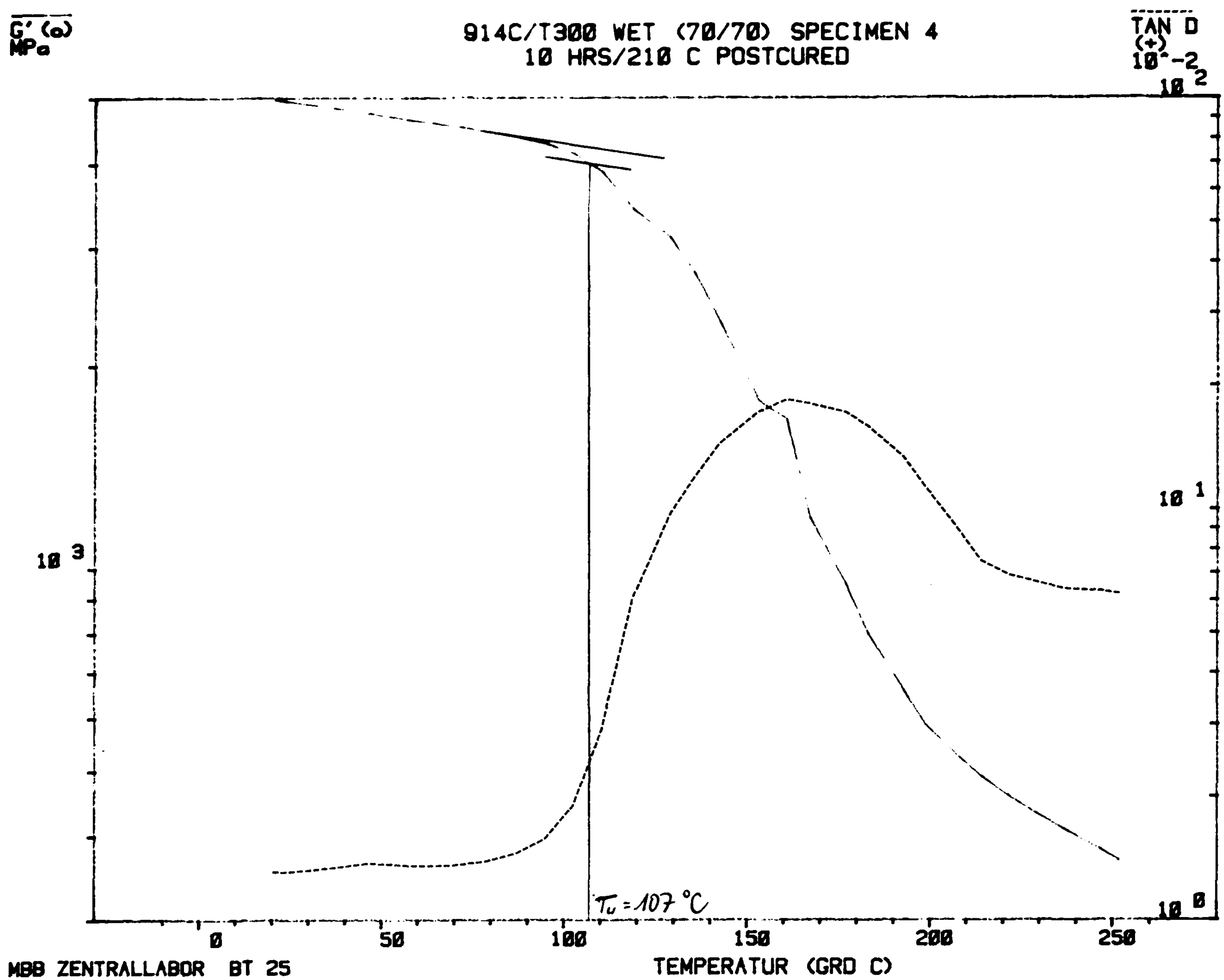
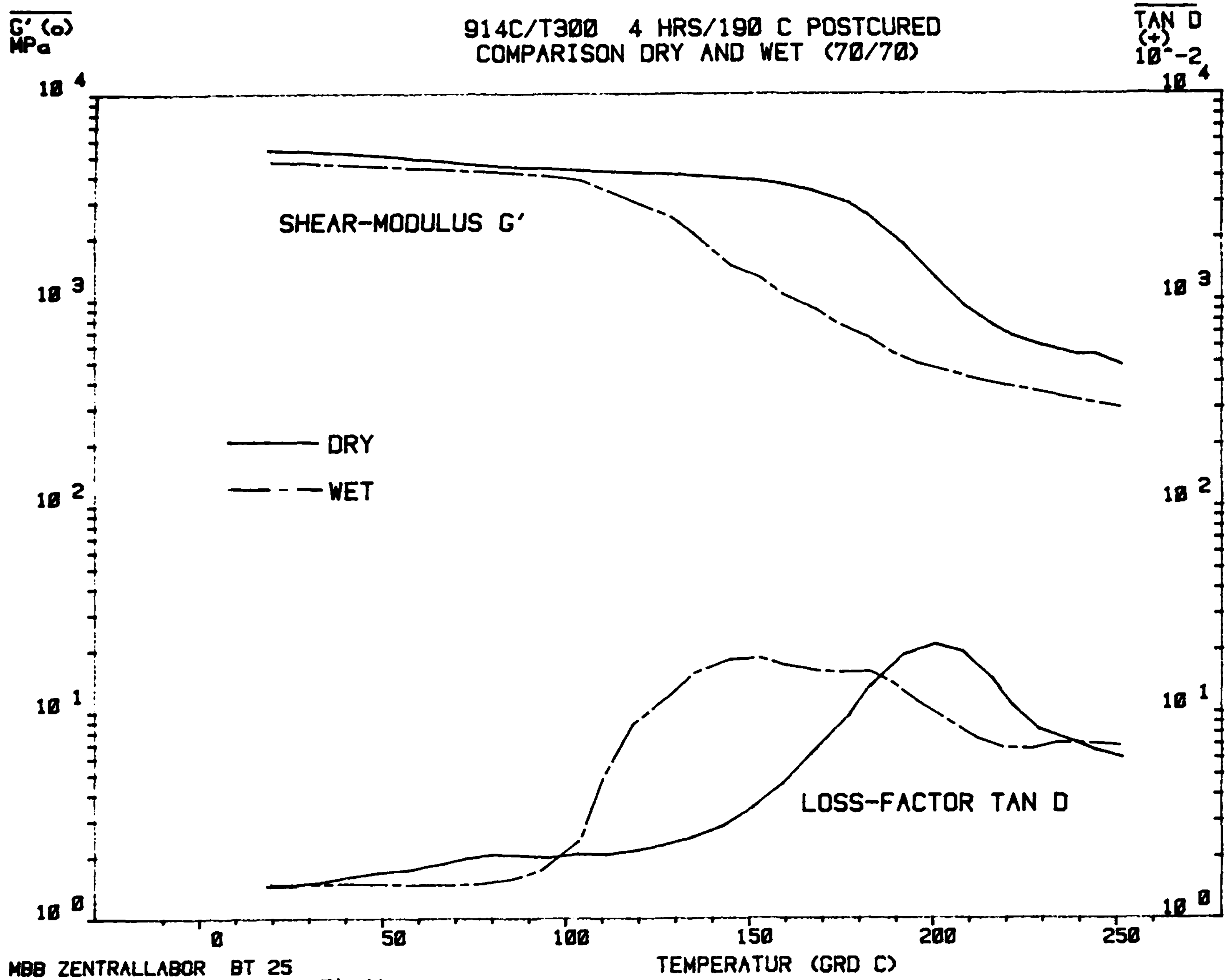

G' (ω)
MPa
914C/T300 WET (70/70) SPECIMEN 4
10 HRS/210 C POSTCURED
TAN D
(+)
10^-2
10 2
10 1
10 0
10 3
0
50
100
150
200
250
T_u = 107 °C
TEMPERATUR (GRD C)
MBB ZENTRALLABOR BT 25

Fig.13


G' (o) MPa
914C/T300 4 HRS/190 C POSTCURED
COMPARISON DRY AND WET (70/70)
TAN D (+) 10^-2
SHEAR-MODULUS G'
DRY
WET
LOSS-FACTOR TAN D
TEMPERATUR (GRD C)
MBB ZENTRALLABOR BT 25
Fig.14

END

FILMED

9-85

DTIC