

## **INFORMATION TO USERS**

**This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.**

**The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.**

**In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.**

**Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.**

**Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.**

**Bell & Howell Information and Learning  
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA  
800-521-0600**

**UMI<sup>®</sup>**



**Rheological Study of Solutions of High Concentrations of  
CarboxyMethyl Cellulose**

**Mohamed Edali**

**A Thesis**

**In**

**The Department**

**Of**

**Mechanical Engineering**

**Presented in Partial Fulfillment of the Requirements**

**For the Degree of Master of Applied Science at**

**Concordia University**

**Montreal, Quebec, Canada**

**June 1999**

**©Mohamed Edali, 1999**



National Library  
of Canada

Acquisitions and  
Bibliographic Services

395 Wellington Street  
Ottawa ON K1A 0N4  
Canada

Bibliothèque nationale  
du Canada

Acquisitions et  
services bibliographiques

395, rue Wellington  
Ottawa ON K1A 0N4  
Canada

*Your file* *Votre référence*

*Our file* *Notre référence*

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-43657-8

Canada

# **ABSTRACT**

## **Rheological Study of Solutions of High Concentrations of**

### **CarboxyMethyl Cellulose**

**Mohamed Edali**

The purpose for this thesis is to provide a complete and comprehensive rheological study for a high range of CMC concentrations. The objective is to reveal the measurements of steady-state parameters, transient shear stress response, and yield stress of Carboxymethyl Cellulose. Also, the thixotropic, viscoelastic behavior, and some of the dynamic responses were included. In order to accomplish this, a Haake-Rheostress 100, Cone-and-Plate Rheometer system was used to get a full set of rheological characteristics of high concentrations of carboxymethyl cellulose solutions (CMC). The concentrations ranged by weight from 5% to 8% of CMC. The rheological behavior of CMC gels at concentrations of 5, 6, 7, and 8 % by weight has been analyzed. This range was wide enough to cover the rheological properties of the highly concentrated CMC solutions. The thixotropic areas and its variations with factors such as concentration and agitation time were obtained. The rheological fingerprints of the samples provided the assigned shear rate and the resulting shear stress correlation in the controlled rate mode of the rheometer.

## **ACKNOWLEDGEMENTS**

The author is grateful to his thesis supervisor, Dr. Nabil Esmail, Professor & Dean of The Faculty of Engineering and Computer science, for his supervision, guidance, and encouragement throughout the course of this research work.

Also, the author would like to express a sincere gratefulness to Dr. Mohamed Al-Meshragi, Assistant Professor and The Chairman of The Department of Chemical Engineering - Naser University - Elkhoms/Libya, for his guidance and support.

Thanks and appreciation are extended to the secretariat of Education of Libya (SESR) for the financial support, and also to the team work of the Canadian Bureau for International Education, for their administration and understanding for the past years of my study.

A very special note of thanks is extended to the author's wife and his daughter, Sarah and his son, Ahmed , for their continued encouragement throughout this endeavor.

## **TABLE OF CONTENTS**

|  |             |
|--|-------------|
| <b>ABSTRACT .....</b>  | <b>iii</b>  |
| <b>ACKNOWLEDGEMENTS .....</b>                                    | <b>iv</b>   |
| <b>TABLE OF CONTENTS .....</b>                                   | <b>v</b>    |
| <b>LIST OF FIGURES .....</b>                                     | <b>vii</b>  |
| <b>LIST OF FIGURES (Continued).....</b>                          | <b>viii</b> |
| <b>LIST OF TABLES .....</b>                                      | <b>ix</b>   |
| <br>   |             |
| <b>1.0 INTRODUCTION .....</b>                                    | <b>1</b>    |
| 1.1 General Introduction of CarboxyMethyl Cellulose Polymer..... | 1           |
| 1.2 Applications of CMC. ....                                    | 2           |
| 1.3 Previous Work on CMC .....                                   | 3           |
| 1.4 The Scope of The Present Thesis .....                        | 5           |
| <br>   |             |
| <b>2.0 EXPERIMENTAL PROCEDURE .....</b>                          | <b>7</b>    |
| 2.1 Preparation of The Solutions .....                           | 7           |
| 2.2 Instrumentation For Rheological Measurements .....           | 9           |
| 2.2.1 Advantages of The Cone and Plate Sensor System .....       | 12          |

|            |   |           |
|------------|---|-----------|
| <b>3.0</b> | <b>RHEOLOGICAL CHARACTERIZATION OF VISCOELASTIC</b> |           |
|            | <b>MATERIALS .....</b>                              | <b>14</b> |
| 3.1        | Shear Flows Classification .....                    | 14        |
| 3.2        | The Most Common Used Flow Geometries .....          | 14        |
| 3.2.1      | Rotational Flow .....                               | 15        |
| 3.2.1.1    | Cone and Plate Flow.....                            | 15        |
| 3.2.1.2    | Parallel Disk Flow.....                             | 16        |
| 3.2.1.3    | Concentric Cylinder Flow.....                       | 17        |
| <br>       |   |           |
| 4.0        | <b>RESULTS AND DISCUSSION.....</b>                  | <b>18</b> |
| 4.1        | Steady-State Shear Flow.....                        | 18        |
| 4.2        | Transient Shear Stress Response: .....              | 25        |
| 4.3        | Thixotropy Test: .....                              | 34        |
| 4.4        | Yield Stress: .....                                 | 50        |
| 4.5        | Creep Recovery Test: .....                          | 56        |
| 4.6        | Dynamic Test:.....                                  | 68        |
| <br>       |   |           |
| 5.0        | <b>CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE</b>   |           |
|            | <b>RESEARCH .....</b>                               | <b>81</b> |
| 5.1        | Conclusions .....                                   | 81        |
| 5.2        | Recommendations For Future Research .....           | 83        |
|            | <b>REFERENCES .....</b>                             | <b>84</b> |

## **LIST OF FIGURES**

- Figure (2-1):** Structural formula for a substituted monomer of CMC.
- Figure (2-2):** Cone and plate sensor system with truncated cone.
- Figure (4-1):** Flow behavior curves of CMC solutions.
- Figure (4-2):** Viscosity curves of CMC solutions.
- Figure (4-3):** Transient shear stress response of 5 % CMC.
- Figure (4-4):** Transient shear stress response of 6 % CMC.
- Figure (4-5):** Transient shear stress response of 7% CMC.
- Figure (4-6):** Transient shear stress response of 8 % CMC.
- Figure (4-7):** Transient shear stress response at shear rate of ( $100 \text{ sec}^{-1}$ ) for CMC.
- Figure (4-8):** Transient shear stress response at shear rate of ( $500 \text{ sec}^{-1}$ ) for CMC.
- Figure (4-9):** CMC thixotropic hysteresis areas by the first technique.
- Figure (4-10):** CMC thixotropic hysteresis areas by the second technique.
- Figure (4-11):** Thixotropy -First technique- at 200 sec three cycles for 6% CMC.
- Figure (4-12):** Thixotropy -First technique- at 200 sec for 6 % CMC.
- Figure (4-13):** Thixotropy -First technique- at 200 sec for 7 % CMC.
- Figure (4-14):** Thixotropy -First technique- at 200 sec for 8 % CMC
- Figure (4-15):** Thixotropy -Second technique- at 200 sec for 6 % CMC.
- Figure (4-16):** Thixotropy -Second technique- at 200 sec for 7 % CMC.
- Figure (4-17):** Thixotropy - Second technique- at 200 sec for 8 % CMC.
- Figure (4-18):** Yield stress response of 6 % CMC at (.09 Pa-4 Pa-.09 Pa) segments.

## **LIST OF FIGURES (Continued)**

**Figure (4-19):**Yield stress response of 7 % CMC at (.09 Pa-4 Pa-.09 Pa) segments.

**Figure (4-20):** Yield stress response of CMC at (.09 Pa-50 Pa-.09 Pa) segments.

**Figure (4-21):** Yield stress response of CMC at (.09 Pa-100 Pa-.09 Pa) segments.

**Figure (4-22):** Creep-Recovery curves of 6% CMC

**Figure (4-23):** Creep-Recovery curves of 7 % CMC

**Figure (4-24):** Creep-Recovery curves of 8 % CMC

**Figure (4-25):** Creep Recovery curves of 5 % CMC at 50 Pa.

**Figure (4-26):** Creep Recovery curves of 6 % CMC at 50 Pa.

**Figure (4-27):** Creep Recovery curves for 7 , 8 % CMC at 1 Pa.

**Figure (4-28):** Creep Recovery curves for 7 , 8 % CMC at 50 Pa.

**Figure (4-29):** Creep Recovery curves for 8 % CMC at 150 Pa.

**Figure (4-30):** Stress sweep [0.1-30 Pa] for 6% CMC.

**Figure (4-31):** Stress sweep at {0.1 - 30 Pa} for 7% CMC.

**Figure (4-32):** Stress sweep at {0.1 - 30 Pa} for 8% CMC.

**Figure (4-33):** Elastic, G' and viscous, G'' modulus for 6% CMC.

**Figure (4-34):** Elastic, G' and viscous, G'' modulus for 7% CMC.

**Figure (4-35):** Elastic, G' and viscous, G'' modulus for 8% CMC.

**Figure (4-36):** Elastic modulus of CMC solution.

**Figure (4-37):** Viscous modulus of CMC solutions.

**Figure (4-38):** Complex viscosity for 6, 7, and 8% of CMC solutions.

## **LIST OF TABLES**

Table (4-1): Flow curve equation constants of CMC% solutions.

Table (4-2): Viscosity equation constants of CMC % solutions.

Table (4-3): Transient shear stress responses at low shear rates for high CMC concentrations

Table (4-4): Thixotropy hysteresis areas ( kPa/ sec) for the first technique

" one cycle of up and down curves" :

Table (4-6): Thixotropy hysteresis areas ( kPa/ sec) for the second technique

" the cycle of up - time curve - and down curves".

# **1.0 INTRODUCTION**

## **1.1 General Introduction of Carboxymethyl Cellulose Polymer**

CarboxyMethyl Cellulose (CMC) is a white granular substance, soluble in water depending upon degree of substitution. Water-soluble CMC is available at various levels of viscosity (10-50000 mPa.S in 2% solution), and is equally soluble in hot and cold water. It is the sodium salt of carboxymethyl cellulose, having a loose number of sodium carboxymethyl groups ( $\text{CH}_2\text{COONa}$ ) introduced to the cellulose molecule to promote water solubility. The principle structural component of the cell walls of plants is cellulose. CMC is the cellulose derivative, which is most widely used. It is made by treating cellulose with sodium hydroxide-chloro acetic acid. CMC hydrates rapidly and forms into clear solution. The single most important property of CMC is viscosity building. Each polymer chain in a diluted solution of CMC is hydrated, extended, and exhibits a stable viscosity. Also, the presence of metal salts has little effect on the viscosity. Solid precipitation occurs for solutions below pH2, and the viscosity decreases rapidly above PH10, but they are stable between pH2-pH10. CMC solutions are either pseudoplastic or thixotropic depending on the type, but most of them are highly pseudoplastic. They show thixotropic behavior; i.e., the viscosity decreases gradually by shearing. CMC is manufactured by many companies throughout the world and has a large market in Western Europe and North

America. As much as several hundred thousand tons per year is produced. Reagents are solid or liquid in CMC, and its sodium chloroacetate (etherifying reagent) is very efficient, making CMC production at normal atmospheric pressures much simpler than that of most other cellulose ethers. These properties of CMC along with its versatility as a thickener, film former, protective colloid, and water-retaining agent, has made CMC the most produced and widely used industrial cellulose ether.

## **1.2 Applications Of CMC**

Large quantities are produced in crude commercial grades without any refining for use in oil-drilling, detergents, and in the paper industry. High-purity grades are employed as food additives, and in the oil industry CMC is used to increase the stability of mud for drilling purposes as it stabilizes the aqueous suspensions of clay due to its high water retention. CMC can be useful as a soil stabilizer, in detergent composition, and as a textile surface protector. In the paper industry, CMC also acts as a strengthener and binder, and increases the water retention of the coating mixtures, thereby increasing grease resistance and the print capability of paper. Various mixtures of low and high level CMC's viscosity can be employed depending on the use. Pigment coats containing purified CMC are applied on the size press and can be up to 10% by weight [23]. In the food industry, it is added as a thickener, or as an emulsion stabilizer to some products such as frozen dairy, dry drink mixes, icing, syrups, and baked goods. CMC

works as a bio-adhesive agent to prolong the expiration period of drugs. In addition, nickel slurry used in batteries (secondary cells) is prepared by mixing a low-density nickel powder with a viscous aqueous solution of carboxymethyl cellulose [22].

