HNBR and Long Term Serviceability in Modern Automotive Lubricants

Part - II : Structure Property Relationships

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ABSTRACT

A study on the viscoelastic properties of Hydrogenated Nitrile (HNBR) was conducted after exposure to nucleophilic and basic constituents in automatic transmission fluid (ATF). Substantial differences in the viscoelastic behavior after aging was observed. A proposed mechanism for the initial formation of an ionomer (isocyanide and / or isonitrile ions), then an imide crosslink is discussed.

INTRODUCTION

The analytical investigation done in Part I of this paper puts forth the hypothesis that Hydrogenated Nitrile (HNBR) rubber in the presence of nucleophilic and basic species, can lead to a chemical reduction of the acrylonitrile group. Lubricant additive packages found in today's automotive fluids contain both nucleophilic and basic constituents. Automatic transmission fluid (ATF) was used in this study.

When subjected to these nucleophilic and basic constituents, the cyano group of HNBR may be converted to an isocyanide or isonitrile ion[1,16]. (See Fig.1). Isocyanide and isonitrile ions carry a partial dipole moment opposite that of their acrylonitrile precursor ($^-C\equiv N^+$)[4]. This charge configuration causes both species to be metastable at best. The presence of water or oxygen, coupled with heat, can further advance these structures to an imide, imine or potentially an aldehyde[1] (See Fig.1). For this paper, the scope will be limited to the proposed mechanism of acrylonitrile sites possibly being converted to isocyanide or isonitrile ions initially, then to an imide crosslink. We will attempt to further investigate what was found in Part I through dynamic mechanical characterization.

EXPERIMENTAL

HNBR samples were formulated and molded as described in the experimental discussion of Part I[16]. Agings were done in Scott blocks using ATF at 150°C, in accordance with ASTM D471. Samples for this portion of the investigation were 3.3 mm thick, compared to 2 mm in Part I. This was done to facilitate dynamic mechanical characterization.

Data was obtained using a Rheometrics™ RDA-II in the torsion rectangular mode. A sample of dimensions' 29.4 mm x 12.8 mm x 3.3 mm was used for each analysis. Data was collected over the frequency range of 0.1 to 100 rad/sec. at a data collection rate of 10 points per decade of frequency at each temperature step. The temperature sweep of the data ranged from -150°C to 150°C for the unaged and 3500 hours samples, and -75°C to 150°C for the remaining samples, using a 4 degrees per step test method.

RESULTS

ELASTIC SHEAR MODULUS SCANS

Figure 2 compares the storage modulus, G', of unaged HNBR with 4 samples aged in ATF for the listed time periods. All of the data is extracted from a temperature sweep scan taken at 0.1 rad./sec..

Initiating the review of data in the low temperature regime, the unaged HNBR exhibits a drop in shear modulus at -35°C. This drop is attributed to the main glass transition temperature, Tg (α relaxation), of the unaged HNBR, and will be referenced by Tg_1, hereafter. All of the aged samples exhibit the same drop in shear modulus at roughly the same temperature.

Progressing through Tg_1 , it can be seen that the transition region for the aged samples becomes broader as the aging time increases (See Fig.2). Samples aged 1500 hours and longer show the establishment of a plateau modulus, between -20°C and 30°C. This first plateau region will be referenced by G_N , hereafter. A second transition, starting at approximately 40°C, appears in samples aged for 1500 hours and longer.

This second transition is not seen in the unaged or 750 hours aged samples. This transition will be referenced as, Tg_2 , hereafter. Continuing above this transition, the long term aged samples enter their equilibrium plateau, commonly referred to as the equilibrium plateau modulus (G_E). The equilibrium plateau modulus had been reached for the unaged and 750 hours samples by -10°C and 20°C, respectively.

One additional note from the elastic shear modulus scans, the equilibrium plateau modulus for the unaged and 750 hour samples appears to be increasing with temperature. We feel this is an artifact of the test procedure and not a "marching modulus" as described in the elastomer industry, which is the result of incomplete cure. This gradual increase is probably due to the onset of aging caused by the long time between measurements at each temperature, approximately 14 minutes.

Returning our focus to the first plateau modulus (G_N) in Fig.2 , initially it could not be determined whether this plateau was due to additional crosslinking of residual unsaturation or other potential crosslinking sites (i.e. tertiary carbon on the acrylonitrile group, unsaturation in 1,2 sites, etc.) after curing. Other potential causes could be increased crystallinity, or some type of ionic behavior.

In Part I of this paper, an investigation was done to determine whether this increase in shear modulus was due to unreacted crosslinkable sites. Twice the typical amount of curative (peroxide) was added to the base polymer matrix and vulcanized[16]. The dynamic scans in Figure 2 indicated the increase in shear modulus was from 1.0E7 dynes / cm^2 to 1.2 to 1.6E8 dynes / cm^2 , a change that could not be achieved solely due to unreacted crosslinkable sites.

This was based on determining the change required in the number average molecular weight between crosslinks (M_C) to achieve such a shift in shear modulus. The calculation was done assuming affine deformation. Having assumed this, the total work done on the network during deformation was then calculated using the equations shown in Table 1[11-15]. Again, we felt this was not a highly probable explanation for the storage shear modulus (G_N) change seen in Figure 2.

When the long term aged samples (1500 hours and greater) reach their equilibrium plateau (G_E), the value is higher than the unaged or 750 hours samples. This difference indicates that some additional crosslinking has occurred (a reduction in M_C). Although this appears to be a small amount on the graph, keep in mind that the y-axis is logarithmic (See Fig.2).

