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Agglomeration increases with silica concentration, amount of silanols on the silica surface and polymer molecular weight. All these observations as well as the relaxation of the different materials are explained with a model in which agglomeration takes place through intermediate chains that link the aggregates to one another. However, low molecular weight suspensions showed a different behavior. This behavior was related to the absence of entanglements and low probability of bridging chains.

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Abstract

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EFFECT OF PARTICULATE FILLERS ON THE RHEOLOGY OF POLYMER MELTS

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Introduction

Polymer suspensions are important for understanding processing of filled rubbers. Even though these systems have been used for many years, there is still not complete agreement on the mechanism of agglomeration and filler-polymer interaction.

The uncured suspensions are more sensitive to the dispersion, structure and surface chemistry of the filler and to the molecular weight of the matrix than the cured rubbers. Thus, the study of the suspension rheology gives a better clue as to the origin of filler agglomeration (ie. formation of finite and/or sample spanning clusters). Our system are concentrated suspensions of aggregates of distributed and colloidal sizes with fractal structure in a polymeric matrix of polydisperse polymer. Adsorption of the polymer onto the filler occurs in the melt state, where strong specific interactions between filler and uncured rubber take place. Thus, an understanding of the rheology of filled unvulcanized rubbers involves studies on colloids and suspensions, polymer characterization and interfaces phenomena.

Initial attempts to model the behavior of these suspensions were based on the work of Einstein on the viscosity of diluted suspensions [1-3]. Corrections due to occluded rubber, bound rubber, or the strain amplification concept helped to extend the use of those simple models up to filler concentrations of 10-20% by volume, although without strong theoretical grounds [4-6]. These models are unable to explain a set of experimental results obtained from different tests.

The filler-polymer interface plays an important role in the reinforcement of

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elastomers. However, the conclusions from the study of one system cannot be readily extended to other systems, since they depend on the nature of filler and polymer. In this particular case, we are looking at suspensions of fumed silica in polydimethylsiloxanes (PDMS). Important contributions to the understanding of the specific interactions silica siloxanes have been made by Chahal and St Pierre [7], Berrod et al. [8] and more recently by Cohen-Adad et al [9,10].

The progress achieved in the study of suspensions is based in observations of spheres or simple asymmetric particles (like rods) in Newtonian fluids. Russel [11] authored a review on the rheology of suspensions where, in spite of the advances done in the area, he points out the inability of present models to treat the multiparticle hydrodynamics that inevitably appears at medium and high concentrations. The situation becomes even more complicated when dealing with flocculated suspensions.

The aim of this work is to relate the morphology of the silica-polydimethylsiloxane suspensions to the observed rheological properties. We will present a model capable of explaining, at least qualitatively, the experimental results as a function of polymer molecular weight, silica concentration, and silica surface chemistry.

Materials

Vinyl terminated polydimethylsiloxanes of polydispersity (M_w/M_n) about 2 were used in this study. All the polymers were supplied by Dow Corning (Midland, MI); except for PDMS1 and PDMS5, which were bought from Petrarch. The materials characterization is presented in Table 1.

Fumed silicas with different surface chemical treatments but similar structure and surface area were used in the study. We used an untreated fumed silica (Aerosil 130, Degussa) and different modifications of it [12]. The main characteristics of these silicas are summarized in Table 2. The silica surface treatments (Table 3) were obtained by reacting Aerosil 130 under mild conditions with disilazanes [12,13], except for Aerosil R972 which is a commercial product obtained from the reaction of Aerosil 130 with dichloromethanes.

Preparation of the Suspensions

Silica and PDMS were mixed at room temperature in a Haake Rheomix 600 with a chamber capacity of 60-70 cm^3 using sigma blades at 35 rpm. The master batch (40 phr, parts of silica per hundred parts of polymer) made from Aerosil R972 and PDMS4 was the only one prepared in a Baker Perkins mixer of 1ℓ of capacity (Midland) using helical rollers

(35 rpm). A dough kitchen mixer was used to dilute this master batch to less concentrated suspensions. Table 4 presents the materials used in this study. The procedure followed for compounding was the same for all the materials and was discussed in another publication [12]. Three hours was the total mixing time since first silica addition until unloading of the filled melt. No additives were used to ease the process. From previous results the average size of the aggregates after mixing is estimated as 0.2 μ [12].

Oscillatory Shear Measurements

Experimental

A Rheometrics System IV in dynamic shear mode was used. Since the samples are of relatively high viscosity, no settling problem is present such that parallel plates and cone and plate geometries were used. Some samples were run using both geometries to verify the results. Cone and plate was used only for the low viscosity samples (low molecular weight PDMS or low silica concentrations).

Sample Loading

Before the sample was loaded in the rheometer, we spread it slowly on a watch glass with a spatula for about 1 minute to eliminate air bubbles. Then, we loaded it waiting approximately 20 minutes before beginning the measurements.

The liquid-like samples were loaded onto the lower plate, so that there was more material in the center of the plate than at its borders. Then, when the lower plate is lifted, the first contact of the filled melt with the upper plate is in the center minimizing possible trapping of air between material and plate. Stiffer samples were loaded in a similar way but spreading half of the sample in each plate to improve adhesion of the polymer to the fixture. Considerable time was required to close the gap in the latter cases. Finally, some specimens were given a disk-like shape before being put between the plates.

It took between one to two hours to close the plates down to the desired gap. Some samples required the use of sand blasted plates to avoid slippage during the test. The loading technique seems to be reproducible. However, it must be noticed that sometimes differences of up to 30% were found in the linear viscoelastic region (LVE) between two runs of the same sample, being particularly noticeable in the case of the most concentrated suspensions or those prepared with high molecular weight PDMS. The reproducibility of a

test is affected by the way the material is loaded and the time of rest before the actual test (it could be insufficient for the complete recovery of the stiff specimens)

General Observations

Aging.

Kosinski [14] observed a decrease in the steady shear stress of silicone-silica suspensions with time. This change was more pronounced in concentrated suspensions and at low deformations. Some samples showed a decrease in the modulus of the uncured composites since the time of preparation (ex: 1×10^4 Pa to 5.5×10^3 Pa in one year for PDMS4+R972 (20 phr), LVE region).

When a sample is deformed and then allowed to rest it recovers and becomes stiffer. The aging effect (modulus decrease) occurs in a different time scale. Recovery took place in the order of minutes to days while aging became noticeable after several months. Considering the size of our samples and the number of tests to be run, portions of used uncured samples were stored for future experiments. This was initially thought to be the reason of the measured decrease in modulus, but it was found that this phenomenon was independent of usage and only a function of the storing time after preparation. This aging did not occur in the pure polymer (stored under the same conditions, closed jars at 3°C). Infrared analysis of the dry silicas showed no changes during that time. Aging took place in the composites irrespective of the surface treatment of the silicas or polymer molecular weight. No conclusive reason was found for this observation. The results presented here were taken during the first three months after sample preparation. Samples were allowed to rest at least one week after being prepared.

Test of Geometry Effects.

Figure 1 shows the storage modulus (G') vs % strain for PDMS2+R972 (20 phr) using different geometries. Parallel plates (diam.=25 mm), cone and plate (diam.= 25mm) and parallel plates (diam.= 50mm) were used in those determinations. From the results shown in figure 1, it can be concluded that the geometry does not have a significant effect on the G' curves. The initial run done using small parallel plates was repeated after the other runs to check reproducibility.

Recovery of Uncured Samples

When working with very stiff materials (high silica concentrations and/or high molecular weight PDMS) we observed the appearance of macroscopic cracks in the samples (melt fracture). Healing of a macroscopic crack is not a fast process, thus, these samples showed a very slow and incomplete recovery. This fracture happens only at large deformations (more than 20% but varying with the material). Sometimes the cracks can be seen just by visual inspection in the edges of the material tested (gap were usually kept between 1 and 2 mm) and can be detected by a sudden drop in the modulus (steep slope).

To observe more easily the cracking process, we tested a very stiff sample: PDMS1+A130 (20 phr). Figure 2 shows a schematic diagram of the different steps involved in the development of the cracks:

a) At deformations lower than 10% strain, the sample was unchanged as the material followed the motion imposed by the upper plate.

b) At about 10% strain no changes were easily detected in the movement of the material, but the border of the sample began to slightly change its shape.

c) A plane in the interior of the gap began to be visible. The upper part of the material accompanied the movement of the upper plate, but the lower part of the sample seemed to have slowed down. Some lines or fine cracks also appeared in the lower part. The regions that became enclosed by those lines appeared almost immobile.

d) Because of the faster or slower movements of the different regions of the material the lines became wider and were easily visible. At this final stage (about 60-80% strain), material was partially expelled from the plates as torn off chips.

e) The sample could be taken out of the plates without too much extra deformation (since it was very stiff to begin with). The specimen showed cracks all along the edges, but not in the center where the strain and the torque were smaller.

There is a macroscopic separation of the material in such a cracking process and to heal the cracks the material should flow to close them. Crack formation in the case described above was practically irreversible, because the material was too stiff to flow without an applied external force.

A sample of PDMS3+R972 (20 phr) was tested. First a strain sweep up to 100% strain at 50 rad/s was done (G'_{LVE} = 41,900 Pa), and then the sample was left to rest. Recovery was measured at different intervals by recording G' at low strain (LVE) at the frequency of the previous test for about 3 to 5 minutes each time. The sample recovered in 22 hours. There was an initial fast recovery in which the sample reached 34% of the original modulus (G'_{LVE} = 14,200 Pa) in about 5 minutes and recovered 52% after 20 minutes (G'_{LVE} =

22,000 Pa). Residual recovery was extremely slow. Suspecting some cracking here too (though so small that could not be seen directly), we reduced the gap immediately after another sweep up to large strain measuring a 83% recovery of the original G' in 24 minutes (G'_{LVE} = 34,600 Pa). By reducing the gap the damaged (cracked) part of the sample is expelled outside the plates and it is eliminated before next test. By doing this, one may completely get rid of the cracks depending on the extent of the cracks and how much the gap is reduced. Finally, we repeated the strain sweep up to large strains, opened the plates and spread the material again. Then, we closed the plates and measured the modulus after 15 min. A complete recovery was obtained this time (Figure 3).

These results point out that an extremely slow recovery after a large deformation may be due to macroscopic crack formation in the sample, and not to the process of microscopic recovery that one is usually trying to measure. One possible way to test the latter would be to do the experiments twice, changing the gap in one of them after the large deformation test and noting if this changes the measured modulus.

Equilibrium Modulus

We tried to use dynamic measurements to obtain $G_{equilibrium} = G(t\rightarrow\infty) = G'(\omega\rightarrow 0)$. However, we found problems using frequency sweeps because the measurements became noisy at low frequencies. The usual solution to this problem is to work at higher temperatures and then use the time temperature superposition principle, but new complications appeared when attempting to use this approach. Since the polymer behavior changes very little with temperature, no new information was obtained with mild increments in temperature. Once the sample was heated to 153°C, irreversible changes took place. The material was cooled down to the initial temperature (26°C) and re-tested. The change in modulus was permanent indicating that some reaction had taken place (Figure 4.a). The same test was performed on the pure polymer. No change was observed in this case (Figure 4.b). A "grafting" reaction involving the silanols of the silica and the backbone of the PDMS was discussed by Berrod et al [10], and it is probably responsible for the observed changes. Our observations are in agreement with their report that the reaction occurs at temperatures on the order of 150°C and above. Figure 4.a. also reveals that the curves at 26°C < T < 110°C differ only in a horizontal shift, that is, time temperature superposition holds in this temperature range. Failure at higher temperatures is due to chemical change of the material. As a result of this chemical modification, we were unable to reach temperatures high enough to obtain information on $G_{equilibrium}$ for the uncured materials.

Results

The samples studied include filled and unfilled uncured materials. The results reported here were obtained at temperatures between 26°C and 30°C unless otherwise indicated.

Uncured Samples

To have a base for comparison when discussing the effects of the reinforcing filler we will present first the behavior of the pure polymer.

Pure PDMS: The strain sweeps of the pure polymers shows (Figure 5.a) that the modulus is strain independent at least in the range of strains covered, 1-100%, except for PDMS1. The drop in the modulus curve for the latter above 30% strain could be due to thinning behavior or to the beginning of edge failure in the sample. There is noise at low strains in G' for PDMS3.

Frequency sweeps for the same samples at 30 °C show only the terminal region. All the materials behave like liquids at room temperature and only the high molecular weight PDMS shows a small part of the entanglement plateau (Figure 5.b).

Composites

Effect of Silica Concentration: We will analyze the behavior of one of the composites, the results obtained for other samples are qualitatively similar.

The first group of samples to be discussed are those made from Aerosil R972 (low concentration of surface silanols) and PDMS4 (mixture of PDMS2 and PDMS3). The concentrations of silica were varied from 0.5 to 30 phr or expressed in volume fractions, 0.002 to 0.12. These volume fractions are based on the density of the polymer and the fumed silica and represent the volume that the silica would occupy if it were a compacted material. The effective volume is much larger due to the open structure of the aggregates.

The behavior of the composites (Figure 6) is very different from the response of the pure polymers. The samples have a large modulus at low strains. The range of LVE is very short, lower than 1 % strain in concentrated samples. At that point the modulus drops until finally at strains close to 100 %, the G' curves seem to be reaching a lower plateau. The value of the critical strain (γ_c) at which the linear viscoelastic region ends was calculated according to three methods described below:

1. Drawing lines tangent to the modulus curve in the LVE region and in the region were the modulus drops. The intersection of the two lines is considered as the critical strain.
2. Obtaining the derivative of the curve G' vs. % strain and assigning the value of the strain where the derivative has a maximum to γ_c.
3. Defining γ_c as the strain at which the modulus is 90 % of $G'_{(LVE)}$.

In all cases we saw a shift of the critical strain towards lower values as the silica concentration increases (Table 5).

Figure 7 shows G" vs strain for the same set of composites (PDMS4+Aerosil R972). The curves look very similar to G' vs strain %. At large strains G" is always larger than G' as it could be expected for a liquid sample. However, at low strains G", is lower than G' for the 20 phr and the 30 phr composites, the materials present a large elastic contribution to the modulus giving a solid-like response at the frequency of the test.