### **1.3 Previous Work On CMC**

CMC has been the topic of much recent research [1-7]. Sikkema and Jannen [4] attempted to prepare CMC's with properties similar to xanthan gum solutions. They synthesized CarboxyMethyl Cellulose that contained "Cellulose blocks" consisting of segments of poorly substituted CMC, giving a physical cross-link in the solution. They manipulated the alkalinity during CMC preparation and produced a complex CMC colloid fiber. The orientability of such colloid fibers would lead to the shear-thinning behavior. Slow agitation was applied to prepare the solutions in this work and studied by using a Weissenberg cone and plate Rheometer. Westra [5] studied the rheological properties of an aqueous solution of Cellulose-CO-CMC segmented block copolymer that had been synthesized. The study revealed properties that are similar to those found in highly pseudoplastic solutions of xanthan gum. A good tool for characterizing the pseudoplasticity of CMC was the Ostwald-De-Waele power law equation. Xanthan gum mimicry samples rheological dependency of the temperature was similar to that of Xanthan and different from that of the usual type of CMC. Young and Shoemaker [3] measured the intrinsic viscosities of aqueous

suspensions of Xanthan gum and CarboxyMethyl Cellulose by using a cone and plate rotational rheometer. The cone angle of the Carri-Med Wieissenberg R20A rheometer was  $2^\circ$  C, and 7.5 cm for the plate diameter. The authors concluded that the reduced viscosities of CMC suspensions and Xanthan gum suspensions within the concentration range of 0.04 - 0.01 % increased with dilution. However, the intrinsic viscosities of Xanthan gum and CMC suspensions decreased with increased shear rate when the molecules became deformed at higher shear forces. Increasing the rigidity of Xanthan molecules at low shear rates could be the reason for the difference in intrinsic viscosity between the two polymers. Abdlrahim et al. [2] stated that due to a need for accurate data on rheological properties of Carboxymethyl cellulose, they had focused their study on measuring the effects of concentration and temperature on CMC rheology. Food processing operations involving mixing, pumping, heating, and cooling, requires this kind of study due to the dependency of the flow characteristics on the fluid viscosity and density. They chose to study the low range of CMC concentration ranging by weight from 0.5% to 2% over a temperature range of 30 to  $90^\circ$  C. High viscosity CMC sodium salt degree of substitution (0.65 - 0.85) and a  $2 \times 10^5$  molecular weight was used. A "Haake model RV20 rotational viscometer was used to apply a programmed 3-cycle continuous sequence shear rate, which increased linearly from 0 to  $500 \text{ sec}^{-1}$  in 10 minutes and decreased from  $500 \text{ sec}^{-1}$  to 0 in an equal amount of time. They concluded that the Power law model was best for describing the flow behavior of CMC and that the power law parameters { m , n } were sensitive to the change in concentration and temperature. Dolz et al [6] analyzed the

thixotropy of CarboxyMethyl Cellulose gels at different concentrations ranging by weight between 1 - 2.5 %. The analysis was in terms of concentration, duration of storage time, agitation time, and temperature. Thixotropic areas variations rate was defined for determining the structural breakdown rate. They believe that the variation rate became negligible after 5 minutes of agitation, and was independent of the rest of the remaining variables. In another publication by Dolz et al.[7], a general method for quantifying the thixotropic behavior of systems with low thixotropy was proposed. This method was applied to Carboxymethyl Cellulose gels with high viscosities. Ghannam and Esmail [1] carried out a complete and comprehensive rheological study of low concentrations of Carboxymethyl Cellulose solutions using the Haake-rheostress Rs100 system. The study included measurements of steady-state flow tests, transient response, yield stress, thixotropy, creep recovery, and dynamic responses of the CMC solutions. The concentrations used were ranging by weight between 1-5% CMC. It was determined that the rheological behavior transformed from Newtonian to shear thinning as the concentrations of the solutions rose. However, when the concentration increased from 4-5% CMC, the thixotropic hysteresis area critically increased and a viscoelastic behavior was observed.

## **1.4 The Scope Of The Present Thesis**

In this work, the rheology behavior of CMC gels at concentrations of 5, 6, 7, and 8 % by weight has been analyzed. The thixotropic areas and its variations with

factors such as concentration and agitation time were obtained. The rheological fingerprints of the samples provided the assigned shear rate and the resulting shear stress correlation in the controlled rate mode of the Rheometer.

At different concentrations, CMC has a wide range of diverse applications such as the production of drilling mud and detergents, in the paper industry, in food products, and pharmaceuticals. The purpose for this report is to provide a complete and comprehensive rheological study for a high range of CMC concentrations. Throughout the testing process, a Haake- RS100 cone and plate sensor system was used.

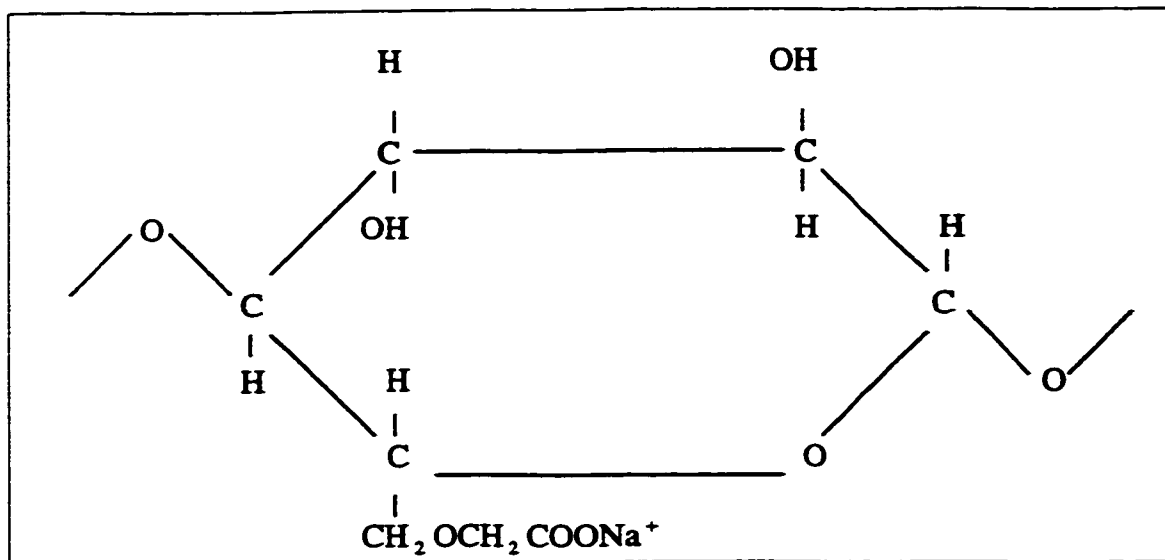
## **2.0 EXPERIMENTAL PROCEDURE**

### **2.1 Preparation Of The Solutions**

Cellulose ethers are high-molecular-weight compounds produced by replacing the hydrogen atoms of the hydroxyl group in the anhydroglucose units of cellulose with alkyl or substituted alkyl groups. Sodium carboxymethyl cellulose (CMC) is one of the most important cellulose ethers in commercial use.

In this thesis, the term Carboxymethyl Cellulose (CMC) is generally used to mean the sodium salt of Carboxymethyl Cellulose. The monomer is designated by the structural formula as shown in Figure (2-1). CMC is prepared by the reaction of sodium monochloroacetate with cellulose in the presence of excess sodium hydroxide. CarboxyMethyl Cellulose can be made in well-agitated water.

The solutions are thixotropic and the viscosity depends on the rate of shear and other variables. The macromolecule behaves as a protective colloid when dissolved in water. The high viscosity of CMC is an advantage where a thickening agent is needed. The industrial grades of CMC occur in the range of D.S. of 0.7 – 1.2, although theoretically the upper limit is three.



**Figure (2-1): Structural formula for a substituted monomer of CMC.**

CMC-sodium salt (medium viscosity) No. C4888, with degree of substitution DS= 0.7 which is the number of hydroxyl groups substituted by glucose units, was purchased from the Sigma chemical company. It is a completely water - soluble polymer and not an ion exchanger, with a viscosity of 2% aqueous solution at 23 ° C : 400 - 800 mPasec. The solutions were studied at concentrations of 5, 6, 7, and 8% (w/w). Each hydrogel concentration was prepared by adding a specific weight of CMC to half a liter of distilled water. Stirring time was required for the gels to be homogenized and this was done at a

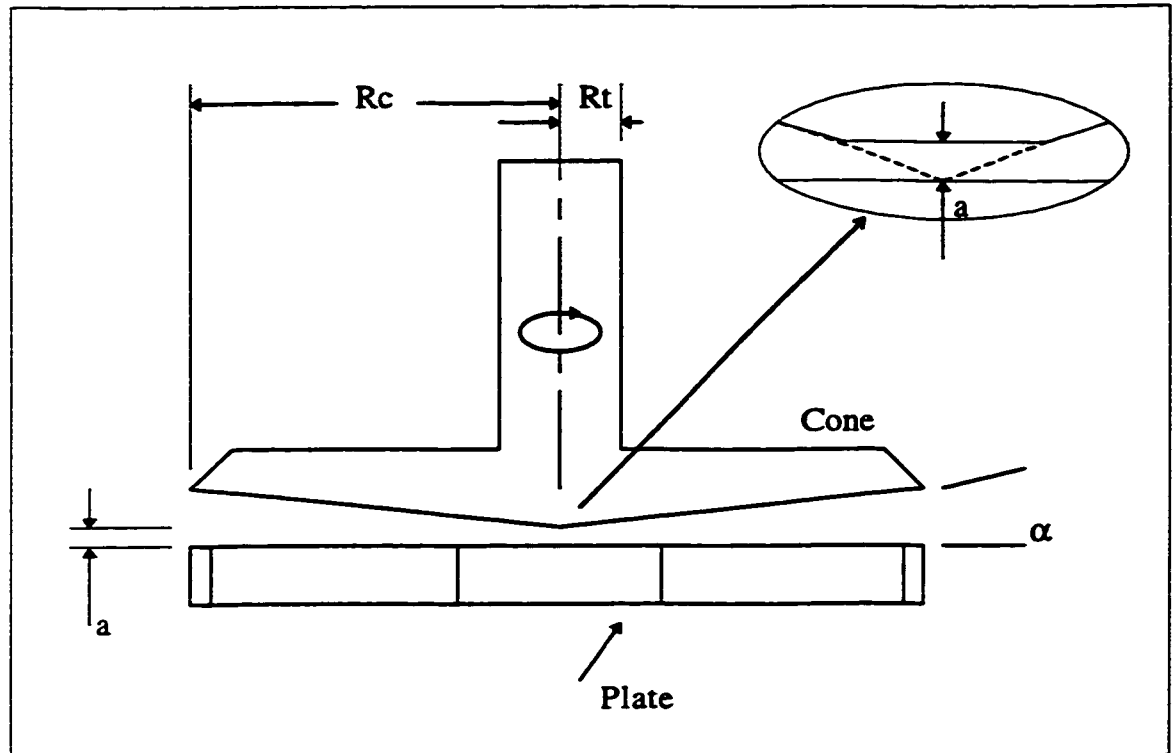
room temperature of 23° C. The experimental measurements were conducted after the samples had been maintained at the same temperature for sufficient time to achieve complete dissolution. For this study, concentrations of CMC were chosen in order to maintain integrity in the results by allowing a range of different effects to be studied.

## **2.2 Instrumentation For Rheological Measurements**

Cone and plate flow is obtained in the region bounded by a flat circular plate and a convex cone whose apex is in initial contact with the plate. However, in practice, the tip of the cone is truncated and a small gap is maintained between the two surfaces. This is to prevent damage to either of the surfaces if they were to rub against each other. A schematic of the cone and plate geometry is shown in Figure (2-2).

Cone angles -  $\alpha = 4^\circ$  in this case - are commonly chosen so that for any point of the cone surface, the ratio of angular speed and distance to the plate is constant. For any point within the gap from the cone tip to the outer ( $R_c$ ), the constant ( $\dot{\gamma}$ ) can be assumed. It is also necessary to truncate the tip of the cone by grounding it off up to a truncation radius ( $R_t$ ) to avoid wear of the cone tip and the center of the plate. As a result, the axial height of the cone is reduced by value ( $a$ ). To prepare the sensor system for a test the cone must be moved downward until

the truncated cone contacts the plate. It is then raised upward to achieve the axial height distance (a) . During running the test, the cone imaginary tip is to touch the plate.



**Figure (2-2): Cone and plate sensor system with truncated cone**

An error occurs when measuring the shear stress or the torque due to removal of the tip of the cone, and the degree of this error is effected by the ratio of the cone surface area to the truncation area. Using parameters taken from measurements by the cone and plate sensor systems, the shear rate  $\dot{\gamma}$ , shear stress  $\tau$

, and viscosity  $\eta$  can be calculated as following [25]:

**A: Shear rate ' $\dot{\gamma}$ '**

$$\begin{aligned}\dot{\gamma} &= M \cdot \omega \\ &= \frac{1}{\tan \alpha} \cdot \omega \\ &= \frac{1}{\alpha} \cdot \frac{2\pi}{60} \cdot n \\ &= \frac{\pi \cdot n}{30\alpha}\end{aligned}\tag{2-1}$$

where :  $\omega$  = angular velocity [rad/sec].