Next, we chose to examine the potential of increased crystallinity. Documented research has shown that highly crystalline materials may give scans similar to the aged scans seen Fig.2[2,3]. However, we could not think of a reasonable hypothesis why one would experience such an

increase in crystallinity. The HNBR tested was a crosslinked amorphous elastomer. Aging was done in a free, undeformed state at elevated temperature, conditions not suitable for significantly increasing crystallinity in an elastomer.

There are proposed theories and discussions that the highly saturated grades of HNBR (< 1% unsaturation remaining after hydrogenation of the NBR precursor) give high ultimate strengths due to strain crystallization of the mostly olefinic backbone. Again, this does not seem to be a plausible mechanism for the shear modulus changes seen in Figure 2, as the strain applied to the samples was extremely small (0.1%) and elastomers do not crystallize in shear.

The final hypothesis to investigate was ionic effects. Review of prior work on the viscoelastic characterization of ionomers, mainly the research of Eisenberg and Navratil[6-9], Yeo and Eisenberg[10], and Ward and Tobolsky[5], showed results that closely parelleled our results. This coupled with the results proposed from Part I of this paper, led us to investigate this hypothesis further.

The research of Eisenberg et.al.was on styrene-based and perfluorinated ionomers. Tobolsky et.al. researched copolymers of α-olefins and carboxylic acids. Their viscoelastic and dynamic mechanical data closely resembles what we have found in aged HNBR. Two key hypothesis from their work which we used as a fundamental basis for ours are: 1) neither the ion size nor valence, play a major role in influencing the viscoelasticity of the polymer matrix. The concentration of the ionic species present is the predominate factor. 2) The formation of ionic behavior may cause the material to behave thermo-rheologically complex. Thereby, Time - Temperature Superposition (TTS), could break down in most cases, but not in every case. The concentration of ionic species present dictates whether TTS is valid or not.

Having established what we could propose from the elastic shear modulus scans, and how that led us to investigate the characterization of ionic species and ionomers, we next reviewed our scans in light of the findings of Eisenberg et.al. and Tobolsky et.al..

Eisenberg and co-workers proposed that below a critical ion concentration, these ions probably exist as multiplets and act as pseudo - crosslinks. These pseudo-crosslinks slow down the primary diffusional relaxation mechanism, but still obey TTS. Above the critical ion concentration, the ion multiplets act as crosslinks of finite lifetime and TTS becomes invalid.

Tobolsky and co-workers also found the same results in their α-olefin and carboxylic acid copolymers at least five years prior to Eisenberg's published findings.

To examine this concept of TTS failure with the presence of ionic character, we went back and attempted to do TTS on the elastic shear modulus scans of the unaged HNBR, and samples aged 1500 hours and 3500 hours. The scans were not compensated for the change in Tg because, there was very little change after aging. The results are shown in Figs. 3a,b and c.

Using Tg_1 as the reference temperature, all of the scans were shifted using the WLF equation. None of the samples showed "strict" adherence to the WLF equation. Again, two features are apparent.

This follows the same type trend that Eisenberg and Tobolsky found in their investigations.

LOSS SHEAR MODULUS SCANS

Figure 4 compares the loss shear modulus, G", of unaged HNBR and samples aged in ATF at 150°C for the listed time periods. All of the data is extracted from a temperature sweep scan taken at 0.1 rad / sec..

Again, starting the review of data in the low temperature regime for the unaged and 3500 hours samples (See Fig. 4), it appears both have their β-relaxation occurring at -120°C to -70°C. This relaxation is probably occurring in the polyethylene or butadiene segments of the unaged HNBR[2]. The β-relaxation in the sample aged 3500 hours is probably occurring in the polyethylene segments, since we suspect that all of the butadiene segments have been reacted

after this amount of test time. None of the other samples were analyzed below -75°C since our primary area of focus was on Tg_1 and above.

The α-relaxation, Tg_1, of the unaged sample occurs at -35°C. After aging up to 3500 hours, Tg_1 is essentially the same, or shifted very slightly to higher temperatures (< 1°C). The primary difference between unaged and aged scans being the breadth of the transition region.

Between the unaged sample and the sample aged for 750 hours, the transition region has already begun to widen (Fig.4). After 1500 and 2500 hours, there is the clear development of a second transition, earlier designated as Tg_2. This was seen in Eisenberg's work, thereby we are proposing that this second peak is due to an increase in ion concentration (i.e. isocyanide or isonitrile ions), but still below the critical ion concentration.

Continued aging out to 3500 hours, the intensity of this peak diminishes and the loss modulus curve takes on a different profile, an inflection point develops (Fig. 5a and b). Eisenberg found the same type behavior in his loss shear modulus versus temperature scans, although he was working with a styrene-based polymer. His research proposed that, below a critical ion concentration, a second peak in the loss modulus curve would exist (what we earlier referenced as Tg_2). Above the critical ion concentration, no distinct second peak in the loss modulus curve would be observed, instead an inflection point would appear. (See Fig.4)

Comparison of our loss shear modulus scans to those of Eisenberg's would indicate the possibility that at up to 2500 hours, the ionic species formed is below the critical ion concentration. Continuing the aging to 3500 hours, the critical ion concentration is exceeded, thus changing the profile of the loss modulus curve.

DISCUSSIONS

This initial investigation into the aging of HNBR in nucleophilic and basic environments has made it apparent that the nitrile moiety is subject to attack in these environments. Chemical literature has shown this not to be a discovery, but maybe an overdue review. Jerry March's "Advanced Organic Chemistry - Reactions, Mechanisms, and Structure" although extremely compartmentalized, is a good treatise to investigate this mechanism.

Further research has already been completed in this area, but was not presented. We have investigated the effects of acrylonitrile content, filler types and levels. Nothing, so far has been found to indicate the attack is not occurring at the cyano group.