The behavior of these materials during a frequency sweep is shown in Figure 8. The strain used was in the LVE region for each sample. The most concentrated sample (30 phr) shows that the modulus is only slightly dependent on the frequency and the curve looks very similar to that of a crosslinked network. At lower concentrations the curves becomes less flat but still show a "plateau" (10-20 phr) which appears to drop near 0.01 rad/s. The measurements became noisy in that region because of the resolution of the apparatus. Thus, it is difficult to determine if the equilibrium modulus is equal to or higher than zero for the concentrated samples.

Effect of the Silica Surface Chemistry: Let us consider first the composites prepared from PDMS4 and different silicas at a constant load of 20 phr (8.1 % by volume). Figure 9 shows the results of the strain sweeps for these samples. Aerosil 130 is an untreated silica, Aerosil R972 is partially treated and Modified Silica 1 is completely treated (Table 2). Comparatively to the modulus (G'_{LVE}) of the composite obtained from Modified Silica 1, the one prepared with Aerosil R972 has a modulus ten times larger and the modulus of the composite made from Aerosil 130 is about 300 times larger. One can clearly see how important the concentration of isolated OH on the silica surface is. Figure 10 shows G" vs strain for these same samples. For the methylated silica and the Aerosil R972 suspensions, G" has a constant value at low strains and then drops, similarly to the G' behavior. However, PDMS4+A130 (20 phr) shows a very clear peak in G", which appears at the end of the LVE region. This maximum in G", which appeared only when working with the untreated silica, may be related to strong agglomeration. Similar feature was shown by

Payne and Whittaker [23] in carbon black filled vulcanized natural rubber. In that case, the peak became more intense with increasing carbon black concentration and degree of crosslinking.

Figure 11 shows the frequency sweep of composites made from PDMS2 and different silicas. The results obtained using Modified Silica 1 and Modified Silica 2 that have the same degree of treatment (all free silanols are reacted) are almost identical.

Effect of the PDMS Molecular Weight: The strain sweep at 50 rad/s of some composites made from Modified Silica 1 (Figure 12) shows that the higher the molecular weight of the polymer the higher the modulus of the composite. However, the picture is not so clear when the results of the frequency sweep are considered (Figure 13). At high frequency the high molecular weight suspensions give higher modulus but at lower frequencies this trend is reversed. The composites made from lower molecular weight polymers show flatter G' vs ω curves than the high molecular weight composites. This difference will be discussed in detail in a separate section.

Discussion

Model: Physical Picture

Adsorption of PDMS on silica was discussed in another article [12], it was reported there that no isolated silanols are left on the silica surface after PDMS adsorption (FTIR), being the bound rubber strongly dependent on the polymer molecular weight and silanol concentration on the silica. We include the bound rubber results here (Table 6), since they are pertinent to this discussion. Based on these observations, we proposed that the silica aggregates are well surrounded by polymer. Furthermore, direct contact between aggregates is not very probable, at least at the concentrations studied. This reasoning leaded us to the conclusion that agglomeration (clustering of aggregates) must be due to linking of the aggregates by the polymer. It is only natural to think that at some critical concentration one cluster will span the whole sample and a physical network will be established. Its formation can be thought as that of a chemical network that evolves from a previous formation of microgels. These physical "microgels" are much larger than those formed chemically in covalent networks and are clusters of aggregates and polymer. The formation of separate clusters is possible even at small concentrations of silica because of the random location of the aggregates and the microscopic heterogeneity of these

mechanically mixed composites. Some aggregates are very close to one another and the polymer can bridge them, while some other aggregates are so far apart from one another that they can not be linked.

Different types of filler-polymer-filler linkages are possible. Figure 14 shows a schematic diagram (not to scale) of the linkages:

a) direct bridging, a chain is adsorbed to two different aggregates,

b) bridging due to entanglement of two chains adsorbed to two different aggregates.

c) bridging due to entanglements of free chains.

All of these types of linkages will effectively increase the modulus of the composite, however types (a) and (b) will also change the qualitative behavior of the uncured rubbers. Because adsorbed chains have reduced mobility their, maximum relaxation time is larger than that of a bulk (non-adsorbed) chain. Thus, the lifetime of bridges of type (a) and (b) is larger than that of bridges type (c). These features alter the response of the material at longer times in a stress relaxation test or at low frequencies in dynamic tests.

The aggregates are polydisperse in size, their size distribution shows a long tail towards the large aggregates which could have an effect on the rheological behavior of the composites. The small aggregates may also strongly affect the behavior since they can act as intermediaries in the polymer bridging of larger aggregates or become the center of a "star" or "microgel". The mobility of these stars would be very low.

A similar model was proposed by Kosinski and Caruthers [15]. Their study was on the steady shear response of suspensions of fumed silicas in PDMS of different molecular weights. They worked with relatively low silica concentrations (1-10 wt%, that is up to about 11 phr). Their model differs from ours mainly in that it does not include direct bridging chains. They focused their attention on the effect of the previous history of deformation on the material response. Some of their stiff samples required times of recovery after continuous shear of the order of one week. These long recoveries may have been the result of melt fracture, especially after continuous shear, as it was observed in our samples after large deformations.

Chahal and St Pierre [7] proposed that the interparticle linkages in silica-silicone composites were due to direct filler-filler contacts or to polymer chains linking the aggregates through entanglements. In this last type of linkages, they distinguished the three types of binding chains described in our physical picture. We think that direct contact aggregate-aggregate is possible at very high silica concentrations (larger than those used in this work) or if there is incomplete dispersion of the filler into the polymer. Since this

would imply incomplete wetting of the filler by the polymer, extensive direct contacts would produce a drop in material properties.

Cohen-Addad et al. studied the adsorption of PDMS chains onto fumed silicas, the composites being prepared by mechanical mixing [9,10]. From the results of bound rubber and swelling experiments, he developed the idea of the presence of binding chains (direct bridging between aggregates). He did a rather crude calculation of the probability of this kind of chains to occur [10]. These calculations lead him to believe that, for a PDMS of $Mn \geq 10^5$ and silica concentrations ≥40 phr, there is a network formed by the aggregates and these bridging chains. Because he did not considered the random location of the aggregates, his is a conservative estimation of the requirements for "network" formation. We have observed that pieces of the uncured material PDMS1+A130 (20 phr) can be swollen, dried and then re-swollen without changing shape. The bridging chains are also present in the formation of clusters of varied sizes even at lower silica concentrations and/or lower PDMS molecular weights.

To verify the validity of the physical picture presented here, we will analyze our experimental results in the frame of this proposed model.

Analysis of the tests on the uncured filled samples:

Frequency Sweeps: From the dynamic results, the relaxation behavior of the sample after a sudden applied strain can be calculated [22]. A comparison between measured and calculated G(t) was done for the composite PDMS4+A130 at 10 phr and 20 phr and we found them in good agreement, being the calculation less noisy at very short times. A qualitative analysis will be done in terms of time or frequency ($t \sim 1/\omega$).

If the connection between aggregates were only through entanglements of free chains, the relaxation times of the linking chains would be the same as those of the pure polymer. The modulus of the composite would be larger than that of the unfilled PDMS but both materials would have essentially the same relaxation spectrum, the only difference given by the adsorbed chains, which represent a small percentage of the polymer (on the order of 10% or less, [12]). The possibility of bridging formation (directly or through entanglement of adsorbed chains) with the consequent agglomeration or even physical network formation increases the value of the modulus, but also changes qualitatively the long time response of the materials (low frequencies). This idea is sketched in Figure 15.

Strains Sweeps: As the strain increases so does the separation between initially close aggregates. At small strains, direct bridges and entanglements are present giving the sample a high G'. At some critical strain (a function of the molecular weight, silica concentration, surface chemistry of the silica, and frequency of the measurement), the separation between the initially linked aggregates becomes so big that the bridges are broken and the modulus begins to drop. During the test new entanglements can be formed, but formation of direct bridges and entanglements of adsorbed chains are reformed more slowly. Under the applied deformation, the adsorbed chains will tend to collapse on the surface of the silica to accompany the movement of the aggregate. At still larger strains the agglomeration is broken down, so that individual aggregates or small agglomerates are possible with "brushes" of polymer coming out from their surface. At this stage another plateau is reached and no more deagglomeration occurs.

Silica Concentration: When the silica concentration increases, so it does the number of bridges between aggregates. Since the aggregates are closer to one another, it is more probable for a given chain to form a bridge. Above some threshold concentration a "network" exists at low strains. If the material is subjected to small deformations under those conditions, the bridges will hold and we observe a linear viscoelastic response (constant modulus). This region is however very short because larger deformations result in the breakage of some bridges or desorption or disentanglement of linking chains. A more rigid network breaks at smaller strains, thus this model would indicate that the critical strain, γ_c, decreases with increasing concentrations of silica (shown in Table 5). If the agglomeration-deagglomeration process is due to the polymer one would expect γ_c to depend on the frequency and to decrease with increasing frequency of the test. This will be discussed in a following section.

Silica Surface Chemistry: No appreciable difference was found between composites prepared with Modified Silica 1 (methyl groups) and Modified Silica 2 (methyl and vinyl groups), both with complete treatment. In the uncured state, the main difference introduced by the surface chemistry is due to the presence of OH groups in the silica.

A silica with a higher concentration of hydroxyl groups adsorbs more polymer chains more strongly, this enables the formation of more bridges between aggregates and a final composite of higher modulus. This agrees with the experimental results of bound rubber, shown in Table 6 and rheological tests shown in Figure 11.

PDMS Molecular Weight (large MW): The higher the molecular weight, the more linkages are possible and so the higher it is the modulus of the material.

The strain sweeps showed that the higher the molecular weight of the polymer the higher the modulus especially in the linear viscoelastic region, also γ_c shifts to larger strains. The frequency sweeps have a similar shape for the composites made of PDMS with molecular weights larger than Men (Figure 13), the differences with composites made from low molecular weight PDMS will be discussed separately.

Low Molecular Weight Composites

Results

Flow Behavior: One observation of the differences of the low molecular weight composites was obtained using a very simple qualitative test. A piece of 0.1 ml of uncured material was deposited on a plain glass surface (extruded from a plastic syringe with the tip cut). Half an hour later the glass was put in vertical position and the flow of the material was observed during one week. At concentrations of 20 phr of Aerosil R972, the suspension made from PDMS3 flows much easier through the syringe (about 3 mm of diameter) than the other samples. Once on the glass, however, the composite made from PDMS2 supports less its own weight than that made from PDMS3.

Rheology: Most of the strain sweeps obtained in this work were done at a frequency of 50 rad/s. At that high frequency, the PDMS2+R972 (20 phr) and PDMS3+R972 (20 phr) composite had about the same modulus value. The frequency sweeps show a complex picture (Figure 16). Composites made from PDMS1 and PDMS2 ($M_w \geq M_{en}$) show a similar behavior, a similar shape of G' vs ω, and so does the one made from PDMS4. However, samples made from PDMS3 and PDMS5 (both with $M_w \leq M_{en}$) show flatter curves that even cross over the high molecular weight G' curves. Notice that the same behavior was also seen in composites made with other silicas (Figure 13).

We decided to further investigate these differences in response with respect to frequency. We did strain sweeps on a single sample at different frequencies for two composites of different molecular weight. Figures 17 a and 17 b show the results obtained for the composites PDMS2+R972 (20 phr) and PDMS3+R972 (20 phr).

PDMS2+R972 (20 phr): The modulus shows a strong dependence on the frequency of the test at high and low strains. The critical strain, γ_c, shifts to larger strains for lower frequencies.

PDMS3+R972 (20 phr): The modulus does not depend strongly on the frequency of the test, lower frequencies were not used because of the decreasing resolution of the measurement. The curves superimpose completely at large deformations, the results obtained at the two higher frequencies are almost identical (considering experimental error), and the critical strain, γ_c, changes only slightly with the frequency. The critical strains for both materials are plotted in Figure 18.

Discussion

The contribution of entanglements and of polymer bridging cannot explain the experimental frequency behavior of the composites made from PDMS3 and PDMS5.

In a sample where the physical connections between aggregates are due to the polymer one would expect a rheological behavior controlled by the polymer response. At large silica concentrations and small deformations the material response should be that of a "viscoelastic network", that is, there should be a strong dependence of G' with the frequency. This was in fact, observed when using PDMS2 (Figure 17 a) and these features are contained in the model.

In a sample where connection between aggregates is due to the filler-filler links or where there is mechanical interlocking of the aggregates, the material behavior should be controlled mainly by the filler response. One would expect an "elastic network" response, that is, G' essentially independent of the frequency of the test. Again, this is what we observed in the response of the low molecular weight composites (Figure 17 b). Our model does not consider this behavior, which should be similar to that of regular suspensions in small molecule solvents.

This difference in frequency dependence is very important in the understanding of the system and in the formulation of a model. It indicates that the relative importance of the forces involved in the agglomeration and reinforcement of a composite change at some critical molecular weight of the polymer, probably at the critical molecular weight for entanglements (M_{en} = 22500 for PDMS [16]). Thus, the conclusions obtained from studies of suspensions prepared with low molecular weight analogs of the polymer are useful to determine the chemical affinity of the surface for the polymer. However, these

studies should not be the sole source of information to determine the forces that lead to agglomeration in polymeric suspensions.

Concentrated suspensions prepared with low molecular weight solvents, but where the filler particles have been coated with high molecular weight polymer (adsorbed or grafted) show some of the characteristics seen in the filled melts. Important elastic contributions (infinite viscosity at low stresses, low frequency plateau [17], bridging chains [18]) appear even at low filler concentrations, when the polymer layers begin to overlap.

In the case of the PDMS3+R972 (20 phr) suspension, the chains are so short ($\sqrt{\overline{r^2}} = 0.073\sqrt{M} = 9.38$ nm [19], using $M = M_w = 16{,}500$) that they are adsorbed forming short or not tails at all (spreading flat onto the surface). This would allow neighbor aggregates to be much closer to each other than in suspensions of higher molecular weight polymers and thus, transitions such as γ_c become more sharp (Figure 17.b). The same effect was seen in composites prepared with silicas of different surface treatment, which tell us that this is an effect that depends quantitatively only on the OH concentration of the silica surface. The negligible frequency dependence of the low molecular weight composites can be explained by the absence of entanglements and long tails in the adsorbed layer and thus the reduced filler-polymer-filler connections in the uncured state.