$n$  = rotor speed [  $\text{min}^{-1}$  ].

$\alpha$  = cone angle [rad].

$M$  = shear rate factor.

**B: Shear stress ' $\tau$ '**

$$\begin{aligned}\tau &= \left( \frac{3}{2\pi \cdot Rc^3} \right) \cdot T \\ &= A \cdot T\end{aligned}\tag{2-2}$$

Where:  $\tau$  = shear stress on the cone [ Pa ].

$Rc$  = outer radius of the cone [m].

$T$  = torque to be measured [N.m].

$A$  = shear stress factor.

### **C: Viscosity ‘ $\eta$ ’**

$$\eta = \frac{T}{\omega} \frac{A}{M} \quad (2-3)$$

Where:  $\eta$  = Viscosity of the sample, [ Pa.s ].

T = torque to be measured, [ N.m].

$\omega$  = angular velocity, [ rad/sec ].

A = shear stress factor.

M = shear rate factor.

#### **2.2.1 Advantages Of The Cone and Plate Sensor System.**

The cone and plate sensor system avoids the complication of having to be cleaned after performing a test. This is an advantage over the cylinder system [as will be mentioned in section 3-2-1-3], where cleaning of the cup and rotor is troublesome and time consuming. In addition, the flow is homogeneous for the cone-and-plate system and the required sample size is normally much smaller than the sample required for some cup-and-rotor sensor systems. This can be an important factor for choosing cone and plate rheometers when the sample to be studied is costly or in limited supply.

The Haake - Rheostress is almost a universally used (CS) rheometer. The RS100 rheometer is used to determine the characterization of viscoelastic fluids in both research and quality control. It features an alternative controlled rate (CR),

and oscillation (OSC) test modes, and is designed with a special low friction roller bearing for the rotor shaft that allows for the testing of fluids at low and high shear rates. Extremely low inertia (shear stress) can be applied on the samples tested by the rheometer controlled stress mode. Easy optimization of test parameters can suit very many samples with different rheological behavior by the interchangeable sensor systems. The RS100, with its digital encoder capable of processing 1 million per revolution, can detect any deformation of the samples. Even the lowest strains or shear rates can be measured due to the high rheometer encoder resolution. The RS100 is a computer controlled system that provides oscillating stress inputs and autostrains as well as swapping between both the CS and CR modes. It also controls the variable axially positions a cone versus plate lift speed, manually or remotely. A thermal gap size compensation for any of the sensor systems is provided by a microprocessor - control. Both test routines and data evaluations can be evaluated on the "Haake Windows" software. The rheometer has an extreme degree of sensitivity and is a very powerful research instrument for rheologically complicated fluids, especially fluids of medium visco-elasticity. The tests performed by the RS100 allow an insight into the molecular structure of materials with both viscous and elastic characteristics. Moreover, the thixotropy of samples by means of the hysteresis between the up and down ramp curves can be successfully determined by the RS100 - CR mode.

## **3.0 RHEOLOGICAL CHARACTERIZATION OF VISCOELASTIC MATERIALS**

### **3.1 Shear Flow Classification**

Firstly, shear flow is defined as a flow in which the shearing surfaces move isometrically, i.e., the distance between any two particles on the surface remains constant. Secondly, the volume of every element in the fluid remains constant, i.e., the flow is incompressible .

The curve to which the flow direction is everywhere tangent is called the stream line or line of shear. The shear flow is unidirectional when the stream lines coincide with material lines. Rheological steady shear flow is unidirectional shear flow in which the shear rate  $\dot{\gamma}$  is independent of time for a given particle. The flow is homogeneous if the shear rate  $\dot{\gamma}$  does not vary from particle to particle. Simple shear flow is unidirectional flow in which the shearing surfaces are planes and the flow is homogeneous.

### **3.2 The Most Commonly Used Flow Geometries**

There are a group of geometries that can generate unidirectional flow under certain assumed flow conditions. They can be used to determine certain

rheological material functions that fall into two classes - rotational flow, and rectilinear flow. In this study, rotational flow is discussed.

### **3.2.1 Rotational flow**

#### **3.2.1.1 Cone and plate flow**

This flow geometry is one type of rotational flow and is used extensively in the rheological characterization of viscoelastic materials. The sample is contained between a cone and a plate. Both of these have the same radius ( $R$ ), and the cone rotates with an angular velocity ( $\omega$ ). The torque ( $T$ ) is required to turn the rotating member, and the total normal force ( $F$ ) is the exertion by the fluid on the plate or cone. In this geometry, the angular velocity ( $\omega$ ) is small enough that the inertia forces can be neglected. The cone angle ( $\alpha$ ) is sufficiently small that the shear rate can be assumed to be homogeneous throughout the gap. Also, the free surface at the edge is spherical with a radius of curvature equal to the cone radius.

The homogeneous shear rate between the cone and the plate is the principle reason for the advantage of this geometry, which simplifies the interpretation of data.

There are three major problems associated with the assumptions

previously described. First, the uniform shear rate approximation is valid if the cone angle is less than  $4^\circ$ . However, a larger angle is desirable to limit the damping effect of the fluid on the normal stress measurements. Another problem is the secondary flow that results from fluid inertia due to a large cone angle and edge effects. Lastly, the edge effect problem is caused by the fact that the geometry necessarily has finite dimensions. The field is influenced by the existence of the free surface. This problem is dependent on the cone angle and the angular velocity used in the shearing. Surface tension is likely to contribute to an error occurring in the measurement of normal force. The fracturing phenomenon, which is a type of edge effect, arises at higher shear rates. Fracturing surface within the gap can be observed when the material is squeezed out of the gap. Termination of the experiment is usually required due to the occurrence of this phenomenon.

#### **3.2.1.2 Parallel Disk Flow**

The fluid is placed between two parallel circular disks of radius ( $R$ ) and one of the disks rotates with angular velocity ( $\omega$ ). As in the cone and plate flow, the following assumptions are taken into account when using this kind of flow to approximate it as a simple shear. First, the angular velocity is small in order to negate inertia effects. Then the free surface is

cylindrical with a radius ( $R$ ) which is the radius of the plates, and the edge effects are negligible. Unlike cone and plate flow, the shear rate in the gap is not even approximately uniform in the radial direction.

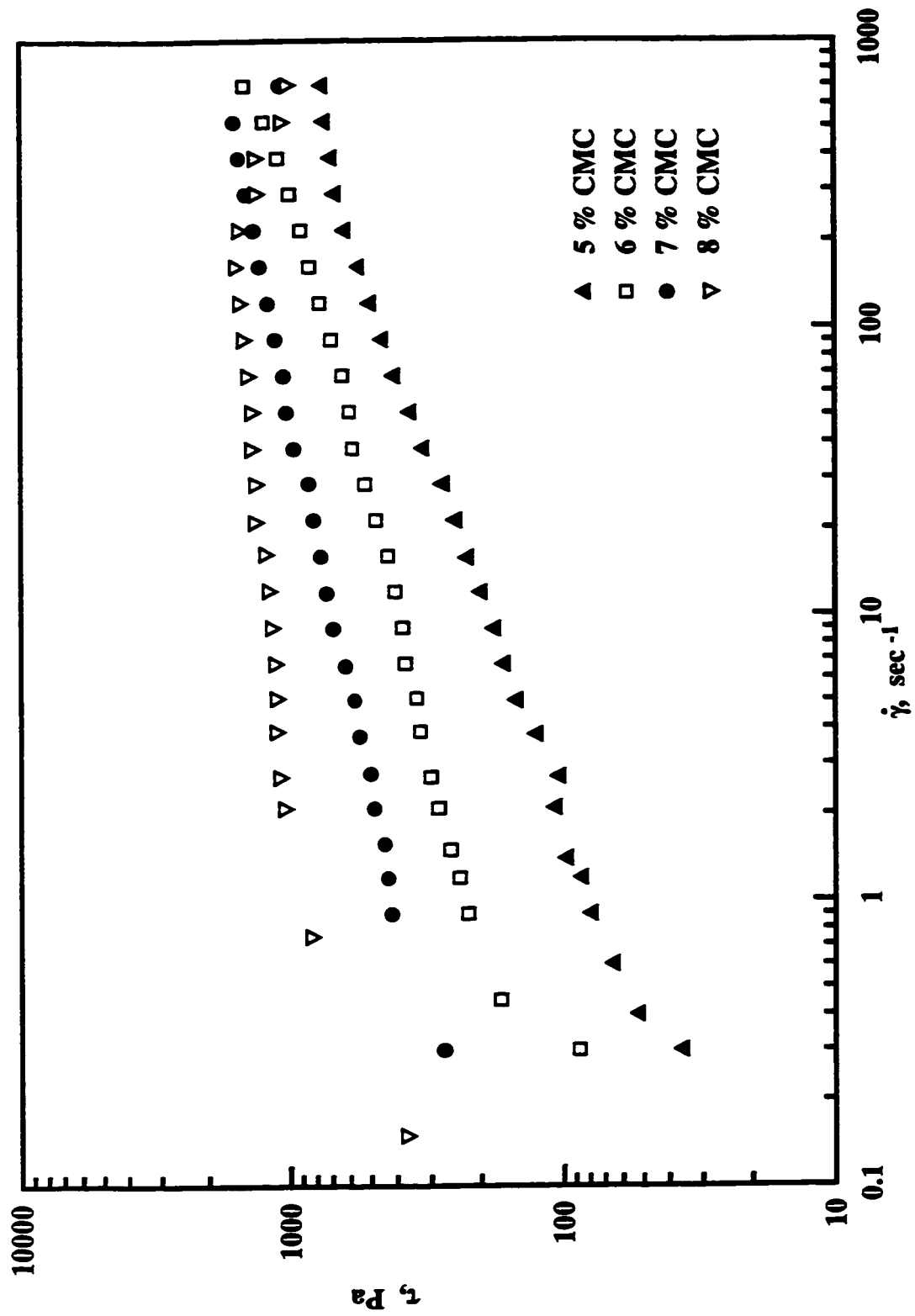
### **3.2.1.3 Concentric Cylinder Flow**

The test fluid is contained between coaxial cylinders having radii ( $R_i$ ) and ( $R_o$ ), with one of them rotating at velocity ( $\omega$ ). The gap between the two cylinders is usually kept very small to minimize the radial variation in shear rate. The torque ( $T$ ) on one of the cylinders is measured during the experiment. If a narrow gap is used, the shear rate is approximately uniform across the gap. On the other hand, if the gap spacing is large, the shear rate is non-homogeneous and its distribution is dependent on the rheological properties of the test fluid, which means that the viscosity of the material must be known before the shear rate can be calculated. In addition to the Weissenberg effect, there is a steady secondary flow within the gap, in which the fluid climbs up the inner cylinder. Concentric cylinder flow cannot be used at higher shear rates because of the deviation from simple shear flow that occurs.

## 4.0 RESULTS AND DISCUSSION

### 4.1 Steady-State Shear Flow

In this test, two main graphs of double logarithmic scales illustrate the rheological fingerprints of the samples under study. These two graphs are the flow behavior curve figure (4-1) showing the relationship between shear stress  $\tau$  and shear rate  $\dot{\gamma}$ , and the viscosity curves figure (4-2) which illustrate the viscosity  $\eta$  decrease with a gradual increase in shear rate. They provide the correlation between the assigned shear in CR mode ranging from 0.15 - 700  $\text{sec}^{-1}$  and the resulting shear stress for CMC solutions in the concentration range of 5 - 8 %. A linear correlation of  $\log(\eta)$  and  $\log(\tau)$  with  $\log(\dot{\gamma})$  exists and the Ostwald-de-Waele equation " Power law" is applied. For CMC solution concentrations of 5%, 6%, and 7% an excellent linearity over three decades of shear rate is observed, from  $\dot{\gamma} = 1 \text{ sec}^{-1}$  up to 1000  $\text{sec}^{-1}$ . Figures 3, 4 from the publication of Ghannam and Esmail [1] show plots for viscosity- shear rate and shear stress-shear rate relationships of aqueous solutions of CMC, which their concentrations ranged by weight % to 1 - 5 % CMC. The behavior of the sample of 5% solution was identical to that in figures (4-1) and (4-2) for the same concentration. It is important to apply a constant shear rate through the flow field during the measurements to study the deformation of molecules as a function of shear rate, and the best tool for providing this is the cone and plate fixtures on a rotational rheometer such as Haake-RS100. The windows software provided with the