O-rings have been obtained that experienced a substantial volume swell (15 - 20%) and increase in shear modulus (from Shore A to Shore D scale). This precludes the fact that the hardening could have occurred first. The swelling occurring first would be within reason, with the formation of some type of ionic species. This would lead to a significant uptake of water, due to a potential (zeta) gradient. Eisenberg et.al. found the same trend with the addition of ionic species to his styrene-based ionomers.

CONCLUSIONS

1. Using dynamic mechanical analysis, the chemical changes of HNBR in the presence of nucleophilic and basic species was characterized to verify the findings from the analytical study.
2. Results from our dynamic mechanical characterization of HNBR aged in ATF, in combination with prior research efforts by Eisenberg et.al.and Tobolsky et.al., we are proposing the hypothesis that the species initially formed through aging is "ionic" in nature. This could be due to the formation of ioscyanide and / or isonitrile ions, before the eventual formation of an imide crosslink.
3. Data indicates that up to 3500 hours in ATF, there is the development of a first plateau modulus, G_N, which we are proposing is due to the formation of an ionic structure; and there

is an increase in the equilibrium plateau modulus, G_E, which we are proposing is the formation of an imide crosslink.

ACKNOWLEDGMENTS

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Table 1. Relationship between shear modulus and molecular weight between crosslinks, and work under strain

$$W = \nu kT/2 \; [<r^2>_c / <r^2>_u] \; [(\lambda_x)^2 + (\lambda_Y)^2 + (\lambda_z)^2 - 3]$$

$$W = (VG/2) \; [(\lambda_x)^2 + (\lambda_Y)^2 + (\lambda_z)^2 - 3]$$

$<r^2>_u$	=	Mean square end to end distance of uncrosslinked Gaussian chain in unperturbed state averaged over time.
$<r^2>_c$	=	Mean square end to end distance of crosslinked Gaussian chain in unperturbed state averaged over time.
λ	=	Extension ratios in principal coordinate axes.
ν	=	Number of molecules in specimen
V	=	Volume of Specimen
k	=	Boltzmann Constant
T	=	Temperature in ° Kelvin
W	=	Work done in Deformation