The crossover of the $G'_{low\ MW}$ and $G'_{high\ MW}$, which would lead, presumably, to a higher $G_{equilibrium}$ for the lower molecular weight composite could be due to a difference in the degree of silica dispersion or to different final size of the aggregates after compounding. The first reason would require the formation of chain like agglomerates of very open structure in the low molecular weight composites, so that the percolation threshold occurs at a lower silica concentration than in the high molecular weight composites. The second reason was tested using SEM of the silica aggregates after compounding, free polymer extraction and subsequent dilution. The micrographs did not show an appreciable difference between the samples obtained from different molecular weights composites.

Kosinski and Caruthers [15] also studied the effect of molecular weight in silica-silicone suspensions. They found that composites prepared with low molecular weight PDMS ($M_w \leq M_{en}$) do not show stress growth maxima under constant shear and that the transient response is independent on the previous deformation history. Molecular weights close or immediately above M_{en} showed both features and finally, high molecular weight composites showed little dependence on the previous history.

Summary and Conclusions

We have reviewed the rheological behavior of silica-PDMS suspensions. Since melt fracture can occur in uncured samples and recovery can be drastically slowed down, extreme care should be taken in the interpretation of recovery results. All the filled materials used here showed aging. This was a very slow process that was detected only several months after sample preparation.

We studied the effect of silica concentration, surface treatment, and polymer molecular weight on the rheological behavior of the samples. A summary of the experimental observations is included below:

1. Silica Concentration:

The addition of silica to the polymer increases its modulus, especially at small deformations. The extension of the linear viscoelastic region decreases with increasing silica concentration. These facts are also affected by the agglomeration of filler, which increases with silica concentration.

2. Agglomeration (secondary structure):

There is an extensive agglomeration when the sample is at rest. At some critical silica concentration there exists a large agglomerate that spans the whole sample. The transition (percolation) is not clear in the silica-polydimethylsiloxane suspensions. The fact that some of the samples do not flow unless an external force is applied is the result of such extensive agglomeration.

3. Silica surface treatment:

In the uncured state, the main factor that modifies the behavior of the filled material is the silanol concentration on the surface of the silica: the higher the silanol concentration the higher the modulus.

4. Polymer molecular weight:

In composites made from polymers of molecular weight larger than M_{en}, it was observed that the larger the molecular weight the larger the modulus of the sample.

A physical model was proposed that takes into account these observations. A diagram including the different types of possible filler-polymer-filler linkages was presented (Figure 14). It is proposed that the forces exerted between aggregates are mainly due to the polymer bonding. This model can explain the larger amount of bound rubber found for higher molecular weight PDMS or silicas with higher OH concentrations [6]. It also can explain the change in the relaxation spectrum of the material. The model was successfully

used to analyze the rheological results of composites made from PDMS with $M_w \geq M_{en}$, but cannot explain the frequency dependence of the low molecular weight uncured composites. The different behavior of low molecular weight was explained as the result of very short tails on the surface of the filler and a negligible concentration of entanglements in the bulk and adsorbed layer. It was pointed out that, for this same reason, the conclusions obtained from suspensions prepared with low molecular weight analogs are valid only to predict specific interactions (chemical, H-bonding, etc.) between silica and polymer. They should not be used to predict the forces between the aggregates, because the important contribution of the entanglements in the polymer and tails on the silica surface are not present when dealing with low molecular weight solvents. The present model is then, useful to understand the rheology of large molecular weight filled melts, typically found in the rubber industry.

Acknowledgements

The authors thank the Office of Naval Research, Grant N00014-88-K-0366 and also Dow Corning (Midland) for the grant and for providing the materials used for this work. Thanks are also due to Degussa for supplying the fumed silicas. Special thanks are given to Dr. John Saam for his suggestions and for valuable discussions. M.I. Aranguren also thanks CONICET for the fellowship that supported her stay in the USA.

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Table 1

Molecular Weights and Polydispersity of the Polydimethylsiloxanes

	M_n	M_w	M_w/M_n
PDMS1[a]	146,000	325,000	2.2
PDMS2[b]	66,400	118,000	1.8
PDMS3[b]	8,900	16,500	1.9
PDMS4[c]	22,600	87,600	3.9
PDMS5	2,000(nominal)		

a. Measured in our laboratories, Waters GPC model 150-C ALC/GPC (1% solution in THF).

b These values were obtained using a PDMS calibration by the Dow Corning laboratories (Midland).

c A mixture of PDMS2 and PDMS3, 70:30 wt % respectively.

Table 2

Characterization of the Fumed Silicas

	BET surface (m^2/g)[a]	% hydroxyl treated[b]	Type of treatment
Aerosil 130 (A130)	133	0	None
Aerosil R972 (R972)	108	10 (30[c])	Dimethyldichlorosilane
Modified Silica 1 (MS1)	112	100	Hexamethyldisilazane
Modified Silica 2 (MS2)	114	100	Divinyltetramethyldisilazane (67wt%) + Hexamethyldisilazane (33wt%)
Modified Silica 3 (MS3)		100	Divinyltetramethyldisilazane

a. Measured by Micromeritics, Inc.
b. Measured by methyl red adsorption [12, 20].
c. From Degussa catalog [21].

Note: The base product for all the treated silicas was Aerosil 130.

Table 3

Recipe for the Silica Surface Treatment

Silica (Aerosil 130) =	50 g
Solvent (Toluene) =	400 ml (grade A.C.S.)
Modified Silica 1:	4 g hexamethyldisilazane (Petrarch, purity 99.6%)
Modified Silica 2:	2.75 g hexamethyldisilazane 1.25 g divinyl tetramethyldisilazane
Modified Silica 3:	4 g divinyl tetramethyldisilazane (Petrarch, purity 98.2%)

Table 4

Materials Used in This Study

	Aerosil 130	Aerosil R972	Modified Silica 1	Modified Silica 2	Modified Silica 3
PDMS1	X	X	X	0	0
PDMS2	0	X	X	X	X
PDMS3	X	X	X	X	X
PDMS4	X	X	X	0	0

The cross means that the composite was prepared, the oval means that it was not. The table does not present the different silica concentrations prepared (in the range of 0-40 phr).

Table 5

Critical strain* as a function of the silica concentration

parts per hundred	1	5	10	20	30
method (1)	11	5	2.7	1.1	0.7
method (2)	4	3.5	2.8	0.8	~0.3
method (3)	13	3.2	2.4	0.9	0.4

* measured at ω=50 rad/s

Table 6

Bound Rubber Expressed as Mass of Adsorbed PDMS/ Mass of Silica

	PDMS M_w			
	16,500	87,600	118,000	325,000
Aerosil 130	0.196 (0.257)	0.653 (0.626)	-----	1.610 (1.613)
Aerosil R972	0.055 (0.064)	0.283 (0.20)	0.216 (0.22)	0.871 (0.837)
Modif. Silica 1	-------	-------	0.151 (~ 0)	-------
Modif. Silica 2	-------	-------	0.167 (~ 0)	-------

- The bound rubber was calculated from the C analysis (MHW Laboratories) of the original silicas and silicas +bound rubber.
- The numbers in parenthesis were obtained in our laboratory from the weight of the silica with adsorbed PDMS after extraction of the free polymer and the amount of silica in the initial sample calculated from the known silica concentration.

Figure 1. Strain sweep of the composite PDMS2+R972 (20 phr) using different geometries: .▲..parallel plates (ϕ=25 mm, gap=1.7 mm), ◇ cone and plate (ϕ=25 mm, β=0.1 rad),○ parallel plates (ϕ=50 mm, gap=1.15), ▽ parallel plates (ϕ=25 mm, gap=1.65 mm).

Figure 2. Development of cracks in the edges of a very stiff sample during a dynamic test. Lines in the samples in a, b, c and d indicate the relative displacement of the upper and lower parts of the sample. a- Sample just loaded. b- Slight edge effect begins at about 10 % strain. c and d- Formation of a crack and immobilized zone (60-80 % strain).
e- Sample at the end of the test.

Figure 3. Recovery of PDMS3+R972 (20 phr) after a strain sweep up to large deformations. Dashed line indicates the original value of the modulus of the composite in the linear viscoelastic region. ▫ Recovery without gap closing. ◆ Gap reduced from 1 to 0.88 mm after a strain sweep up to large deformations. ◇ Gap opened and closed back down to 0.81 mm after a strain sweep up to large deformations.

Figure 4.a. Frequency sweep at increasing temperatures on the composite PDMS1+R972 (20 phr). The final run shows that irreversible changes occured in the material when subjected at 153°C.

Figure 4.b. Frequency sweep at increasing temperatures using unfilled PDMS1. The final curve shows that the material was not affected by high temperatures.

Figure 5.a. Strain sweep for pure polydimethylsiloxanes (ω= 50 rad/s).

Figure 5.b. Frequency sweep for pure polydimethylsiloxanes (% strain =10)

Figure 6. Strain sweep of the composites made of PDMS4 and Aerosil R972. Silica concentrations are given in phr (parts of silica per hundred parts of polymer) and percentage by volume.

Figure 7. Loss moduli of the composites made of PDMS4 and Aerosil R972 (strain sweep at ω=50 rad/s).

Figure 8. Frequency sweep on the composites made of PDMS4 and Aerosil R972 (the % strain was chosen within the LVE region of each material).

Figure 9. Effect of the silica surface chemistry: Strain sweep (G' vs. %strain) of composites prepared from PDMS4. All the filled samples contain 20 phr of silica. The surface OH concentration on the silicas increases upwards.

Figure 10. Strain sweep (G" vs. strain) of composites made from PDMS4. The figure shows G" for the same materials used in Figure 9.

Figure 11. Frequency sweep of composites prepared from PDMS2. Filled materials contain 20 phr of silica.

Figure 12. Strain sweep (G' vs. % strain) of the composites containing 20 phr of Modified Silica 1 (ω= 50 rad/s)

Figure 13. Frequency sweep of composites prepared from Modified Silica 1 and different molecular weight polydimethylsiloxanes. See that the trend in the curves is different for the low molecular weight PDMS.

Figure 14. Schematic diagram of the different types of contact filler-polymer-filler that would lead to agglomeration of individual aggregates. Each groups of particles in the diagram represents an aggregate (primary structure in the rubber). The drawing is not done to scale. The number of particles per aggregate is much larger than what it is shown here. a) Direct bridging, b) bridging by entanglement of adsorbed chains, c) bridging by entanglement of non-adsorbed chains.

Figure 15. Schematic diagram showing (a) a summary of experimental results, (b) the effect of aggiomeration due to entanglements of non-adsorbed chains and (c) agglomeration due to direct bridging and/or entanglements of adsorbed chains.

Figure 16. Frequency sweep of composites containing 20 phr of Aerosil R972 and different molecular weight polydimethylsiloxanes. Dashed curves correspond to the regular results obtained for high molecular weight PDMS. Not-connected points correspond to anomalous results obtained for low molecular weight matrices. Compare to Figure 13.

Figure 17.a. Strain sweep of PDMS2+R972 (20 phr) at different frequencies.

Figure 17.b. Strain sweep of PDMS3+R972 (20 phr) at different frequencies.

Figure 18. Critical strain, γ_c, vs frequency for the composites PDMS2+R972 (20 phr) and PDMS3+R972 (20 phr).

Fig. 1

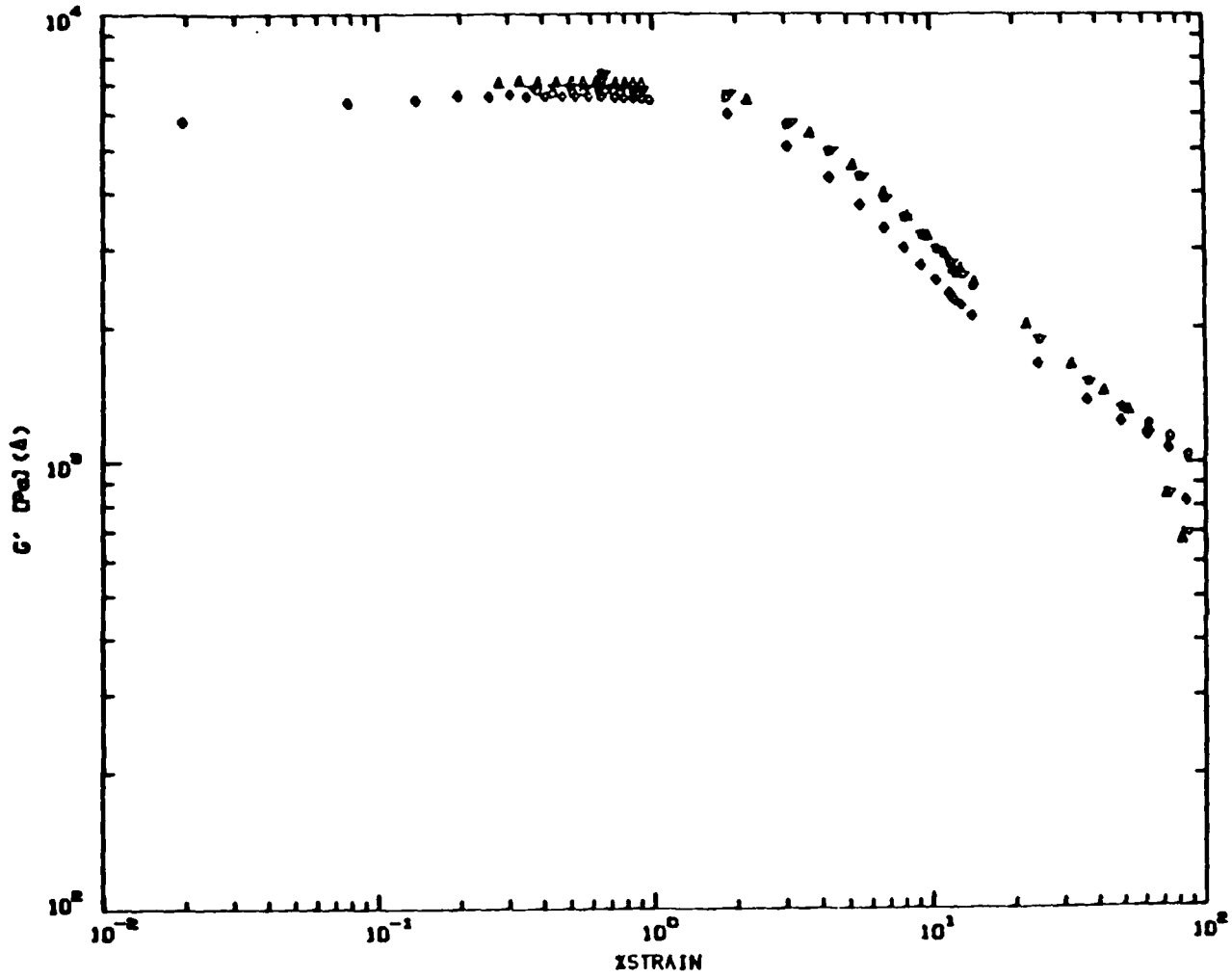


Figure 2.