**Figure (4-1) : Flow behavior curves of CMC solutions**

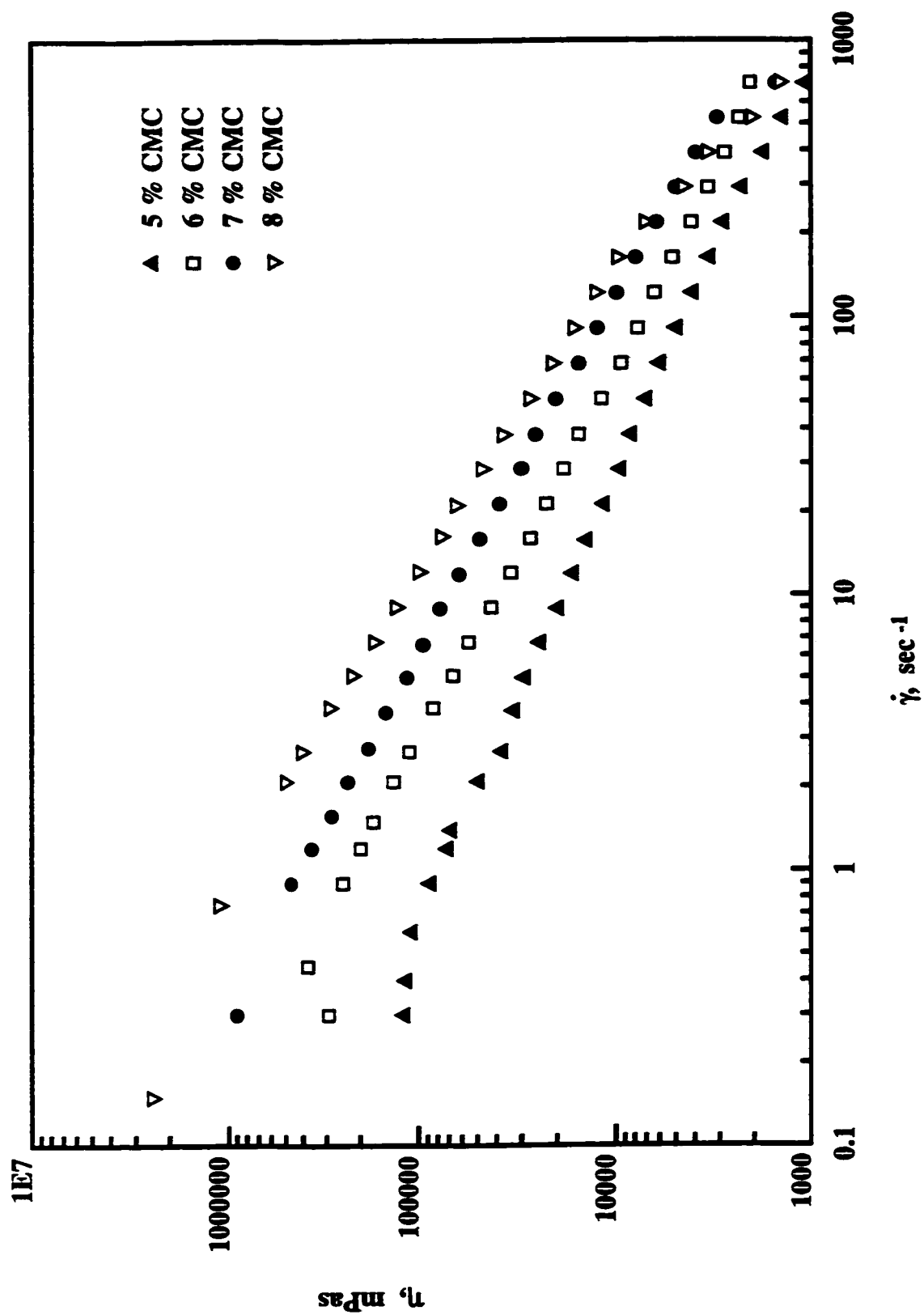


Figure (4-2) : Viscosity curves of CMC solutions.

RS100 rheometer was a very helpful tool for the handling and evaluation of results. In order to determine the best-fitting option in the evaluation of the results, the Ostwald- de- Waele equation is used as the suitable model. It can be written as:

$$\tau = k (\dot{\gamma})^n \quad (4-1)$$

Where:  $\tau$  = Shear stress, Pa  
 $\dot{\gamma}$  = Shear rate, sec<sup>-1</sup>  
 $k$  = consistency index, Pa s<sup>n</sup>  
 $n$  = flow behavior index

Rheologically, table (4-1) shows both  $k$  and  $n$  constants of the Ostwald-de-Waele equation for concentrations from 5 - 8 % CMC and indicates the drop of flow behavior index from (0.38-0.092). This also is a clear indication of the strong Pseudoplastic behavior of CMC concentrations above 5 %. On the other hand, the evaluation of the flow curve measurement confirms that the power law model is the best fit for CMC concentration range 5% to 7%. The analysis is mathematically illustrated in table (4-1). An 8% CMC concentration is the point where the hyperbolic model should be used over the Power law model.

Power law model equation:  $Y = a \cdot X^b$  (4-2)

Hyperbolic model equation:  $Y = a \cdot b/X$  (4-3)

**Table (4-1): Flow curve equation constants of CMC% solutions.**

**A: Rheologically: “Ostwald-de-Waele model”**

| CMC% | K   | n     |
|------|-----|-------|
| 5    | 75  | 0.38  |
| 6    | 200 | 0.28  |
| 7    | 410 | 0.21  |
| 8    | 880 | 0.092 |

**B: Mathematically: “Power law model”, and “\* 8 at Hyperbolic model;**

| CMC% | K    | n    |
|------|------|------|
| 5    | 75   | 0.38 |
| 6    | 200  | 0.28 |
| 7    | 410  | 0.21 |
| * 8  | 1300 | -150 |

In figure (4-2), the viscosity curve for each concentration appears to be in shear thinning behavior that drops in the range of 1000,000 - 100,000 mPa.s at low shear rates for the CMC concentration set to a low viscosity range close to 1000 mPa.s. It is clear from figure (4-2) that from the gradual increase in shear

rate from  $0.15 - 300 \text{ sec}^{-1}$ , the lines of all the concentrations (5 - 8 %) are getting closer to each other. Moreover, at high shear rates, a viscosity curve of 7 % suddenly begins a strong drop to a lower viscosity following that on the plot a similar drop for 8 % viscosity curve but at lower shear rate of  $300 \text{ sec}^{-1}$  where the mathematical model has been changed. The mathematical constants for the viscosity curve model " Power law " of CMC concentrations is stated in table (4-2).

**Table (4-2): Viscosity equation constants of CMC % solutions:**

**A: Rheologically: " Ostwald-de-Waele "**

| CMC% | K      | n     |
|------|--------|-------|
| 5    | 75000  | 0.38  |
| 6    | 200000 | 0.28  |
| 7    | 410000 | 0.21  |
| 8    | 880000 | 0.092 |

**B: Mathematically:        " Power law model "**

| CMC% | K      | n      |
|------|--------|--------|
| 5    | 75000  | - 0.62 |
| 6    | 200000 | - 0.71 |
| 7    | 410000 | - 0.78 |
| 8    | 880000 | - 0.91 |

The flow and viscosity behavior of CMC concentrations higher than 5% become complex due to their effect on the molecular structure. This trait is of importance to the commercial industry using CMC. In addition, it is important to closely investigate the flow curve behavior of the concentration used in order to solve any hydrodynamic problems related to the flow of the material and to predict its potential degree of success in its application.

## 4.2 Transient Shear Stress Response

Transient rheological behavior is a very characteristic time effect, leading to a complex relationship between stress and rate of deformation. Transient shear flow provides more information about the viscoelastic response of the material than can be obtained in the shear stress experiments. Stress overshoot can occur if the shear rate is sufficiently high. For polymeric liquid and concentrated solutions, the overshoot can be explained in terms of a transient entanglement network. These entanglements are the local interaction between the macromolecules that are continuously being destroyed and reformed at rates depending on the deformation field.

In linear viscoelasticity, i.e., when the deformation is slow or small, the stress function grows until a steady state is reached. If the rate of deformation is large enough, the equilibrium entanglement density becomes strain-rate dependent, and non linear viscoelastic behavior is observed. Initially, the stress growth function follows the curve of linear viscoelasticity until a critical strain,  $(\gamma_{\max})$  is reached where maximum stress is observed.

In a regular liquid, applying a constant shear rate leads to the beginning of immediate flow. The rheological liquids and from the graphs in figures (4-3) to (4-6), one can easily notice the slowly developing shear stress at low shear rates in different time intervals and that this interval becomes shorter if shear rate is increased. After this time interval, a constant shear stress response is reached

and the flow is called steady when the shear stress continues to remain constant with no inertial effect, and drops to zero when flow is stopped. Transient behavior time can be long and comparable with the flow duration. Therefore, in some cases it is a mistake to characterize properties of a liquid only by its flow curve. For this reason, it is important to study the relationship between  $(\tau, \dot{\gamma})$  after the completion of transient processes to describe and understand their cause and effect.

In this work, the transient response test was carried out with the RS100 rheometer. The controlled rate (CR) mode and time curve option for a duration of 5 minutes for each shear rate was applied on the samples. The shear stress results was  $\tau = f(t)$  at constant shear rates ranging from  $0.15 - 500 \text{ sec}^{-1}$  for each CMC concentration. These plots show the existence of the rheopexy behavior which is a time dependency of shear stress and that shear stress increases rapidly to a constant value for each concentration tested. Rheopexy is a characteristic behavior of viscoelastic liquids of a thixotropic structure and is due to the limited structural breakdown at low shear rates. CMC concentration at shear rates higher than  $10 \text{ sec}^{-1}$  do not exhibit rheopexy as shown by this test, even for this high range of concentration. The gradual increase or decrease in the resulting shear stress can be attributed to the structure recovery. Transient shear stress responses were detected for all the concentrations over different time intervals. For a 5 % CMC solution, the response was identical to the one plotted in figure 5 in the Ghannam and Esmail [1] publication for low shear rates. Figures (4-3) to (4-6)