$$G = NkT / 2 \; [<r^2>_c / <r^2>_u] = \rho RT / M_C$$

G	=	Shear modulus of specimen
M_C	=	Number average molecular weight between crosslinks
N	=	ν/V
ρ	=	Density
R	=	Gas constant
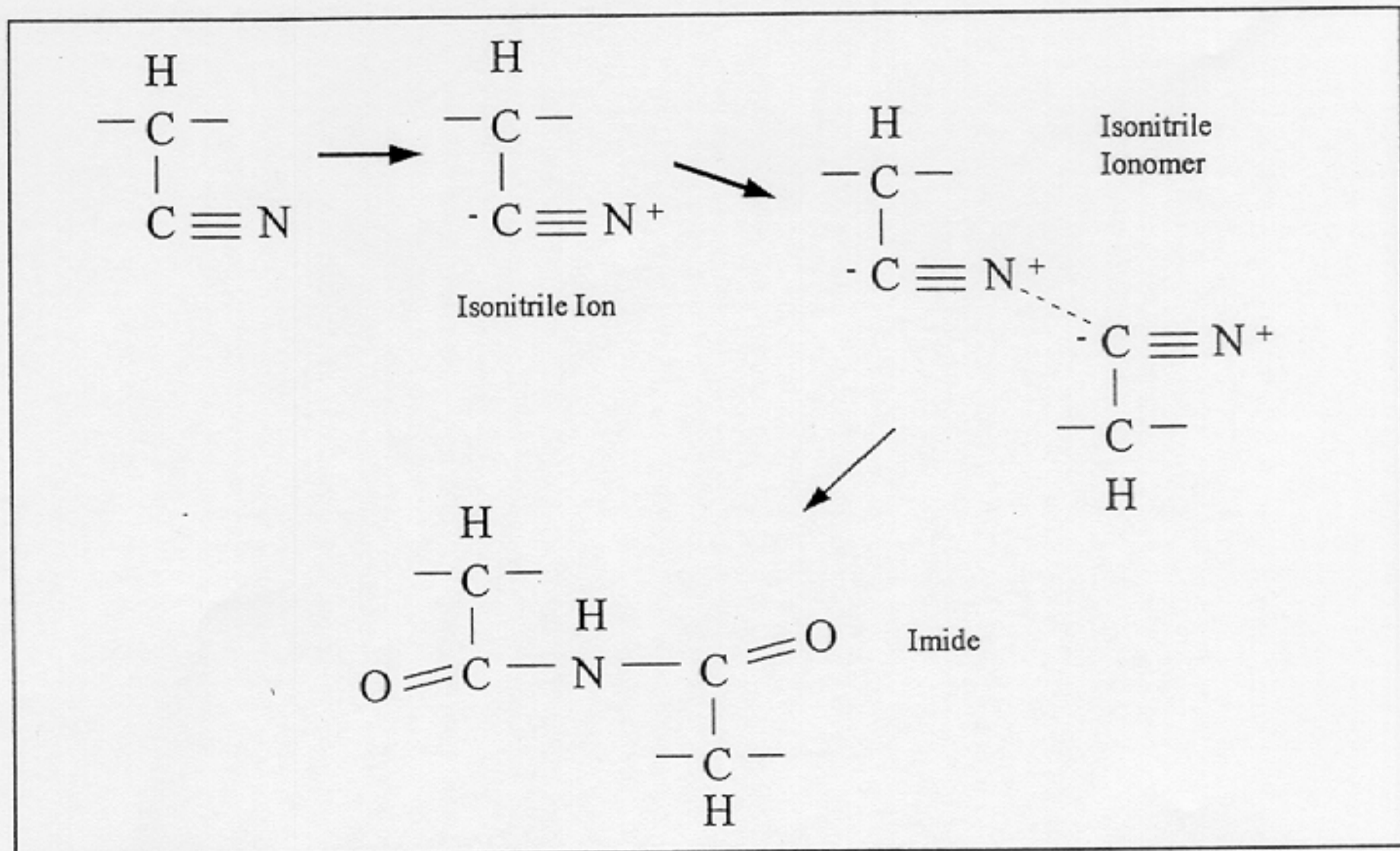
Fig. 1. Schematic of the proposed mechanism for degradation of HNBR -- conversion of HNBR to isonitrile ionomer and subsequently an imide
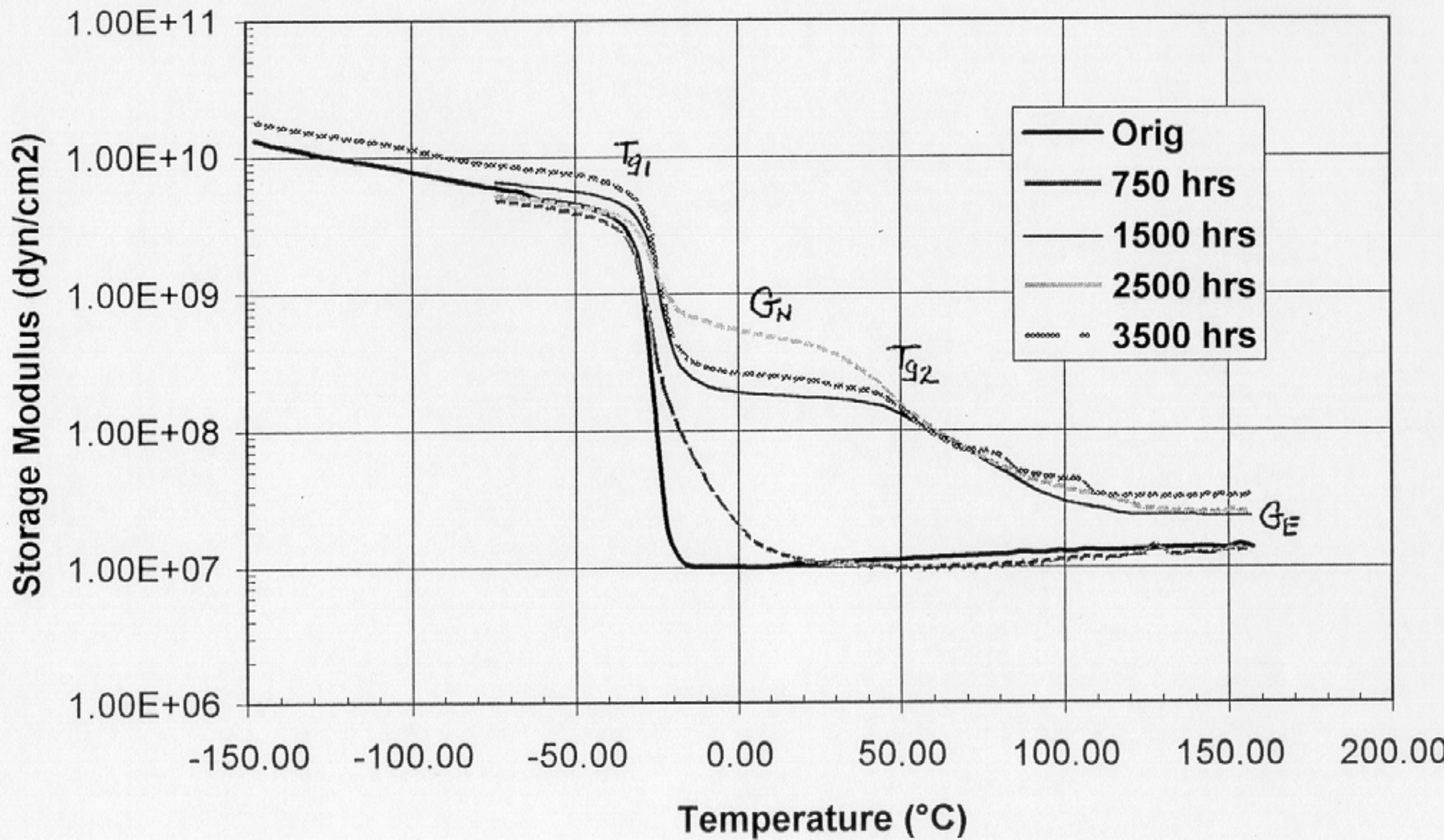
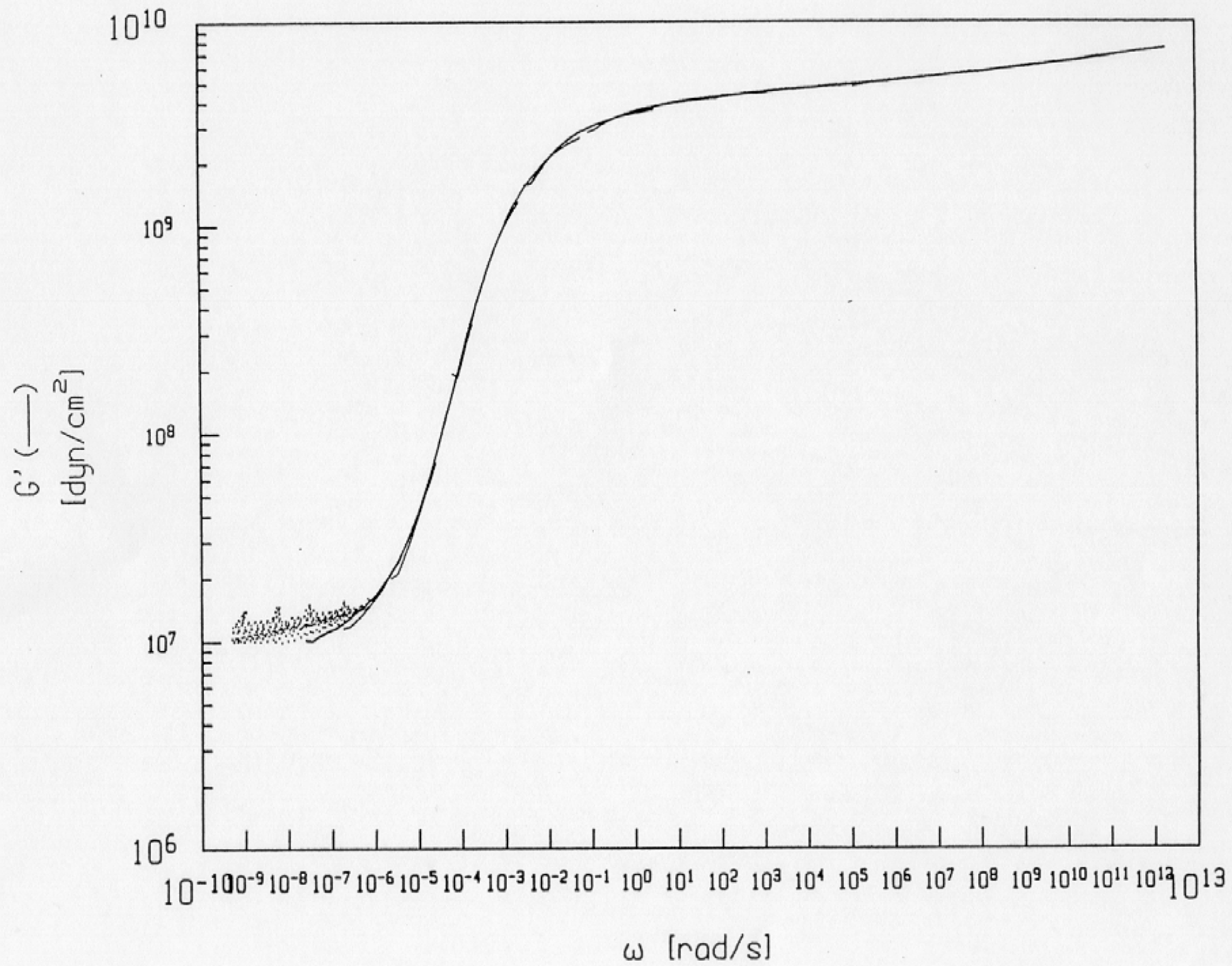Fig. 2 Storage modulus of the HNBR compound at various aging times