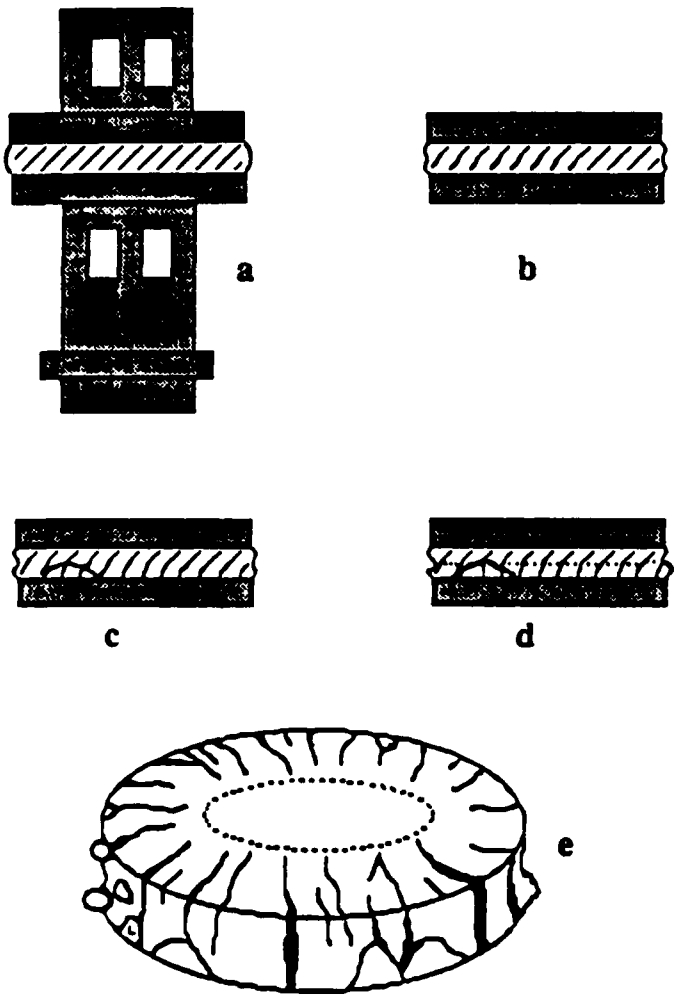


Figure 3

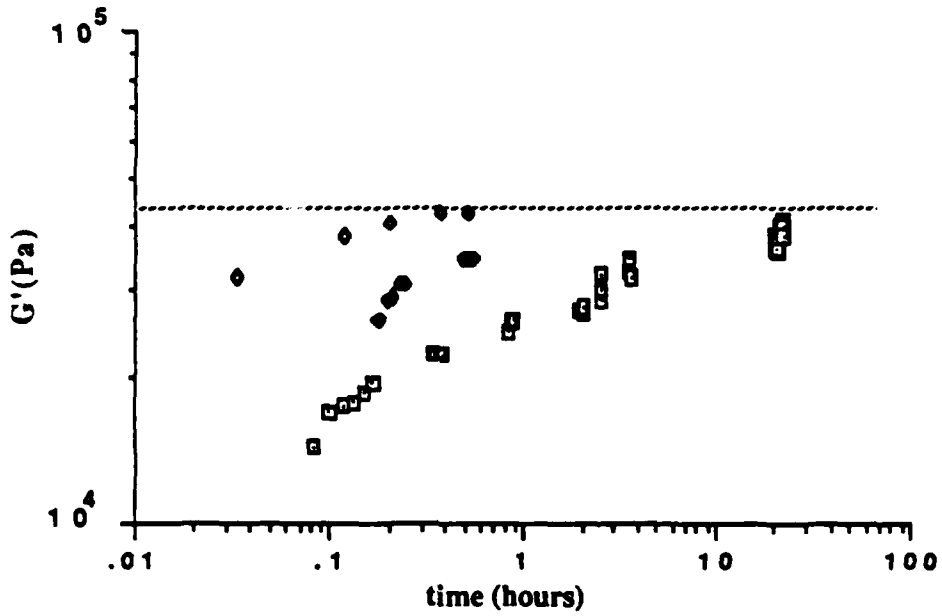
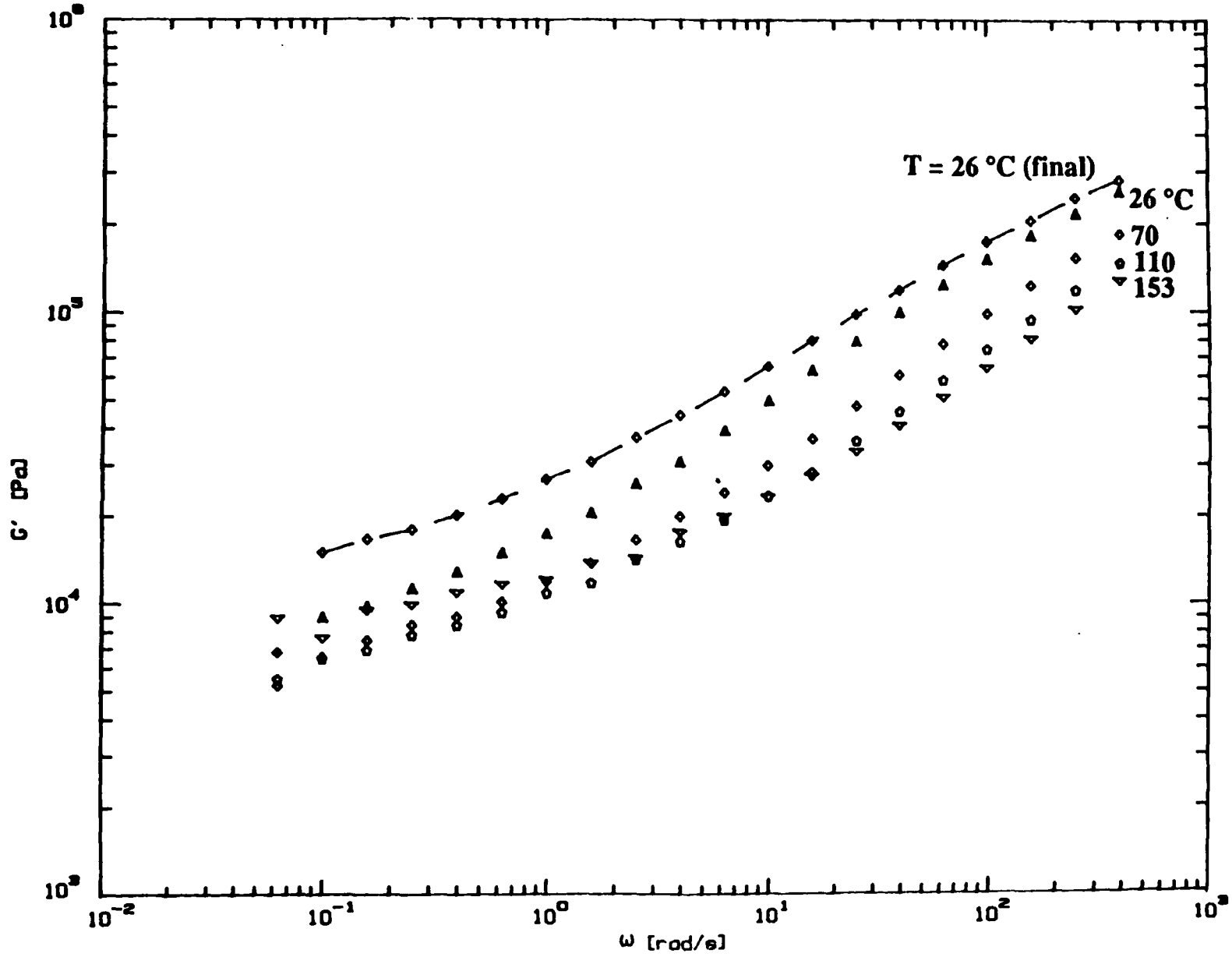


Figure 4a.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26 °C
70
110
153
G' [Pa]
ω [rad/s]
10^{6}
10^{5}
10^{4}
10^{3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}

Figure 4.b.

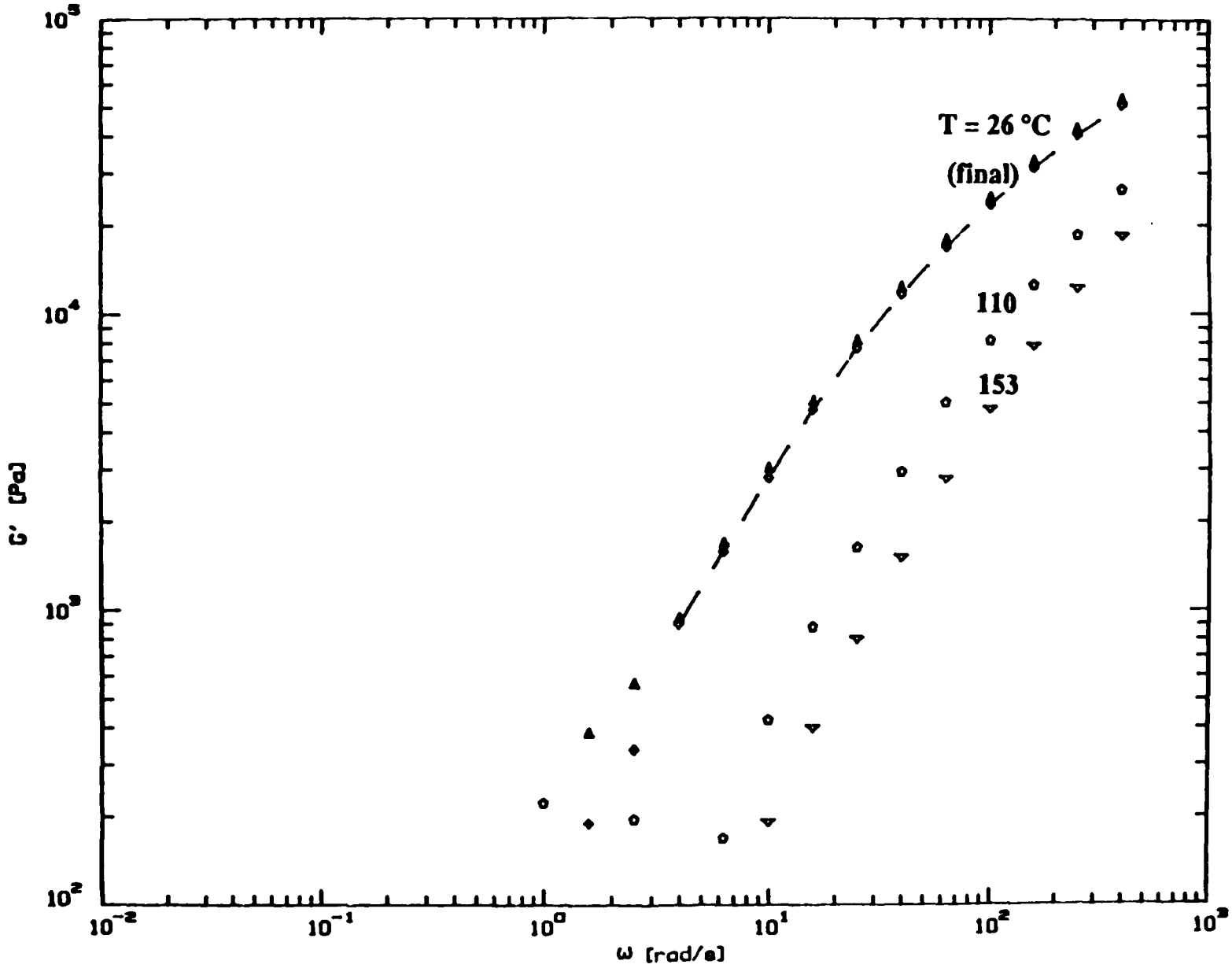

T = 26 °C
(final)
110
153
G' [Pa]
ω [rad/s]
10^5
10^4
10^3
10^2
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3