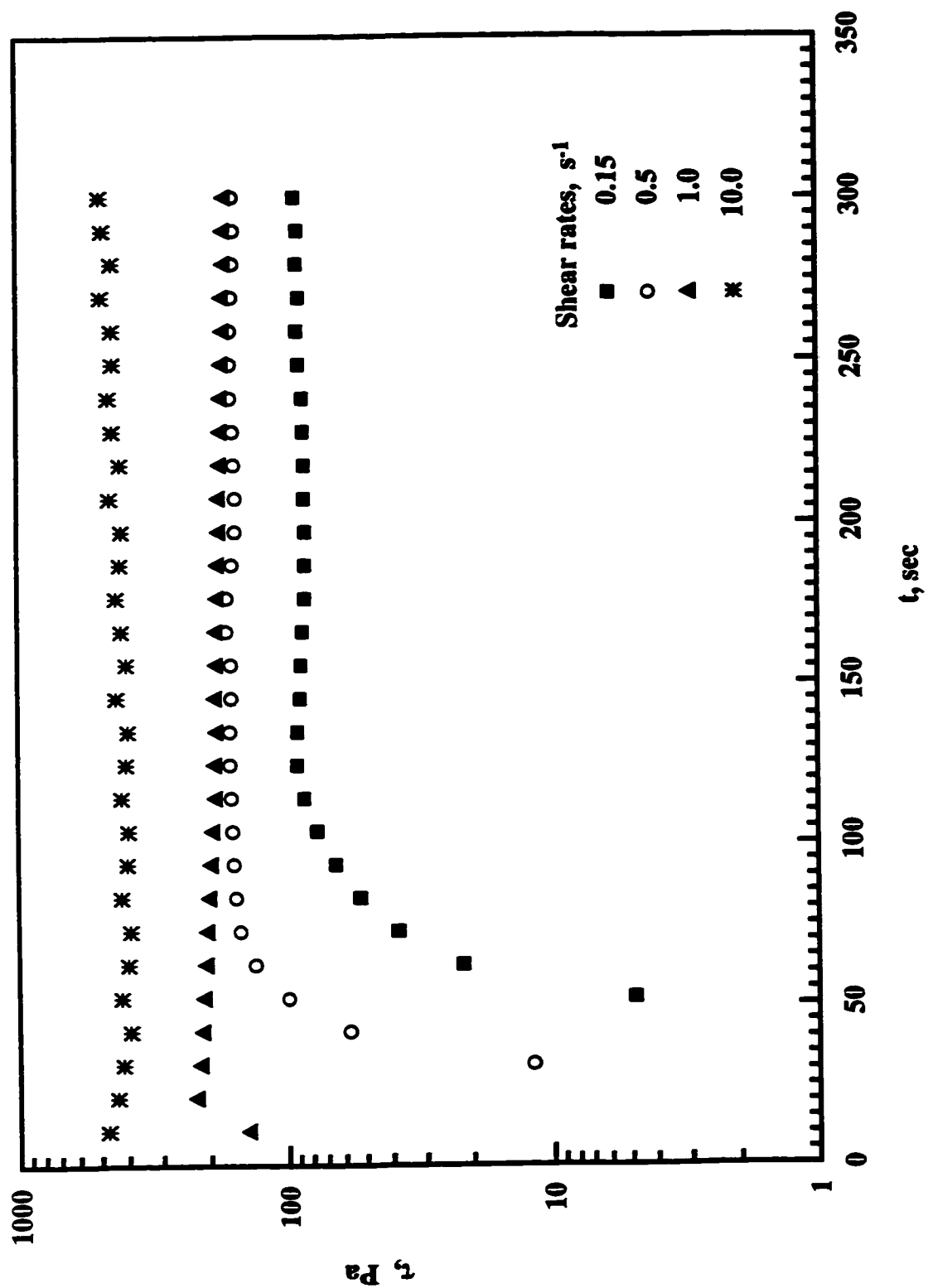
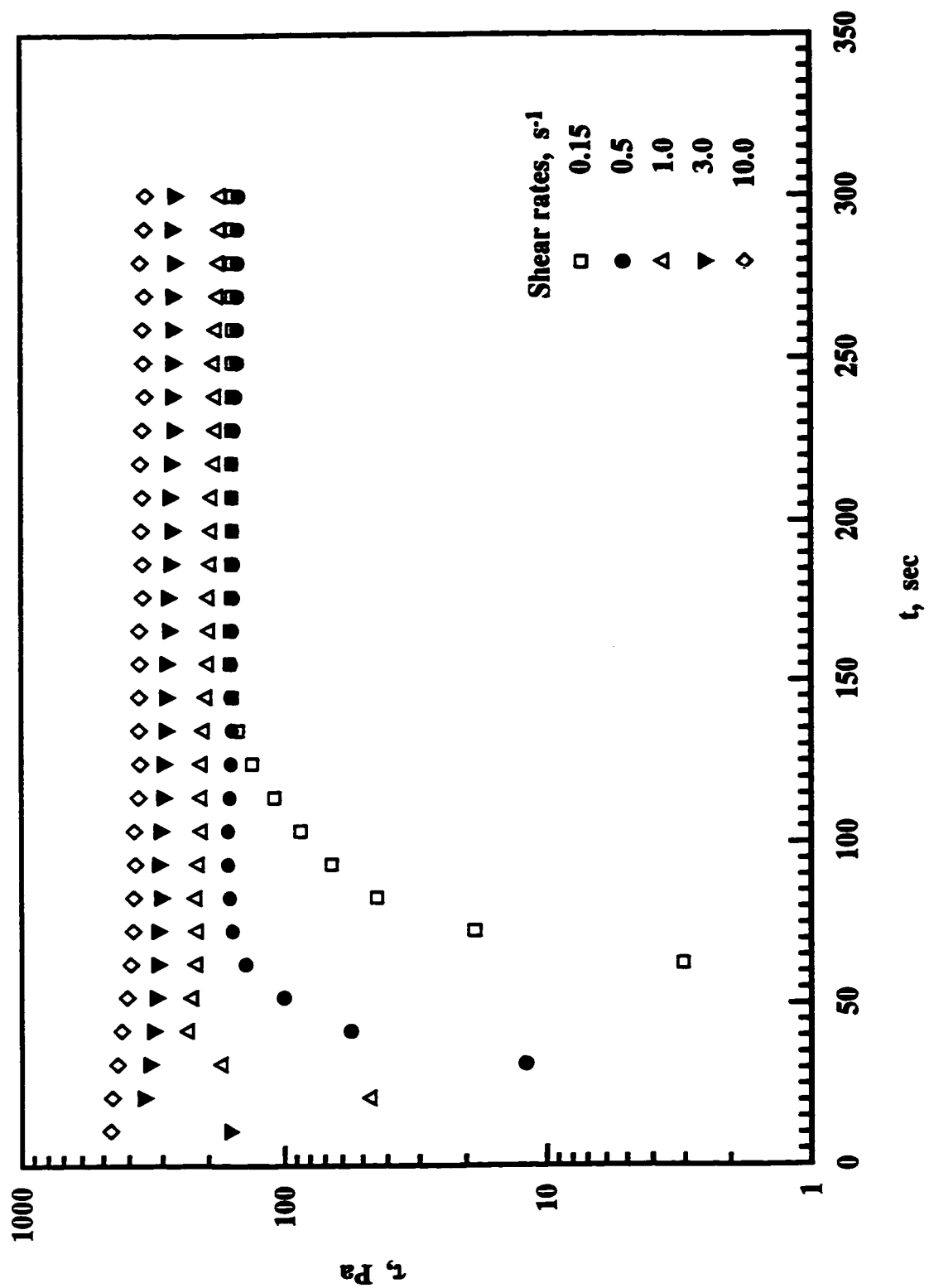
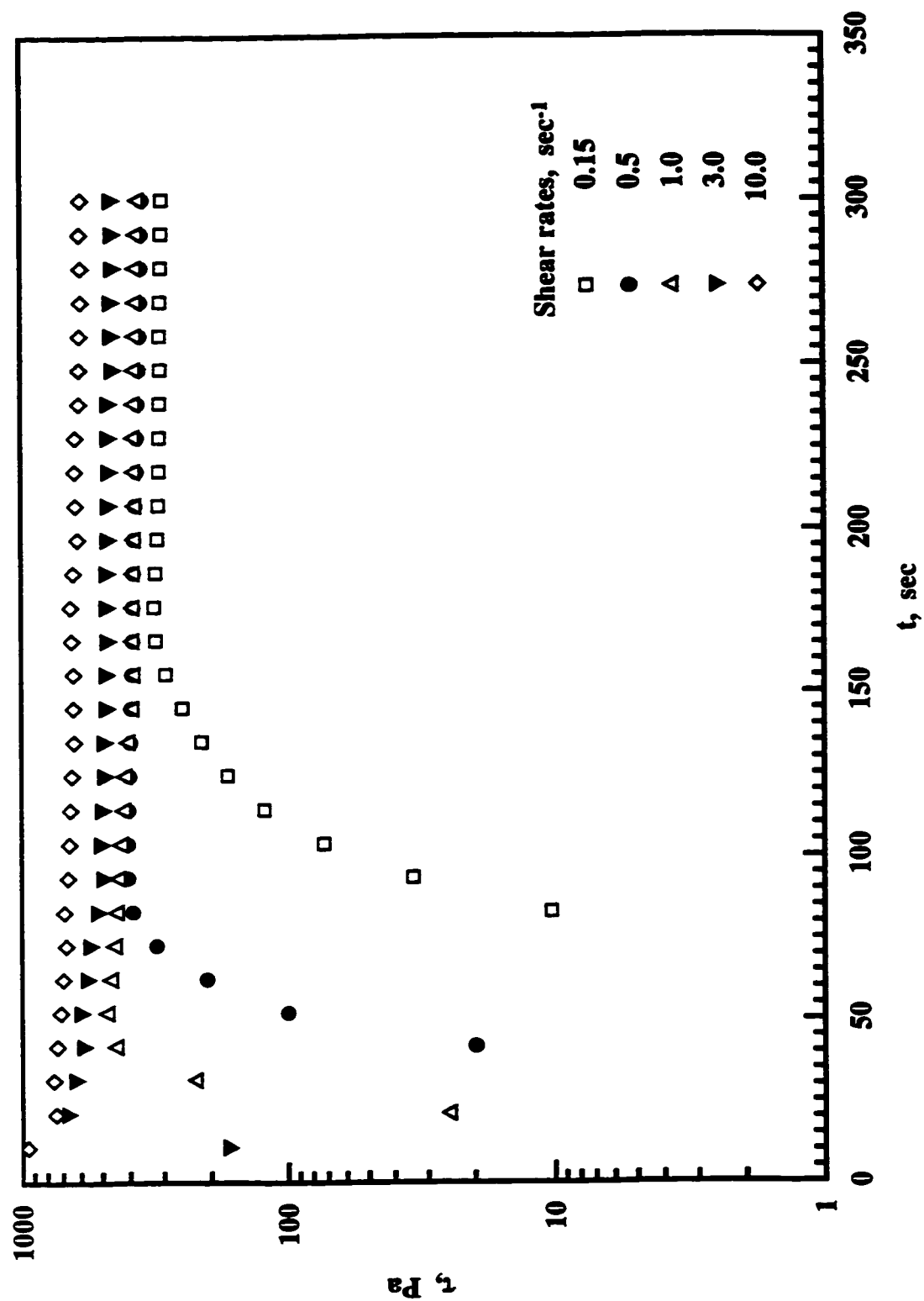


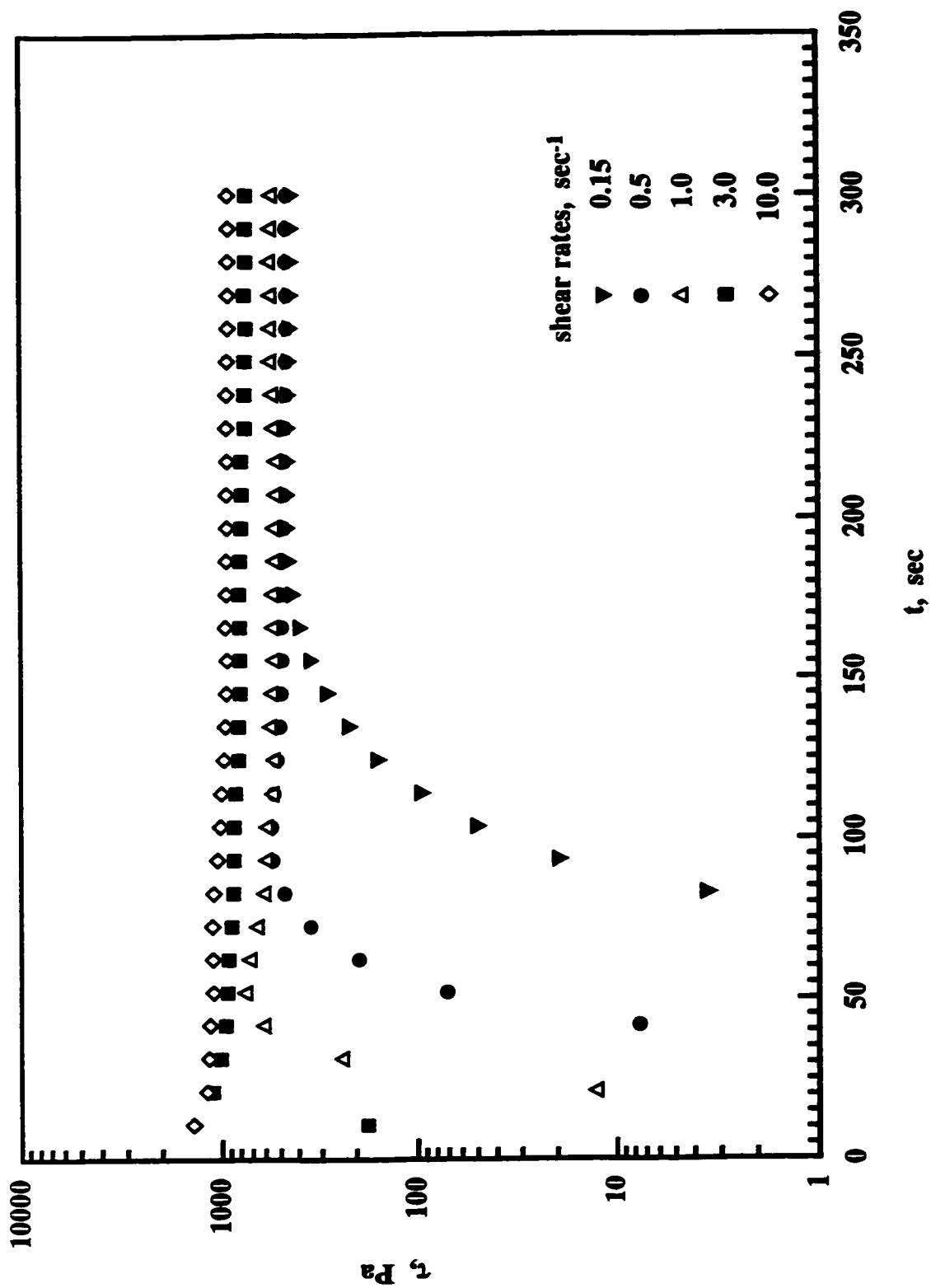
Figure (4-3) : Transient shear stress response of 5 % CMC.