Fig. 3 a) Storage modulus Master Curve for the Original HNBR compound
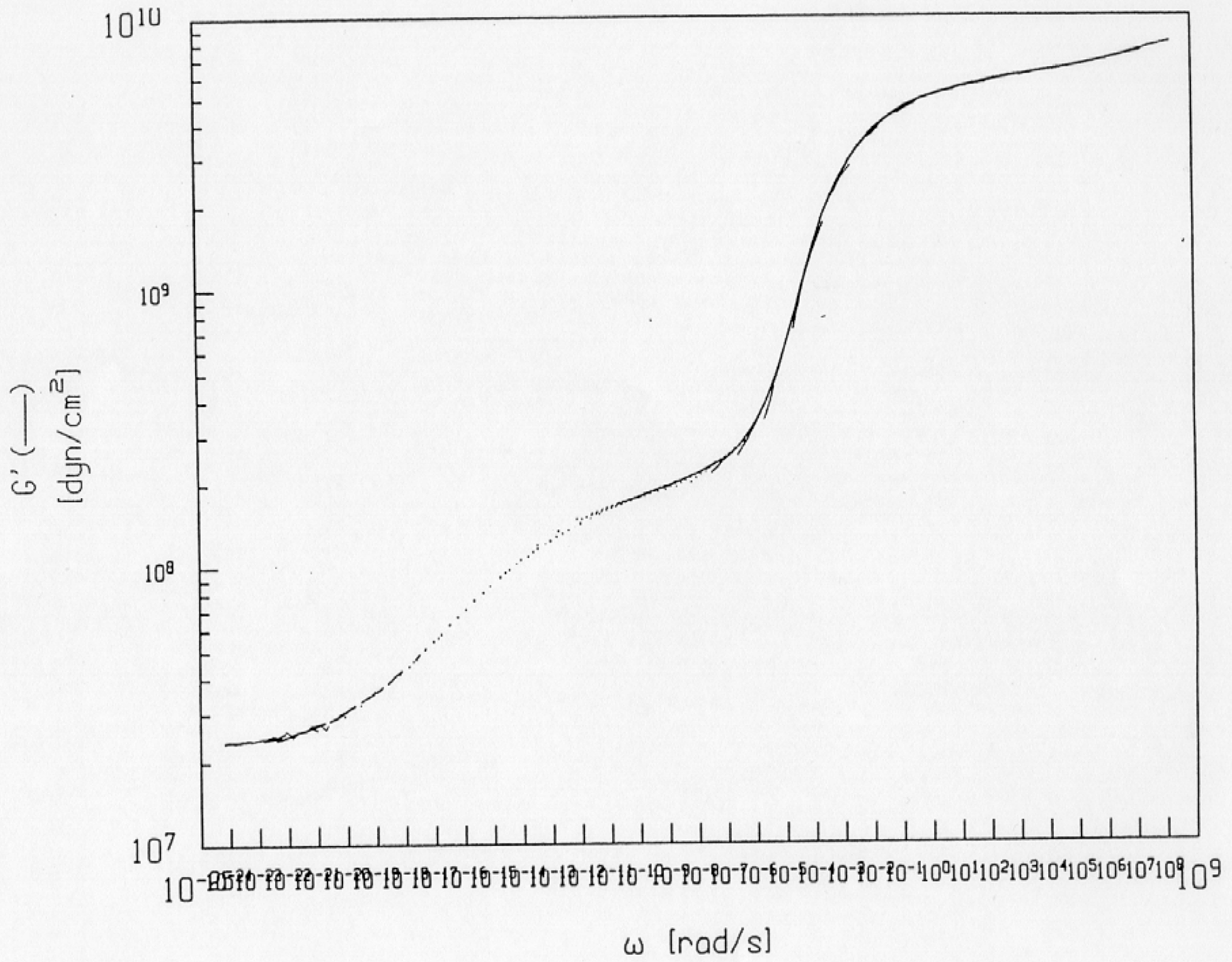
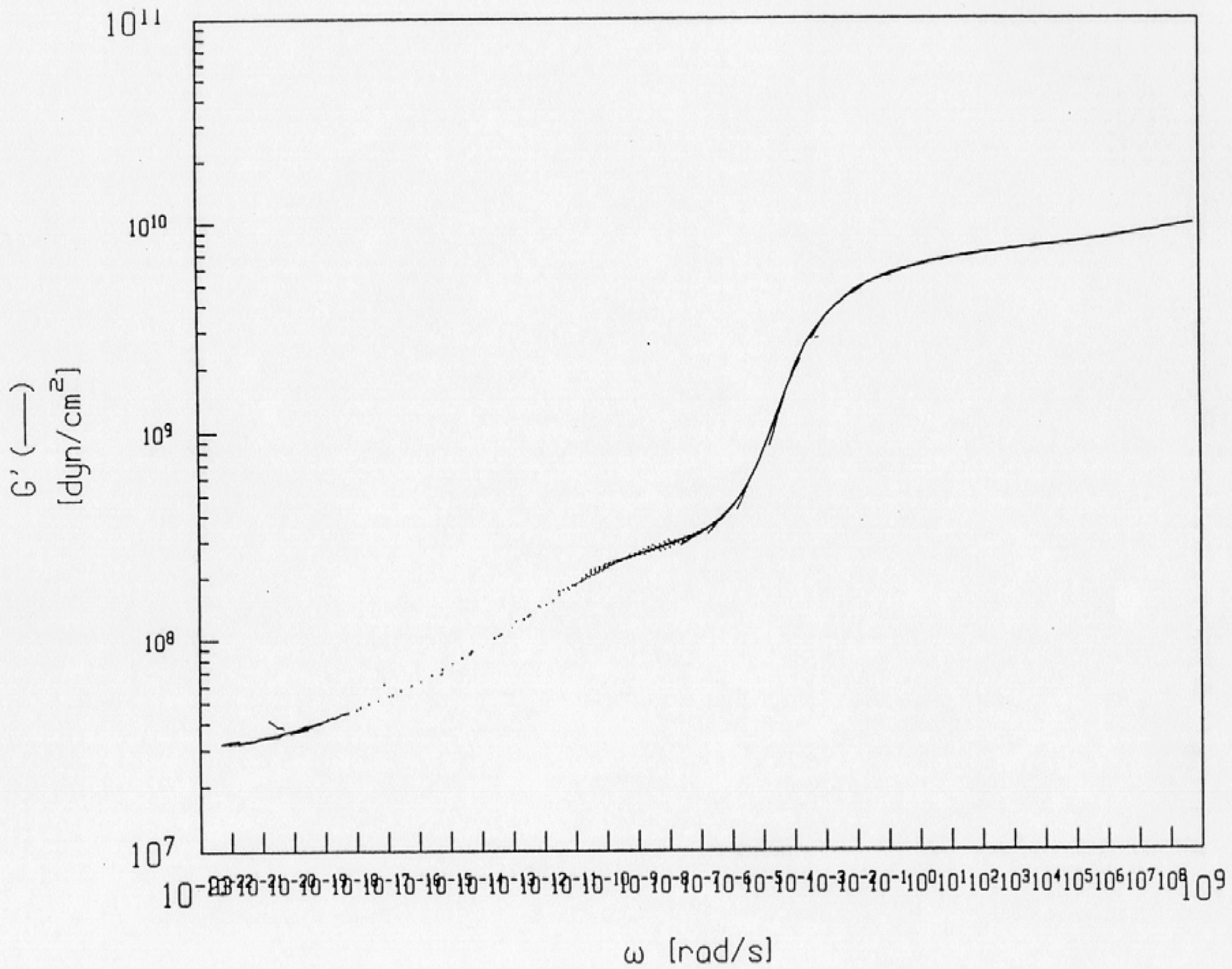Fig. 3 b) Storage modulus Master Curve for the HNBR compound after 1500 hours of aging