Figure 5.a

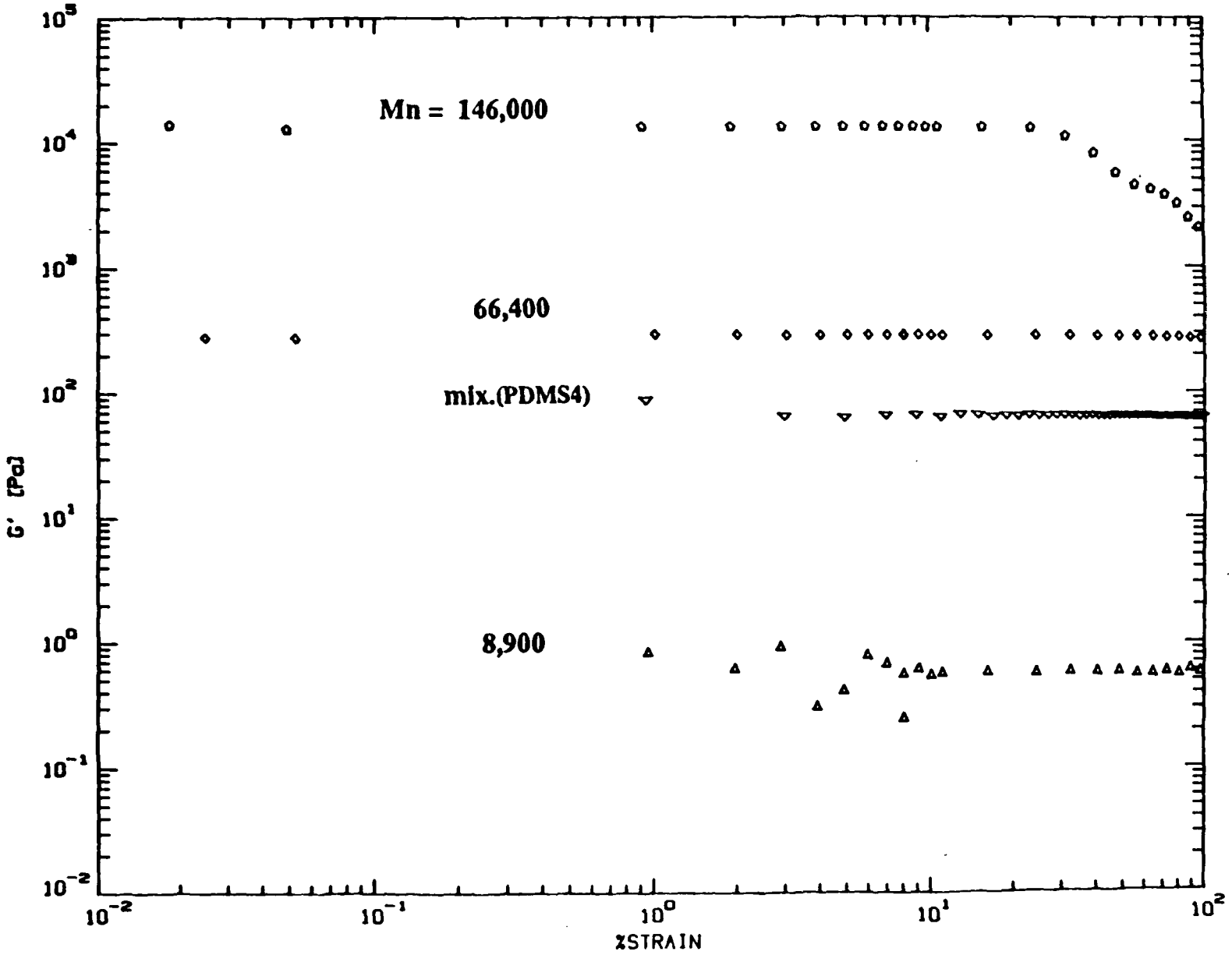
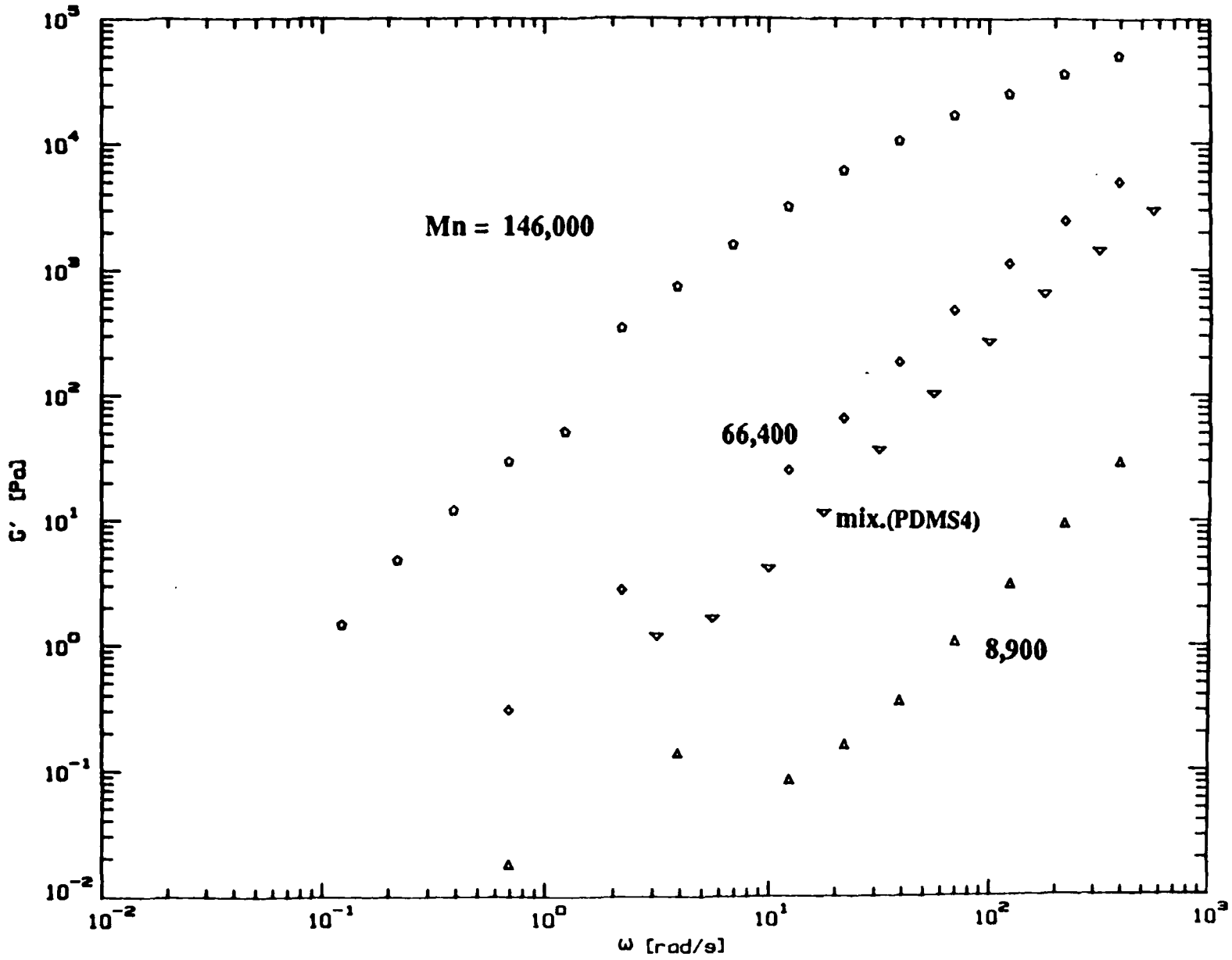

Mn = 146,000
66,400
mix.(PDMS4)
8,900
G' [Pa]
%STRAIN
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-2}
10^{-1}
10^0
10^1
10^2

Figure 5.b.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mix.(PDMS4)
8,900
G' [Pa]
ω [rad/s]
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10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}

Figure 6.

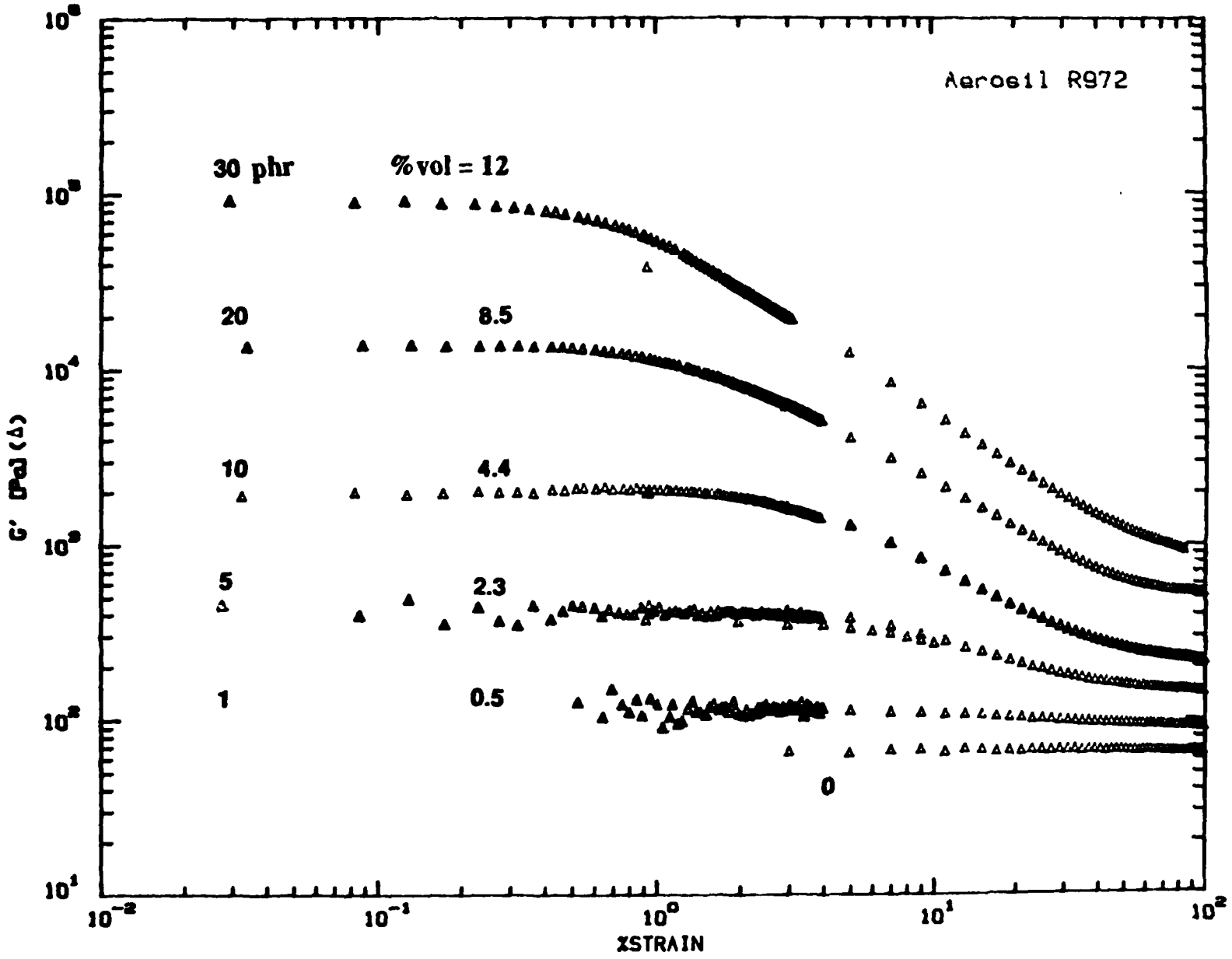

Aerosil R972
30 phr
%vol = 12
20
8.5
10
4.4
5
2.3
1
0.5
0
G' [Pa] (Δ)
%STRAIN
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}

Figure 7

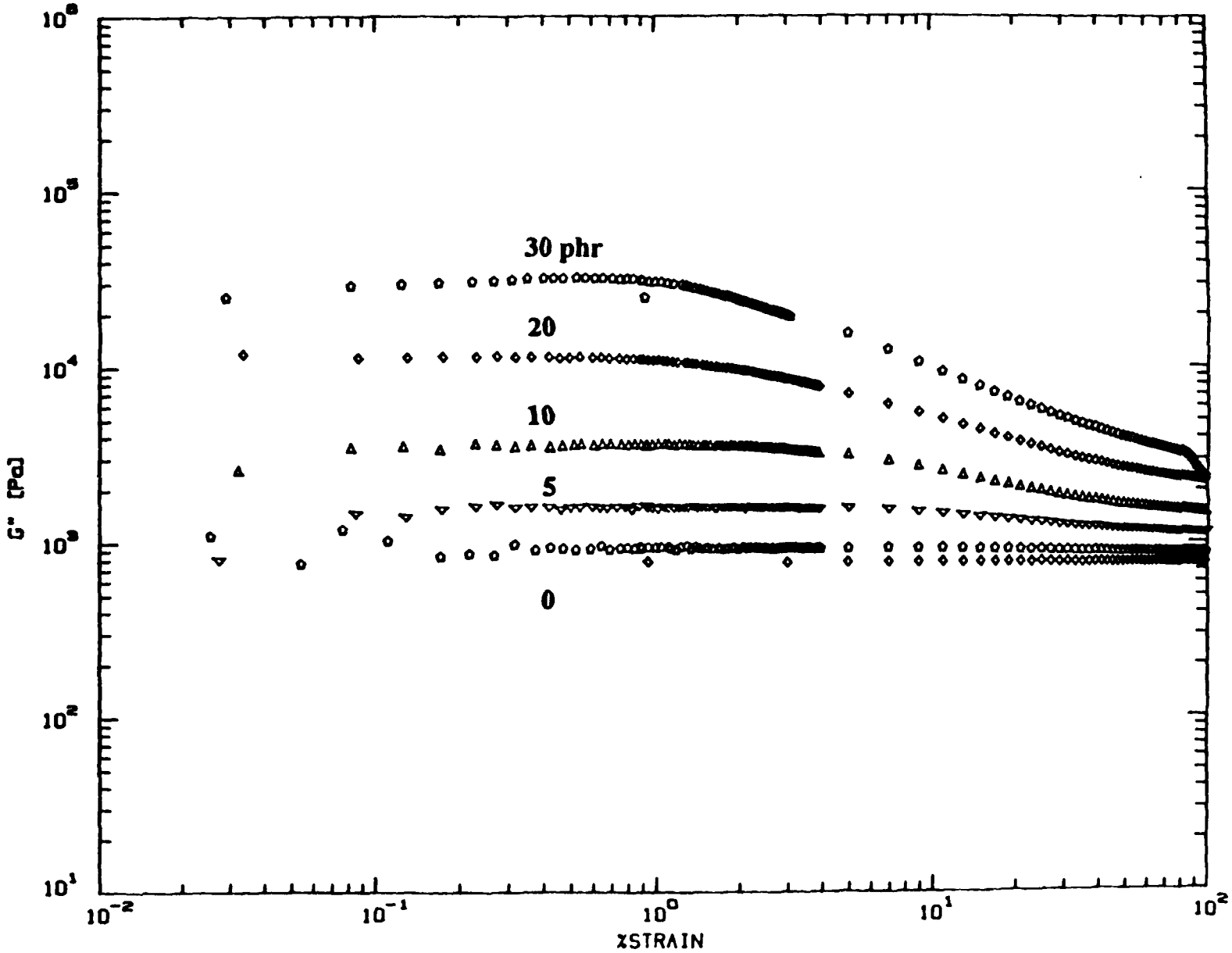

30 phr
20
10
5
0
G" [Pa]
%STRAIN
10^6
10^5
10^4
10^3
10^2
10^1
10^{-2}
10^{-1}
10^0
10^1
10^2