**Figure (4-4) : Transient shear stress response of 6 % CMC.**



**Figure (4-5) : Transient shear stress response of 7% CMC.**



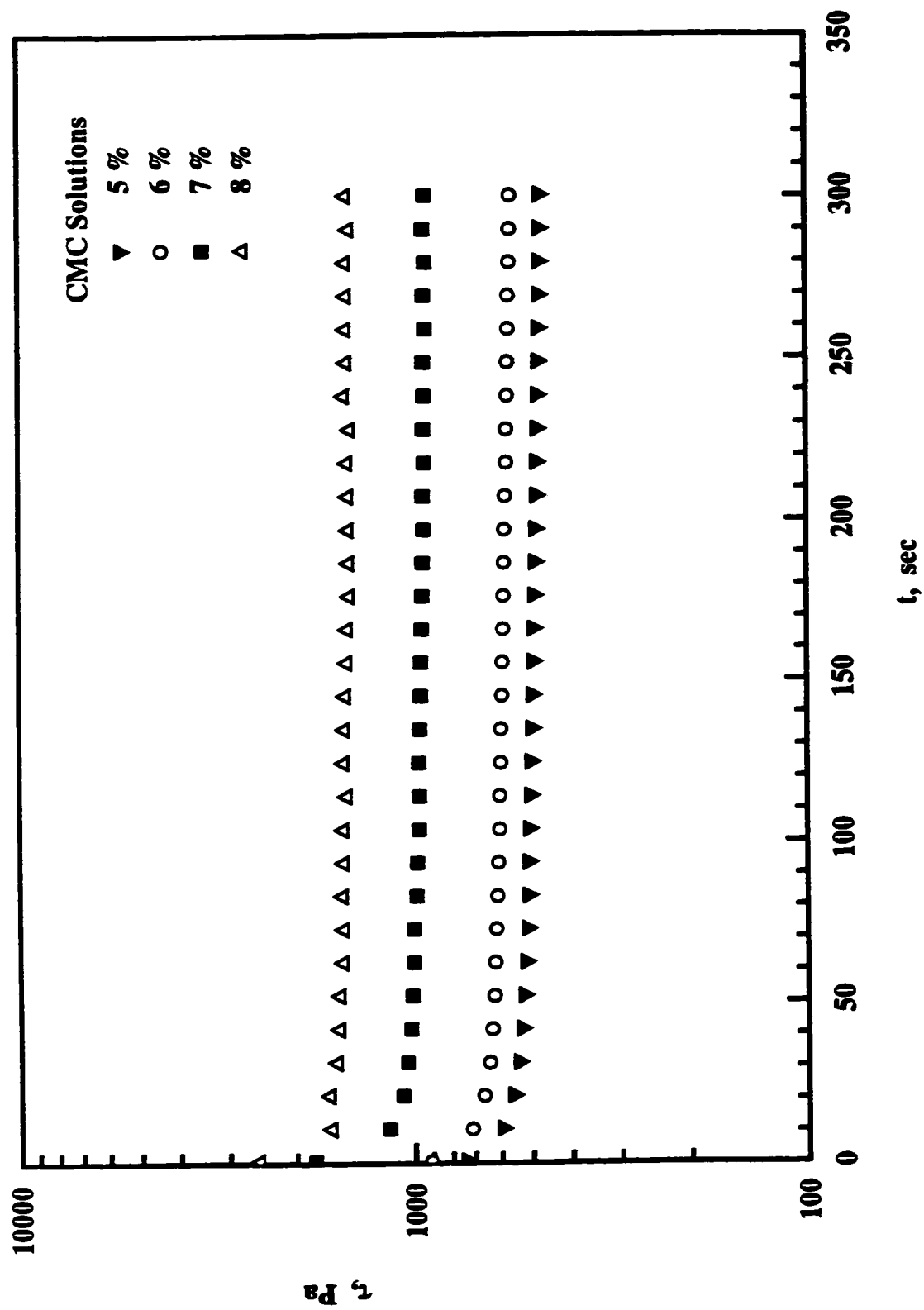
**Figure (4-6) : Transient shear stress response of 8 % CMC.**

of this study show that the steady response of shear stress was reached depending on the concentration of CMC sample, and the shear rate applied over different time durations as illustrated in table (4-3).

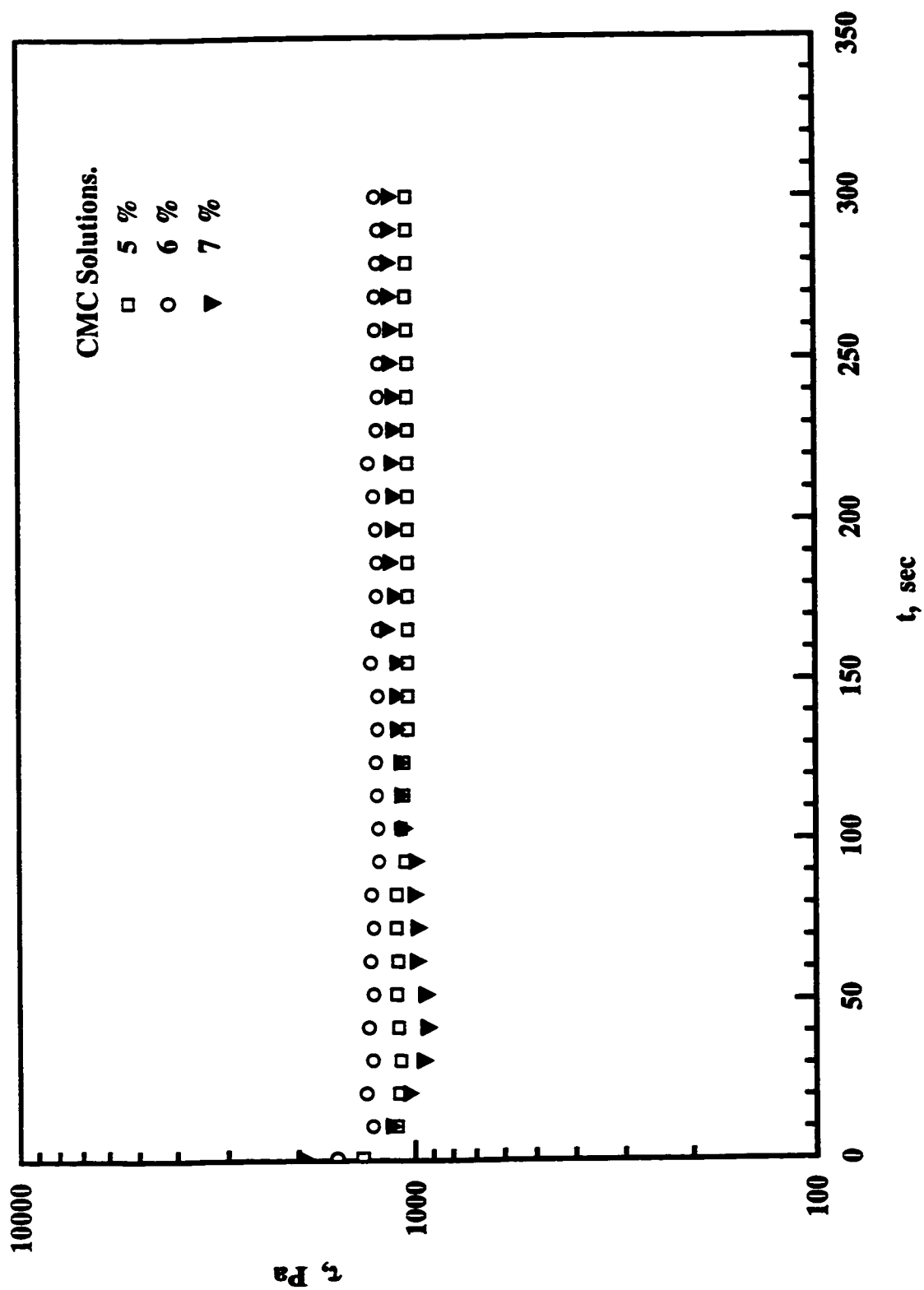
**Table (4-3): Transient shear stress responses at low shear rates for high CMC concentrations.**

| CMC % | Shear rates, $\text{sec}^{-1}$ |        |       |       |
|-------|--------------------------------|--------|-------|-------|
|       | 0.15                           | 0.5    | 1     | 3     |
| 5     | 25sec                          | 85sec  | 25sec | -     |
| 6     | 145sec                         | 90sec  | 40sec | 20sec |
| 7     | 170sec                         | 100sec | 55sec | 25sec |
| 8     | 195sec                         | 115sec | 65sec | 30sec |

The only response was detected for shear rates applied over  $10 \text{ sec}^{-1}$ , a shear stress overshooting in the first 30 seconds of  $100 \text{ sec}^{-1}$  shear rate applied as can be noticed in figure (4-7). No definitive trend response was found when shear rate reached a high range as plotted in figure (4-8) where the shear rate applied on the samples was  $500 \text{ sec}^{-1}$ . This may be due to the structural breakdown at the high shear rates exerted.



**Figure (4-7) : Transient shear stress response at shear rate of (100 sec<sup>-1</sup>) for CMC.**



**Figure (4-8) : Transient shear stress response at shear rate of ( 500 sec<sup>-1</sup> ) for CMC.**

### **4.3 Thixotropy Test**

Thixotropy of a material can be defined as the tendency of a substance to change from a gel state with high viscosity to a lower viscosity as a result of applying a high shear rate. An important characteristic of thixotropy is its capacity to re-thicken when the material is left at rest. Viscosity of some materials changes due to the occurrence of structural transformations when shear is applied and may continue to change after the cause of the structural deformation is ceased. Generally, changes in material properties can be reversible, but some changes are irreversible and permanent. In the case of viscoelastic fluids, there is a complication with their thixotropy structure in the nonlinear region due to the reversible change of their microstructure that responds to exerted shear. For that, one has to understand the original definition of thixotropy, which mainly is the reversible change from a flowable fluid to a solid like elastic gel. The practical use of materials in paints, coatings, adhesives, etc., rely upon the properties of viscosity such as the increase in the rested state and its decrease in the case of applying a constant shear rate. Moreover, these kind of materials are time-dependent fluids, which means that their thixotropic structure can be broken-down in a matter of seconds but takes hours to fully recover to a gel state. Rheologists study thixotropy-agitation time relationship in order to have a clear picture of the material's behavior. In paints, for example, full recovery to a gel structure is needed as fast as possible to prevent the paint layer from sagging off

the wall. In another example, additives are added to drugs to get a thixotropic syrup that prevents dissolving or separation of drugs from the syrup base.

The best way to study thixotropy of materials is by performing a loop test. This involves increasing the shear rate linearly from minimum to maximum value and then returning it back to the minimum value that the rheometer being used can apply. This test is repeated on the same sample to get a second and third or more up-and-down cycles. The loop test must be repeated in order to avoid the danger of the thixotropic structure breakdown not having been achieved in one cycle. Solution status of a gel thixotropic material is an important point to get when the hysteresis areas of up-and-down curve cycles decrease till they coincide and the area is zero, where the thixotropic structure is completely destroyed. The hysteresis area is known to be the measure of thixotropy and it is the area between the up-and-down curve in the plot of  $\dot{\gamma}$  -vs.-  $\tau$ .

The test for thixotropy done for this study was carried out using the RS100 rheometer in the mode of controlled shear rate, where the shear rate is programmed to increase from  $0.15 \text{ sec}^{-1}$ . This is the minimum value the apparatus can apply to its maximum value of  $700 \text{ sec}^{-1}$  to give the up curve. The down curve is immediately ramped down from  $700 \text{ sec}^{-1}$  shear rate to  $0.15 \text{ sec}^{-1}$  in the same time as the up one. CMC concentrations of 5 - 8 % were used in the test samples to study any possible thixotropic behavior as a function of agitation time and concentration.

Two different techniques have been introduced in this test to check the behavior. The first technique involved agitating the sample by 60 sec, 100 sec, and 200 sec for each curve of the up-and-down cycle. In addition, Figure (4-11) illustrates the repeated cycles at 200sec period of shearing from  $0.15 - 700 \text{ sec}^{-1}$  and declining the shearing back from  $700 - 0.15 \text{ sec}^{-1}$  for another 200 sec period. This was repeated three times in order to show us an important approach of practical use of the material. This procedure has been applied for CMC sample concentrations of 5 - 8 %. Also, agitation times of 60 sec, 100 sec, and 200 sec that were programmed in CR mode as a test of three constant time parts. A shear ramp of  $0.15 - 700 \text{ sec}^{-1}$  was maintained in one test, then the shear rate was kept constant in the second part as time curve at  $700 \text{ sec}^{-1}$ , and finally in the third part it was allowed to ramp back from  $700 - 0.15 \text{ sec}^{-1}$ . This procedure was followed in the second technique of the thixotropy test for the CMC concentrations under study. The graphs in figures (4-15),(4-16), and (4-17) show the up-time curve-down curves applied in these techniques at 200-sec shearing time each.

All the CMC concentrations used in the study exhibited a thixotropic effect in both techniques, and confirm the transient test responses which have been demonstrated earlier as a dependent-time material. Furthermore, the conclusion of steady state test, that the high CMC solutions revealed a shear thinning or pseudoplastic material behavior, is confirmed by showing the thixotropic response in this test.