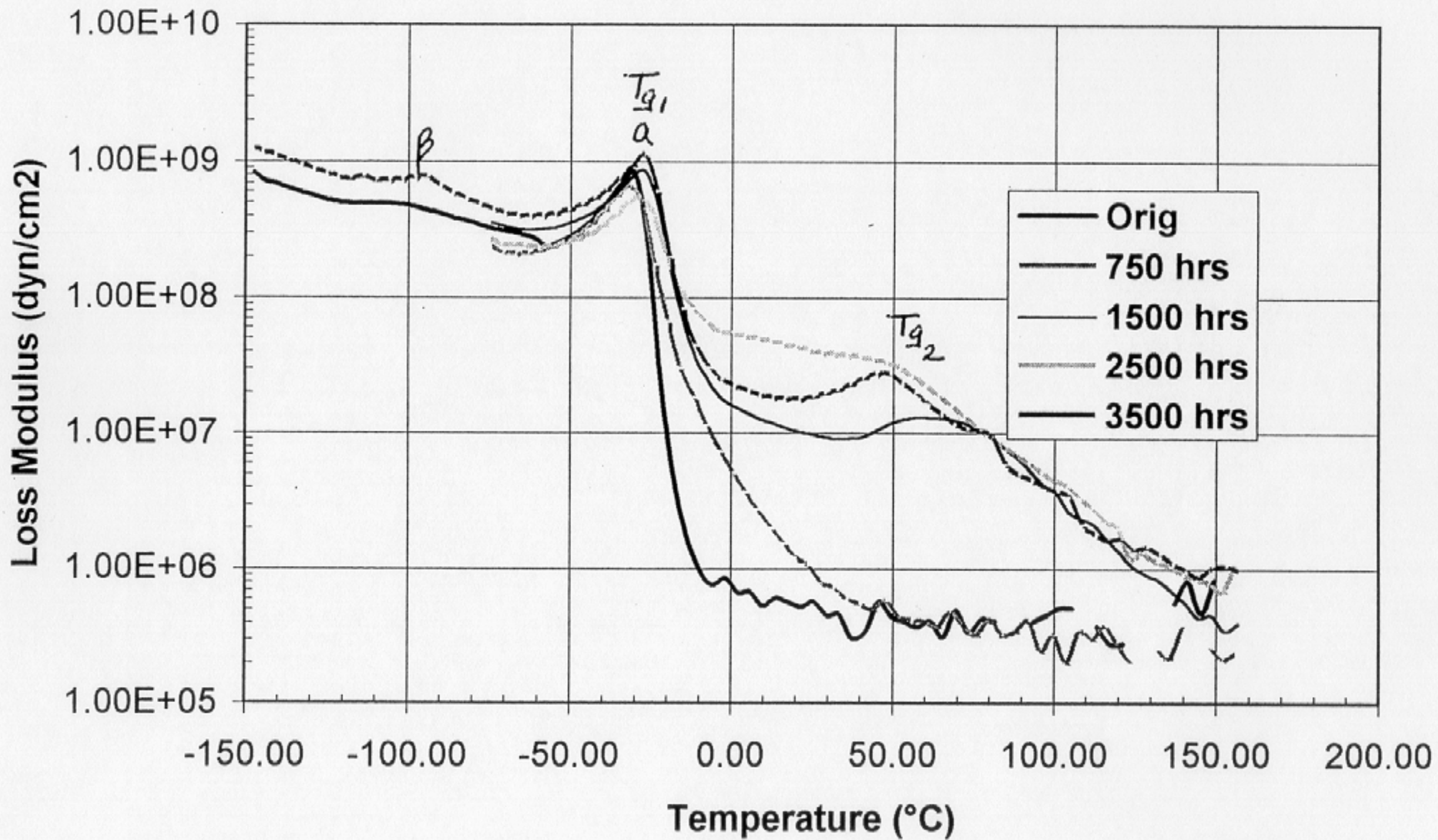Fig. 3 c) Storage modulus Master Curve for the HNBR compound after 3500 hours of aging