Figure 8

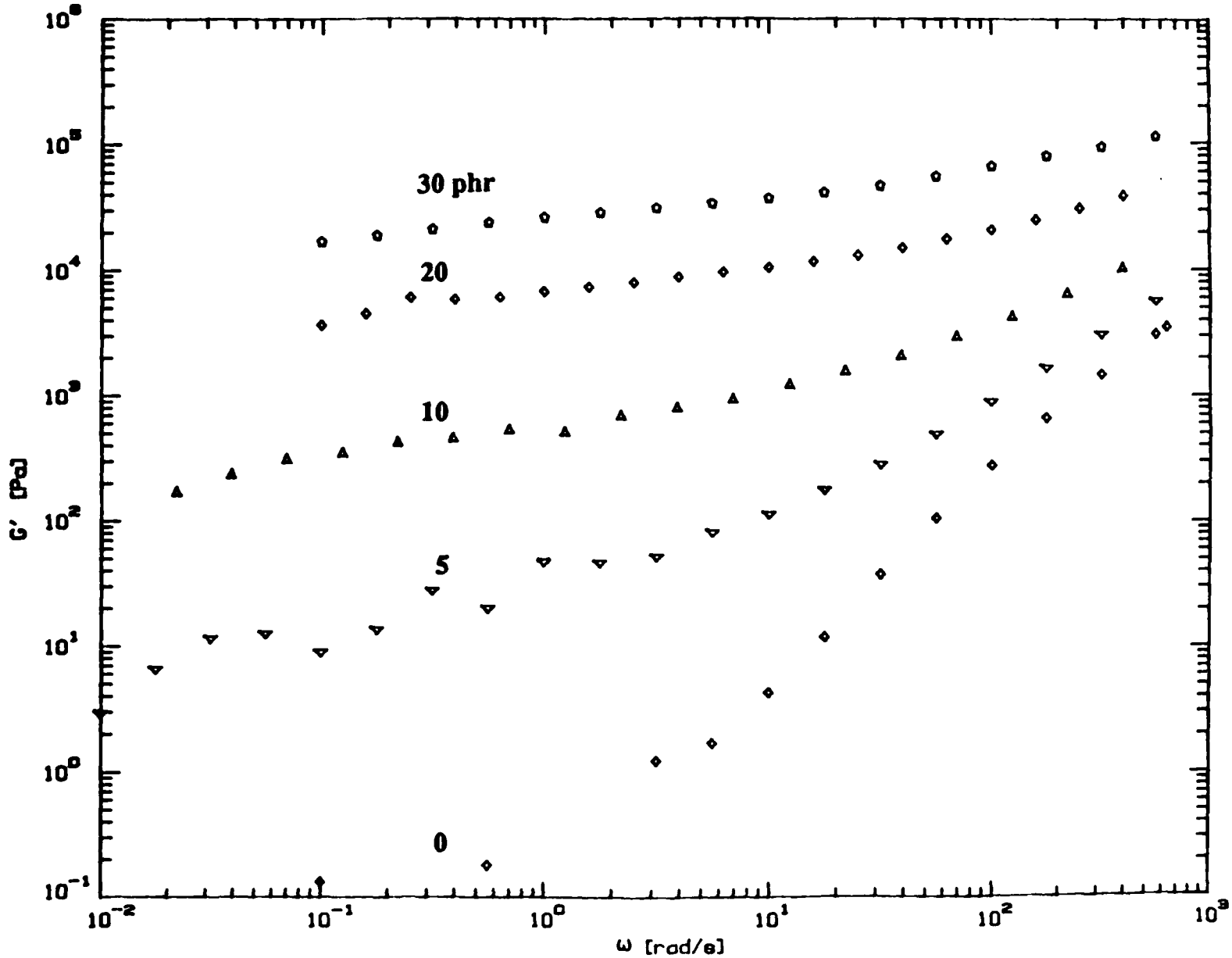

30 phr
20
10
5
0
G' [Pa]
ω [rad/s]
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}

Figure 9

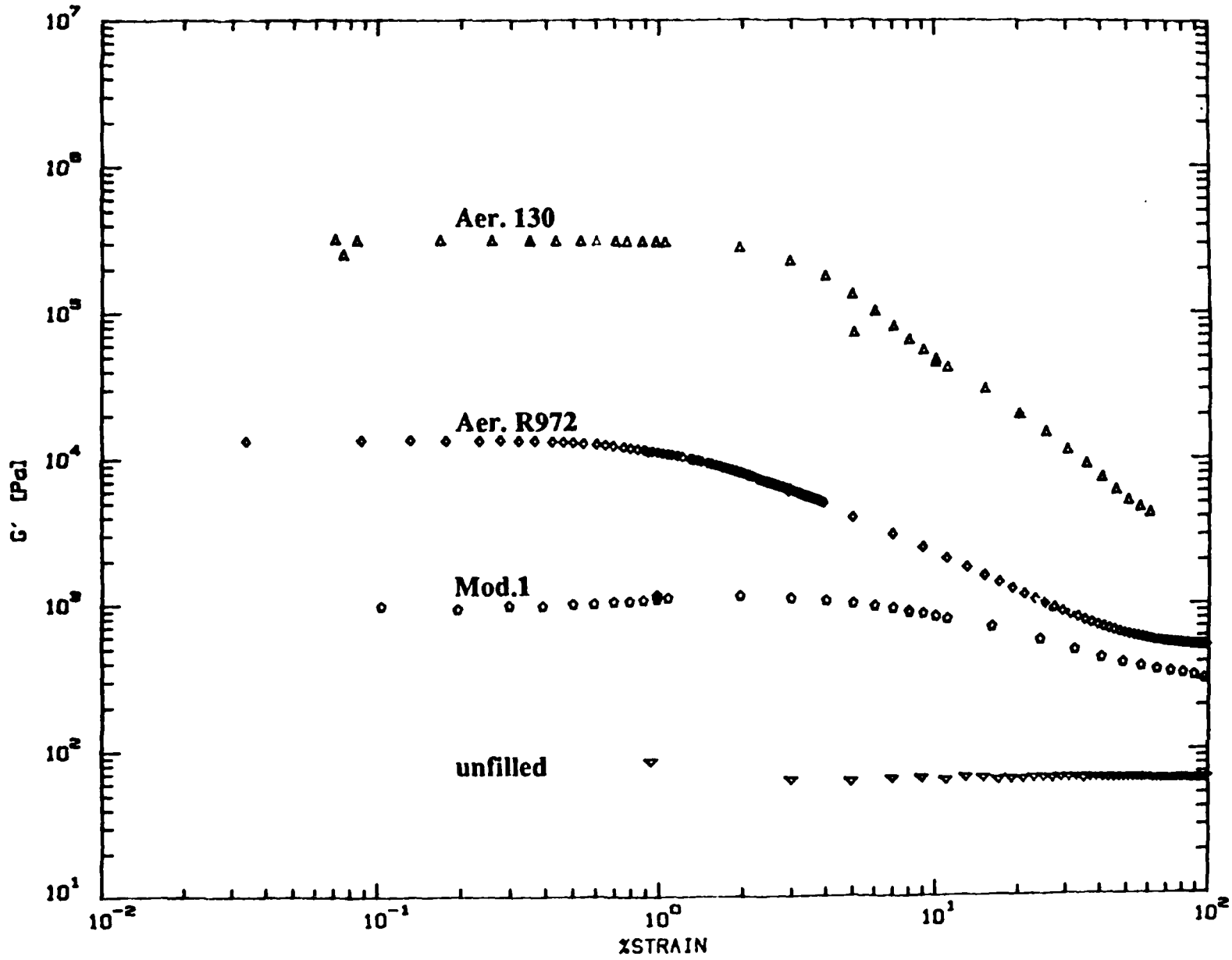
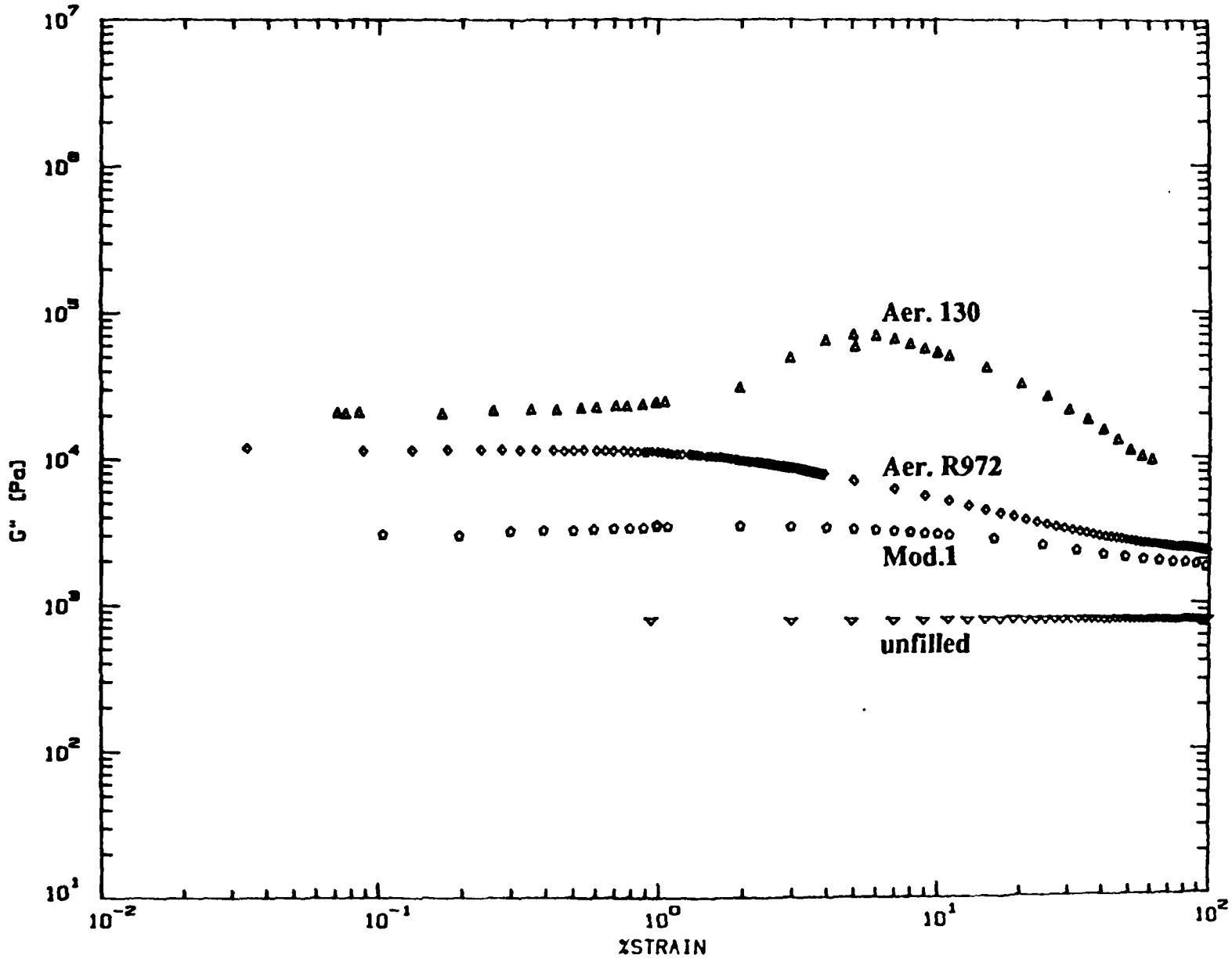

Aer. 130
Aer. R972
Mod.1
unfilled
G' [Pa]
%STRAIN
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^{-2}
10^{-1}
10^0
10^1
10^2

Figure 10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Aer. R972
Mod.1
unfilled
G" [Pa]
%STRAIN
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10^2
10^1
10^{-2}
10^{-1}
10^0
10^1
10^2

Figure 11

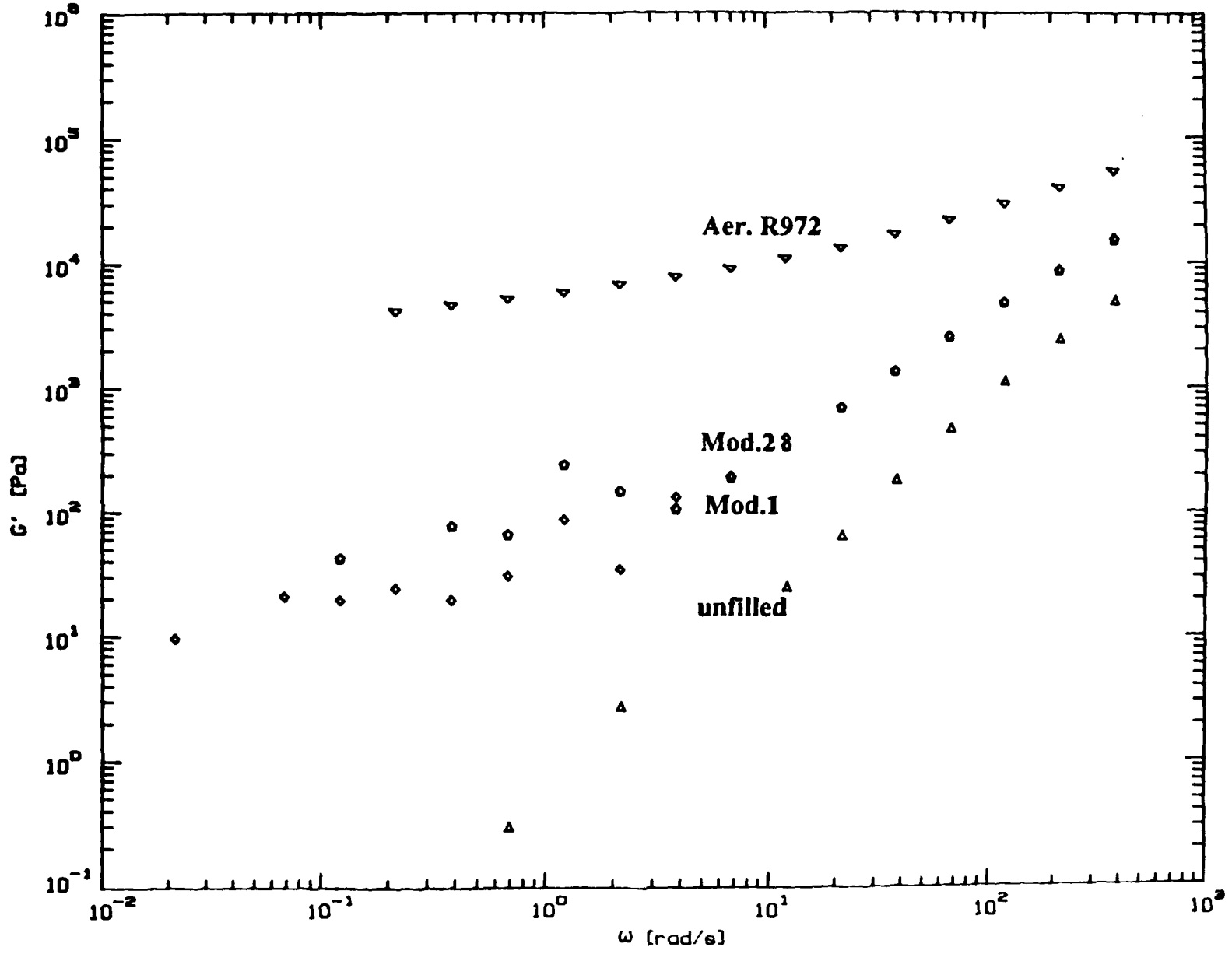

Aer. R972
Mod.2 8
Mod.1
unfilled
G' [Pa]
ω [rad/s]
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}