The integral of the areas under the up and down curve can be easily calculated by using the computer software provided with the Rheometer RS100 under the evaluation option. The software has the ability to calculate the areas under both up and down curves and print the thixotropic area after subtracting one area from the other. Thixotropic area (A) indicates the energy required to break down the thixotropic structure of the material.

$$\begin{aligned}
 A &= \tau * \dot{\gamma} \text{ (Pa 1/sec) } = \text{N/m}^2 \cdot \text{l/sec} = \text{N.m/sec l/m}^3 & (4-4) \\
 &= \text{Work /shear time} * 1/\text{volume} \\
 &= \text{Energy per unit volume.}
 \end{aligned}$$

Results from the first and second techniques of thixotropy test reveal an existence of variation in the thixotropic areas for the CMC concentration with shearing time. Obviously, by comparing the results obtained in tables (4-4), (4-5), and (4-6) and in figures (4-9) and (4-10) one can find out that for a given shearing time, the thixotropic area of the CMC gels increases proportionately with the CMC concentrations used. The enclosed areas of the curves obtained were considerably large for this high rank of concentration with a very high viscosity. Evaluation of figures (4-9) and (4-10) shows the relationship of the obtained thixotropic hysteresis areas, kPa/sec, with the time of agitation, sec, and CMC concentration. The areas are higher for the higher concentrations. The significant increase in their viscosity can be the reason for that. Moreover, an important aspect must be pointed out that for each curve in figures (4-9) and (4-10), the area decreases with the increase of the shearing time for all CMC

concentrations and this decrease gets sharper with increasing concentrations.

**Table (4-4): Thixotropy hysteresis areas ( kPa/ sec) for the first technique  
" one cycle of up and down curves" :**

| Conc. \ Time | 5 % | 6 % | 7 % | 8 % |
|--------------|-----|-----|-----|-----|
| 60 sec       | 96  | 135 | 328 | 526 |
| 100 sec      | 81  | 122 | 269 | 410 |
| 200 sec      | 78  | 119 | 222 | 317 |

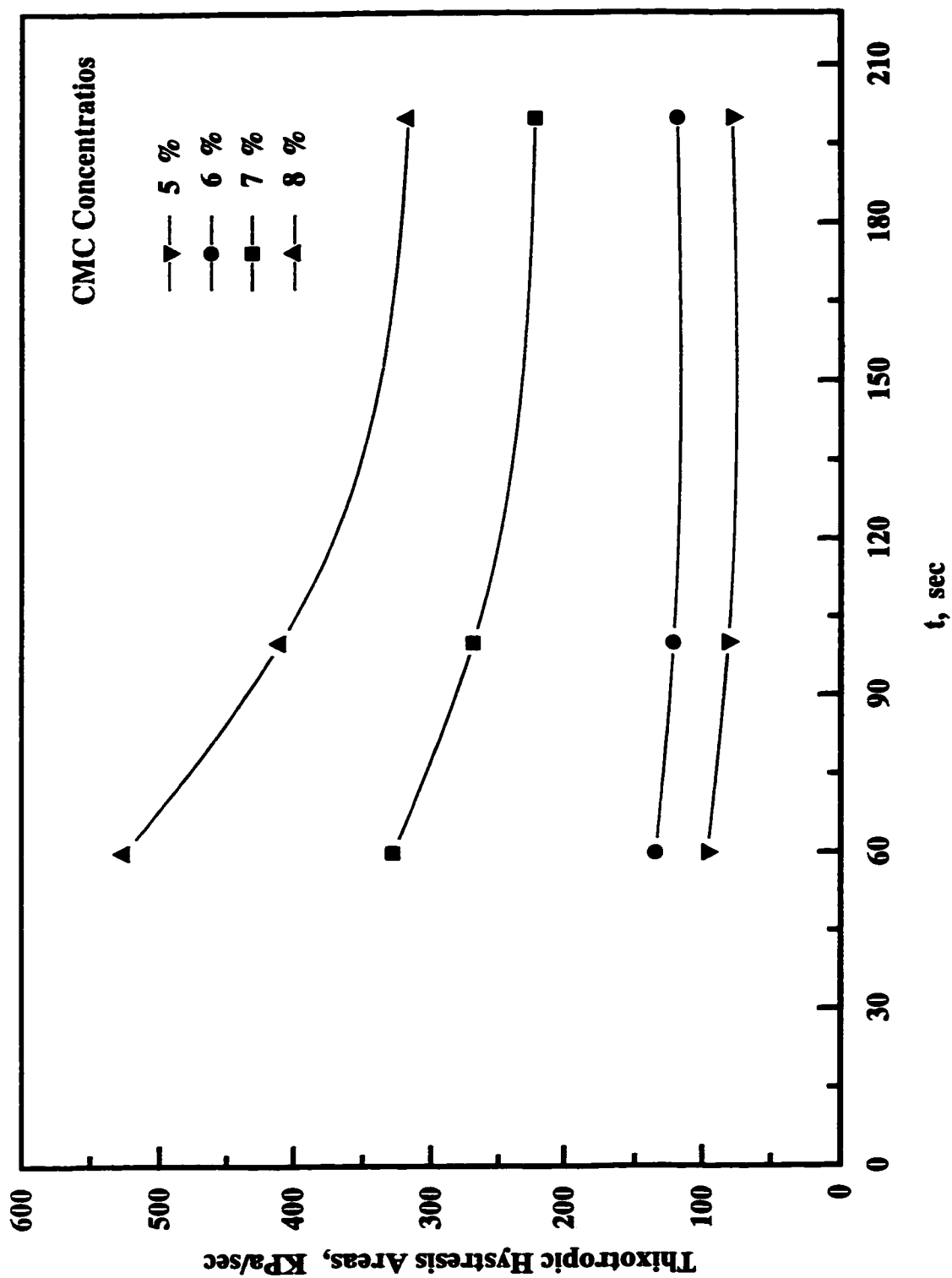
**Table (4-5): Thixotropy hysteresis areas ( kPa/ sec) for the first technique  
" Three cycles of up and down curves" :**

| Conc. \ Time | 5 % | 6 % | 7 % | 8 % |
|--------------|-----|-----|-----|-----|
| 200 sec      | 142 | 209 | 340 | 674 |

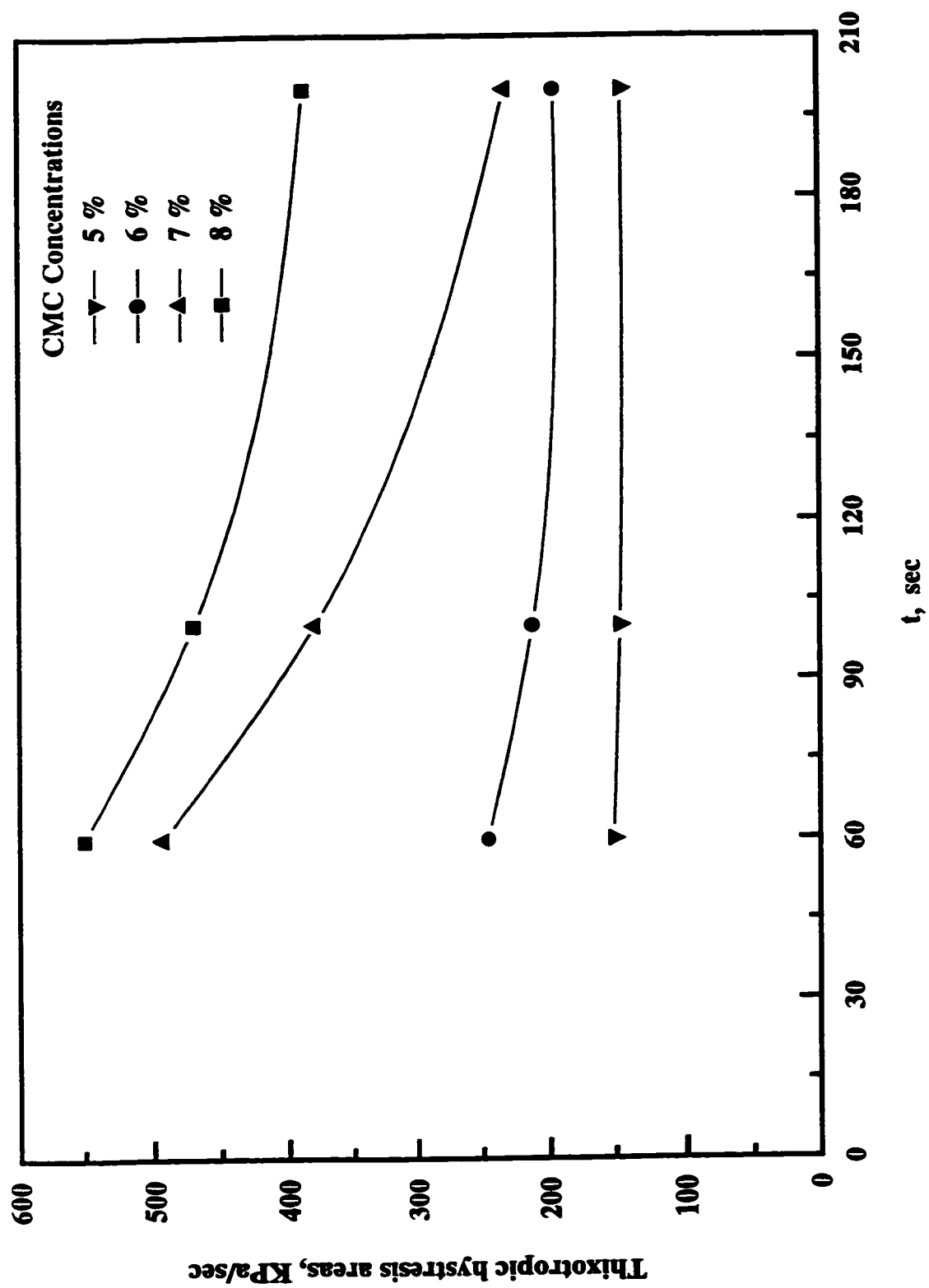
**Table (4-6): Thixotropy hysteresis areas ( kPa/ sec) for the second technique  
" the cycle of up - time curve - and down curves":**

| Conc.<br>Time | 5 % | 6 % | 7 % | 8 % |
|---------------|-----|-----|-----|-----|
| 60 sec        | 151 | 245 | 493 | 550 |
| 100 sec       | 146 | 212 | 380 | 470 |
| 200 sec       | 144 | 195 | 231 | 387 |

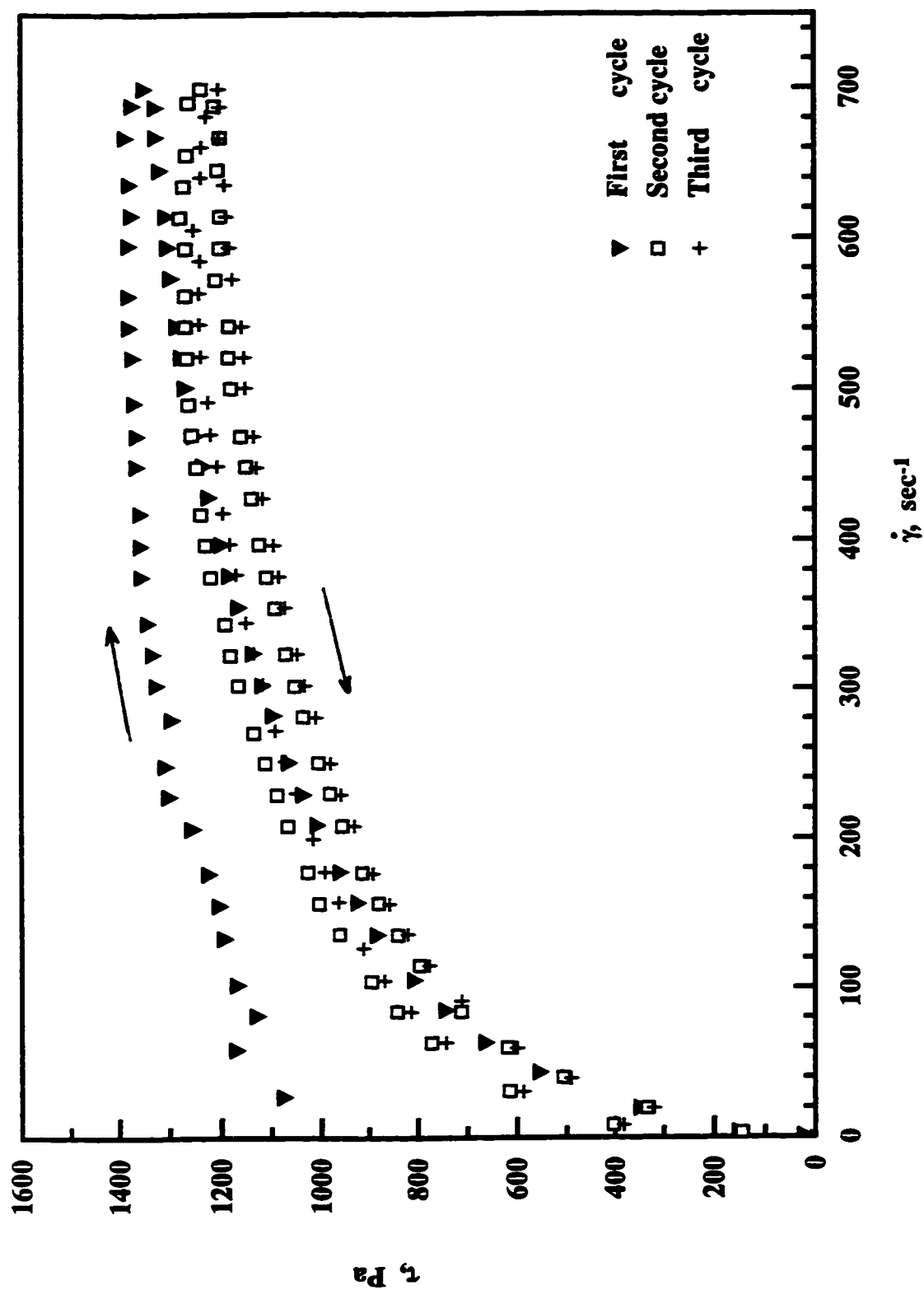
Another significant fact to be taken into account is the relationship of shear stress behavior with the increased CMC concentration in the thixotropy test as illustrated in figures (4-11) to (4-17). Figures (4-13) and (4-14) show the first technique results with shear time = 200 sec for 7% and 8%. They both show a decline of the up curve after 350 sec of shearing time in the 7 % sample and 200 sec for the 8 % sample. The second technique used in the thixotropy test as illustrated in figures (4-16) and (4-17) confirms the result of the first technique that shear stress is affected by an increase in the concentration of CMC.