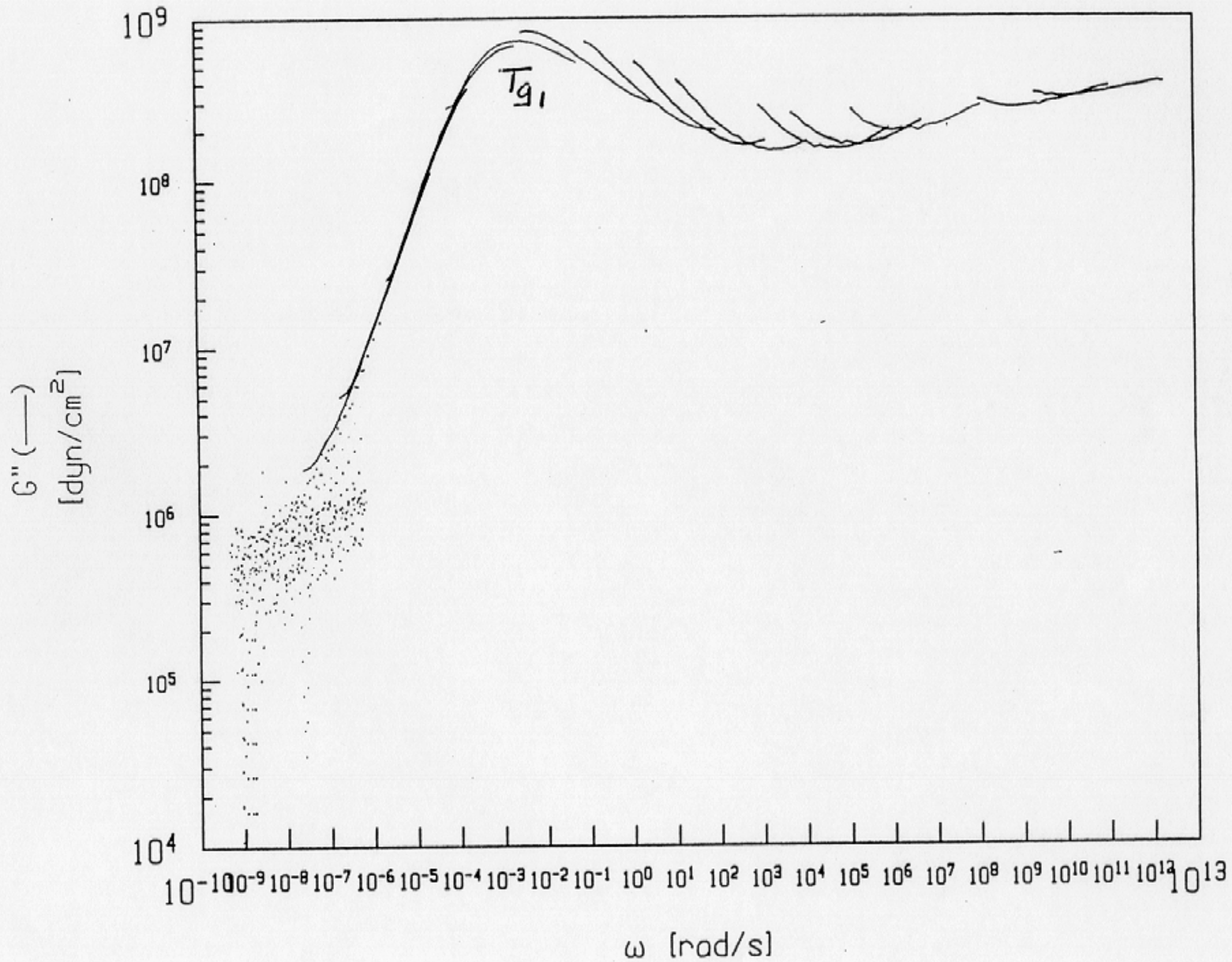Fig. 4 Loss modulus of the HNBR compound at various aging times