Fig 12

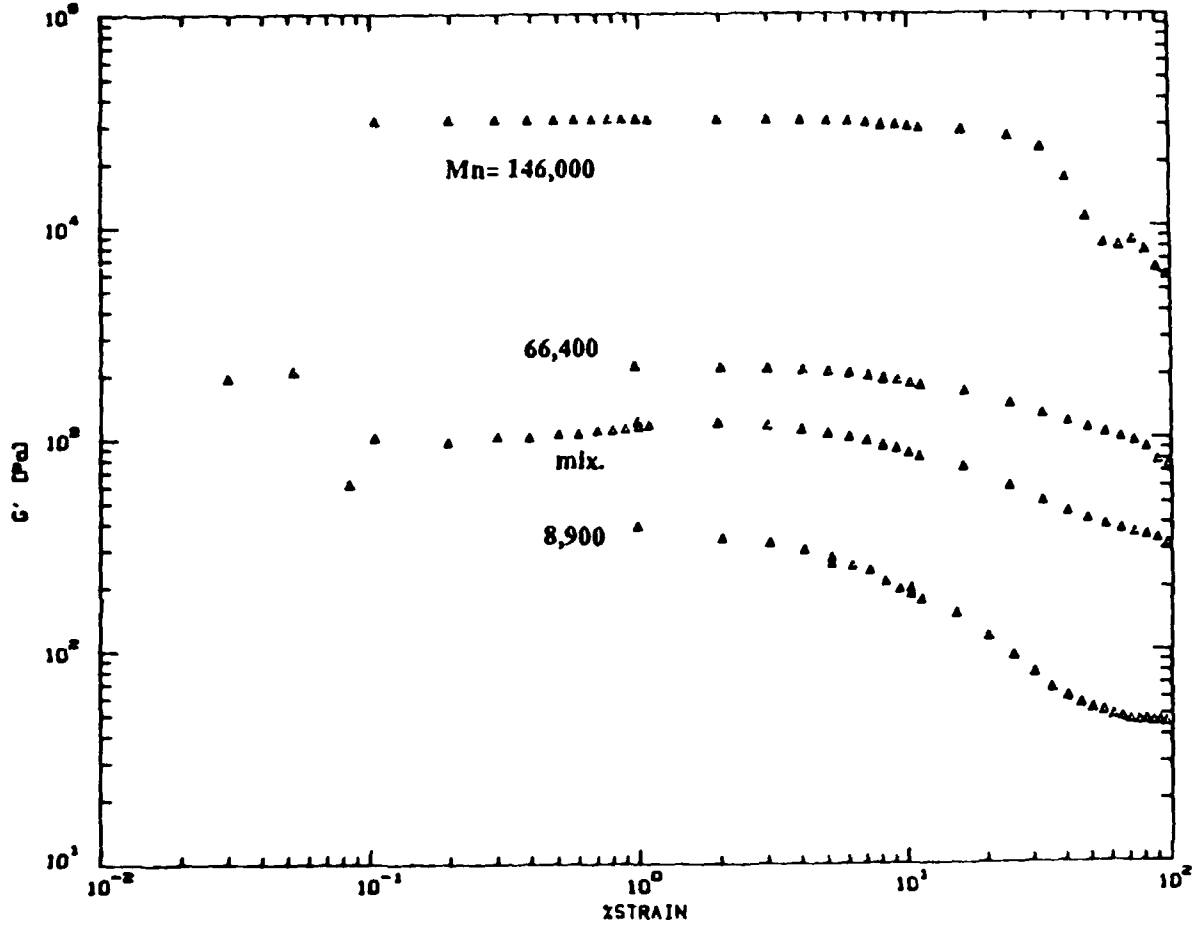
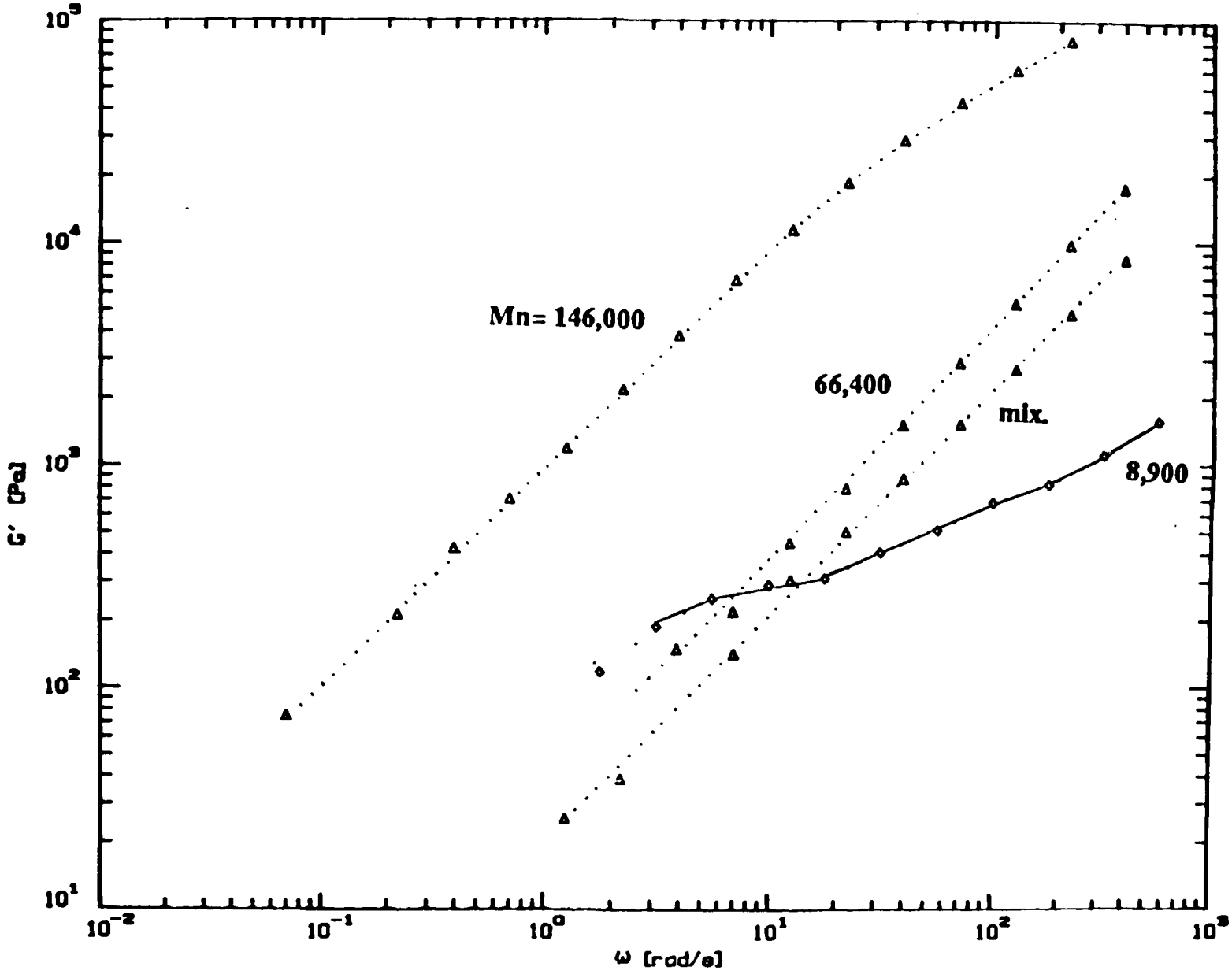


Figure 13


Mn= 146,000
66,400
mix.
8,900
G' [Pa]
ω [rad/s]
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10^4
10^3
10^2
10^1
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3

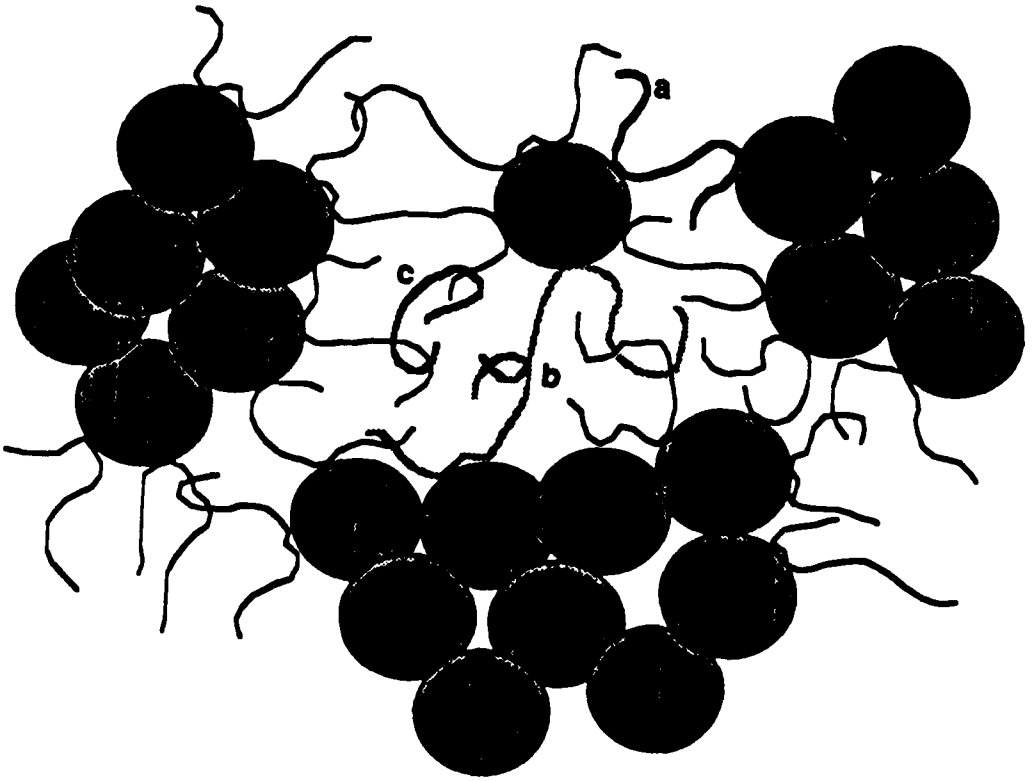


Figure 14

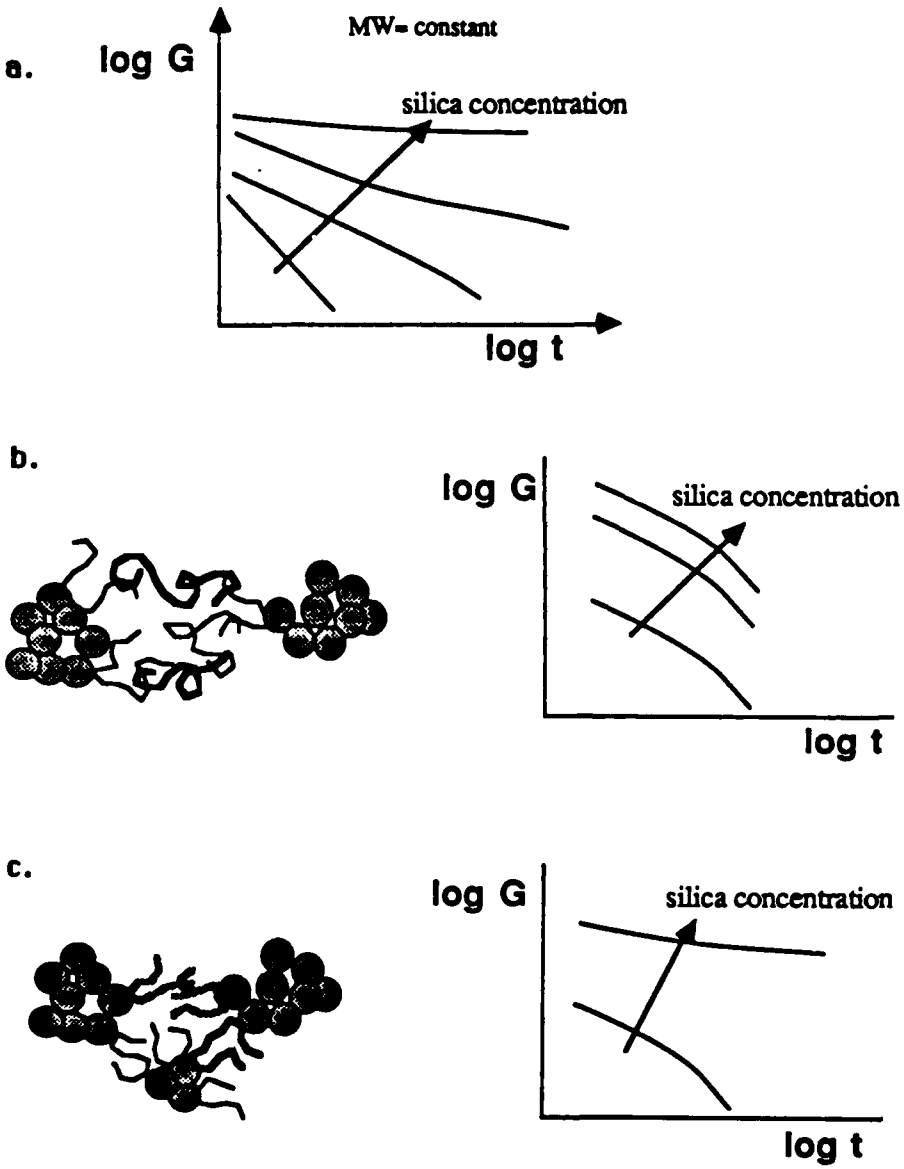

a.
log G
MW= constant
silica concentration
log t
b.
log G
silica concentration
log t
c.
log G
silica concentration
log t