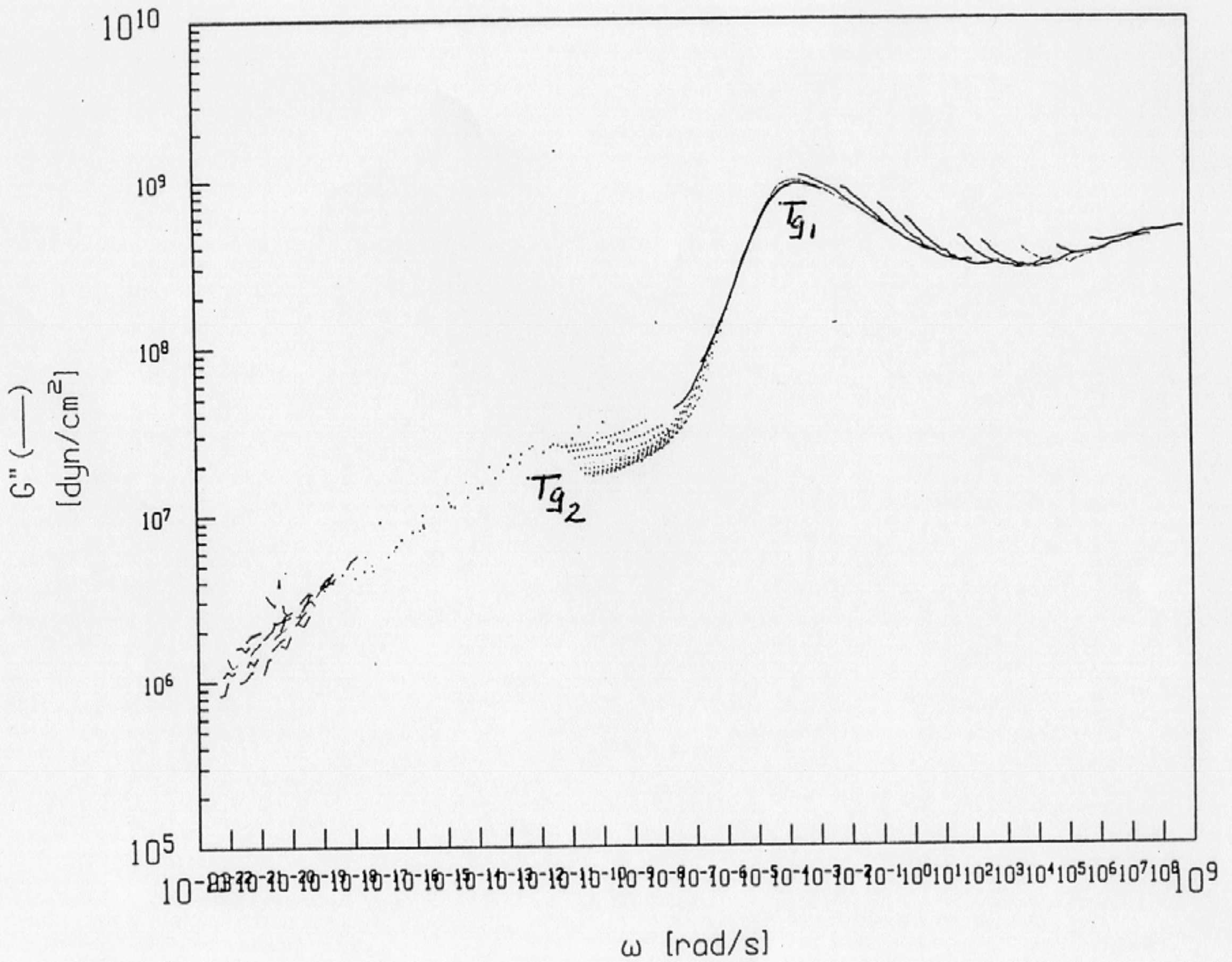Fig. 5 a) Loss modulus Master Curve for the Original HNBR compound

Fig. 5 b) Loss modulus Master Curve for the HNBR compound after 3500 hours of aging