Figure 15

Figure 16

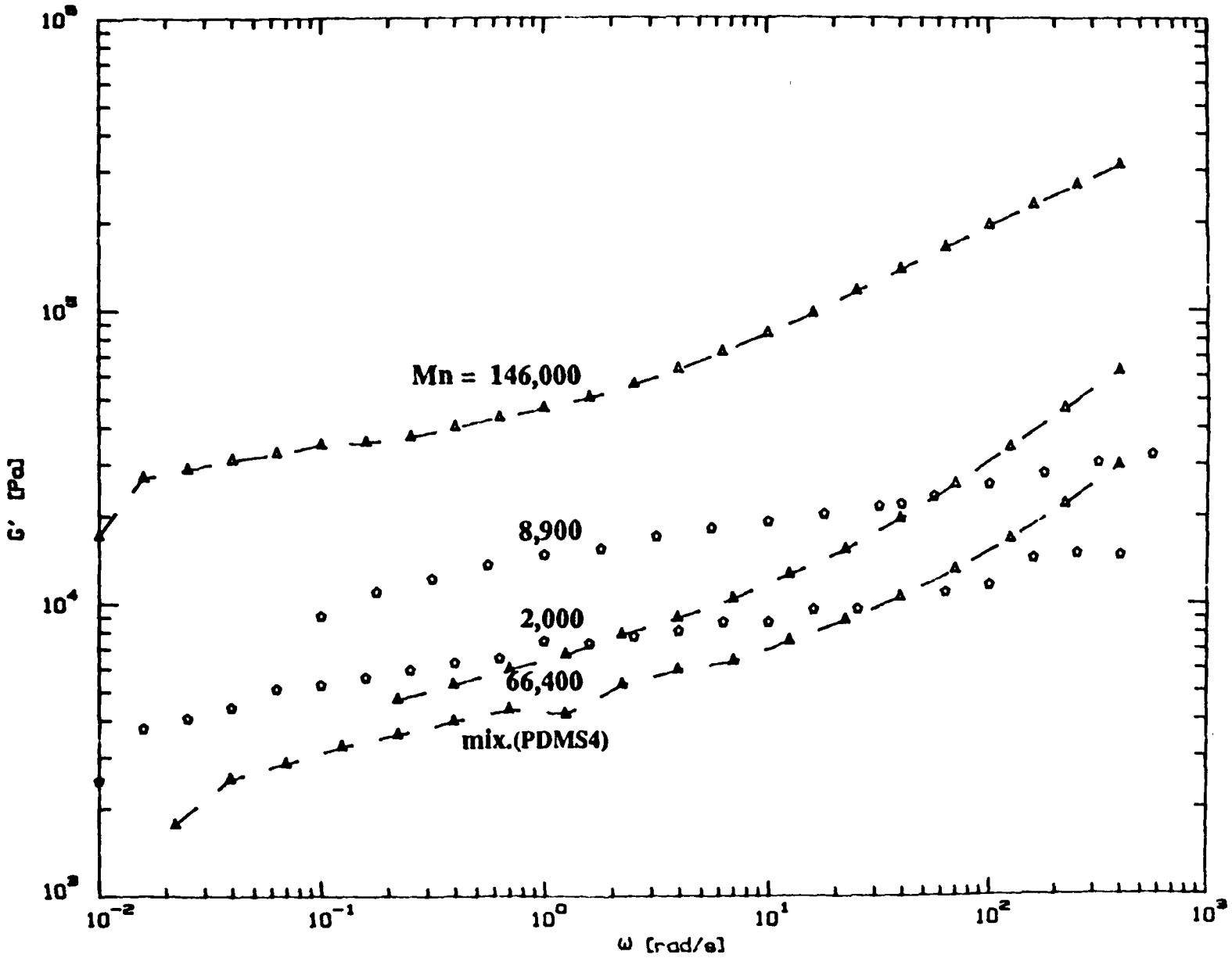

Mn = 146,000
8,900
2,000
66,400
mix.(PDMS4)
G' [Pa]
ω [rad/s]
10^6
10^5
10^4
10^3
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3

Figure 17 a

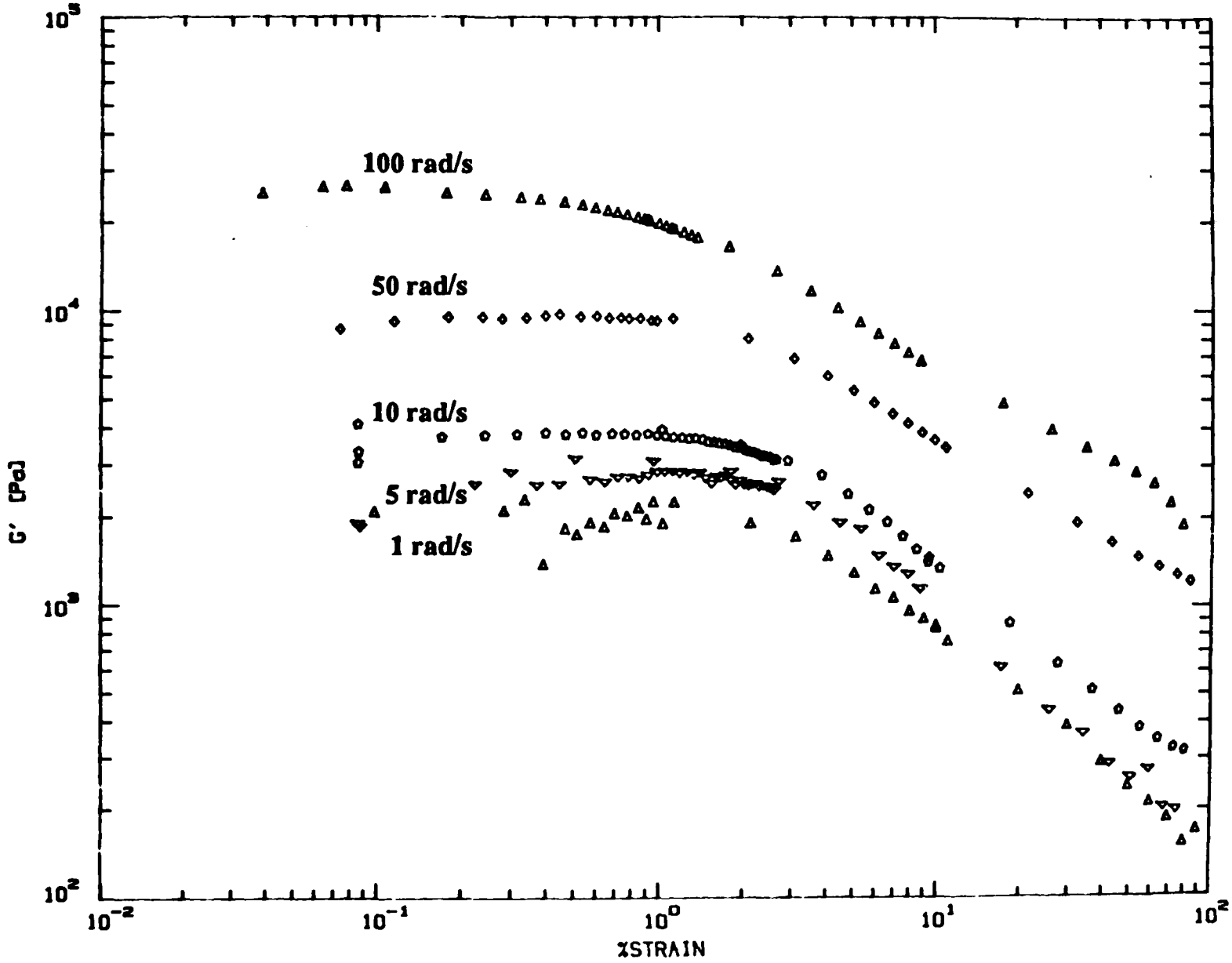
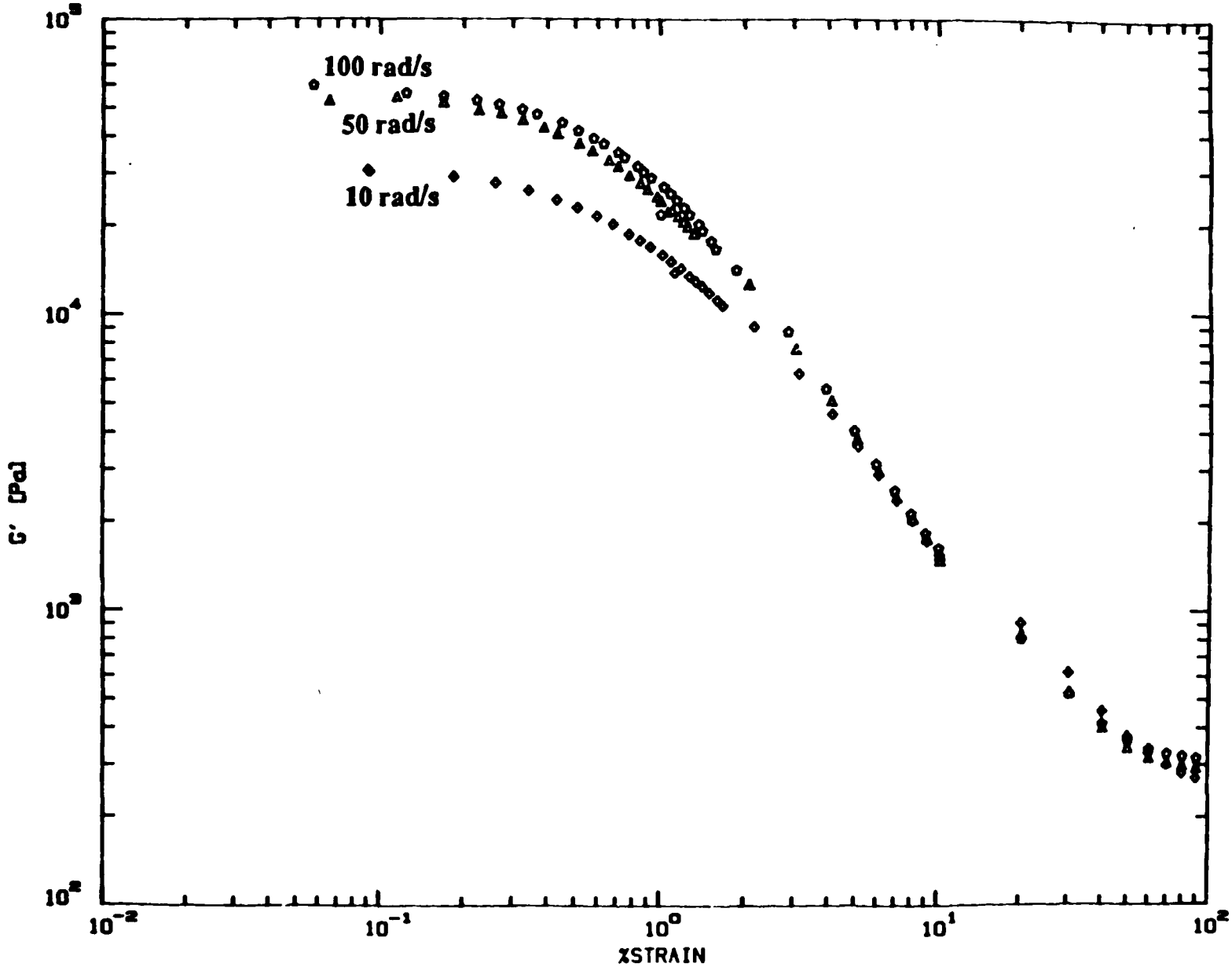

100 rad/s
50 rad/s
10 rad/s
5 rad/s
1 rad/s
G' [Pa]
%STRAIN
10^5
10^4
10^3
10^2
10^{-2}
10^{-1}
10^0
10^1
10^2

Figure 17.b


100 rad/s
50 rad/s
10 rad/s
G' [Pa]
%STRAIN
10^5
10^4
10^3
10^2
10^{-2}
10^{-1}
10^0
10^1
10^2

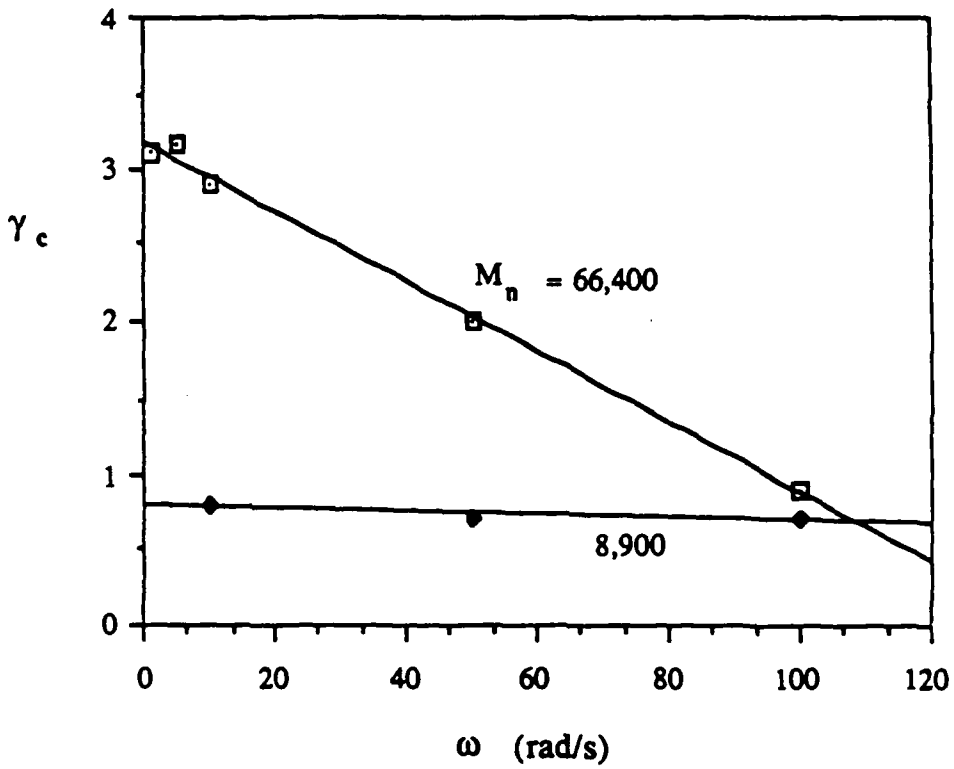


Figure 18

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Ronald A. De Marco

Ronald A. De Marco
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Chemistry Division