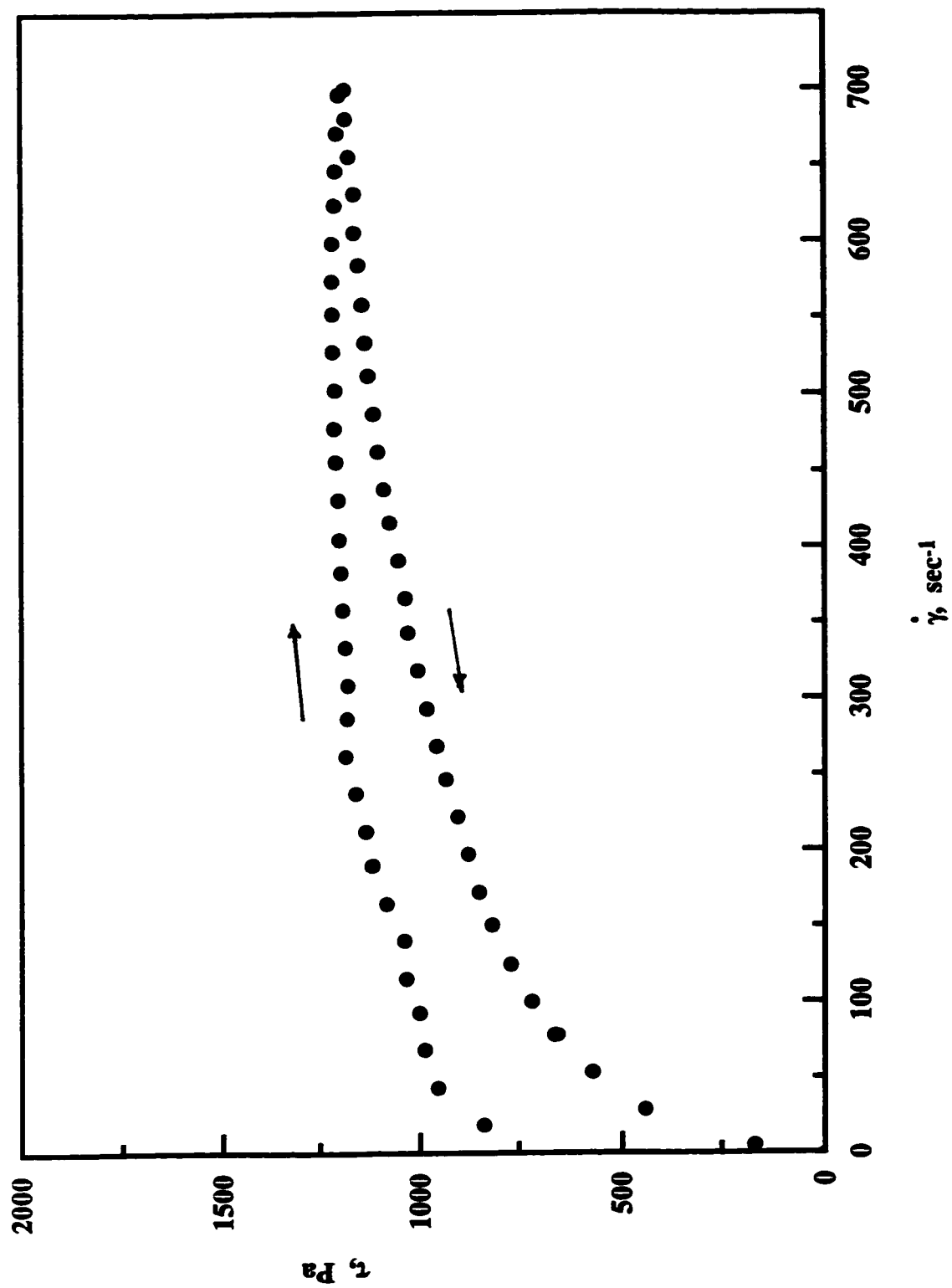
**Figure (4-9) : CMC Thixotropic Hysteresis Areas by the first technique**



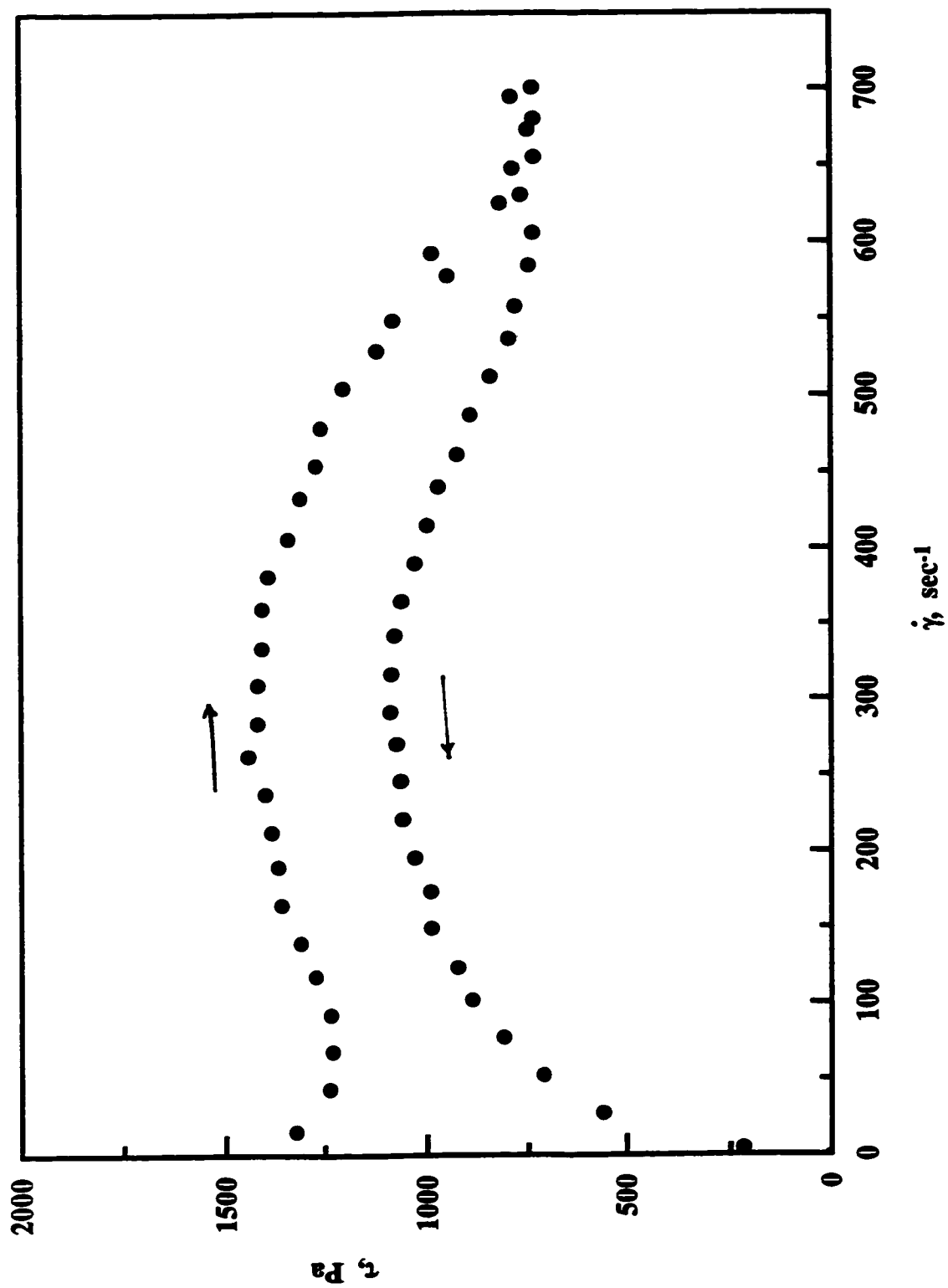
**Figure (4-10) : CMC Thixotropic Hysteresis Areas by the second technique.**



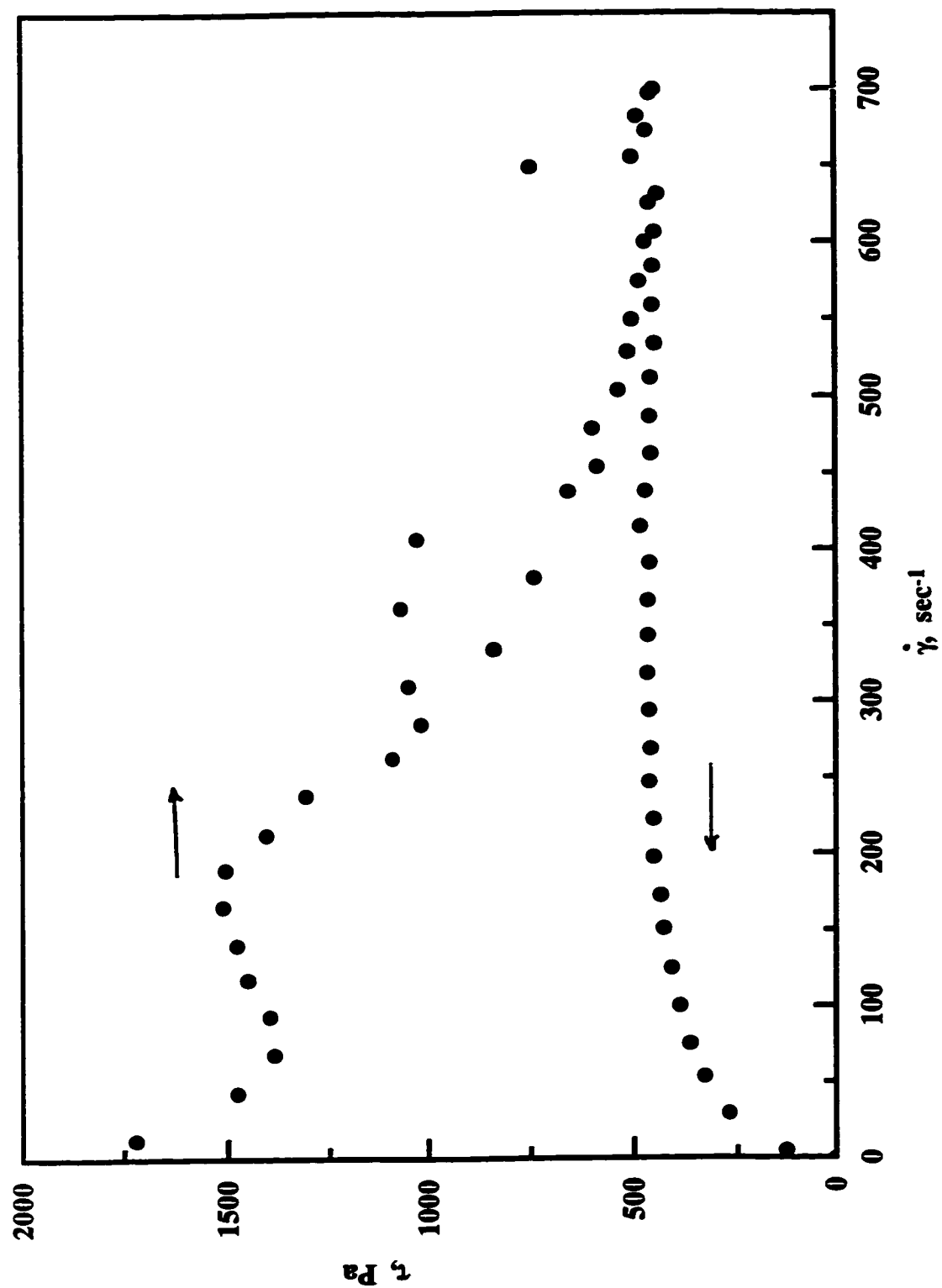
**Figure (4-11) : Thixotropy - First technique - at 200 sec three cycles for 6% CMC.**



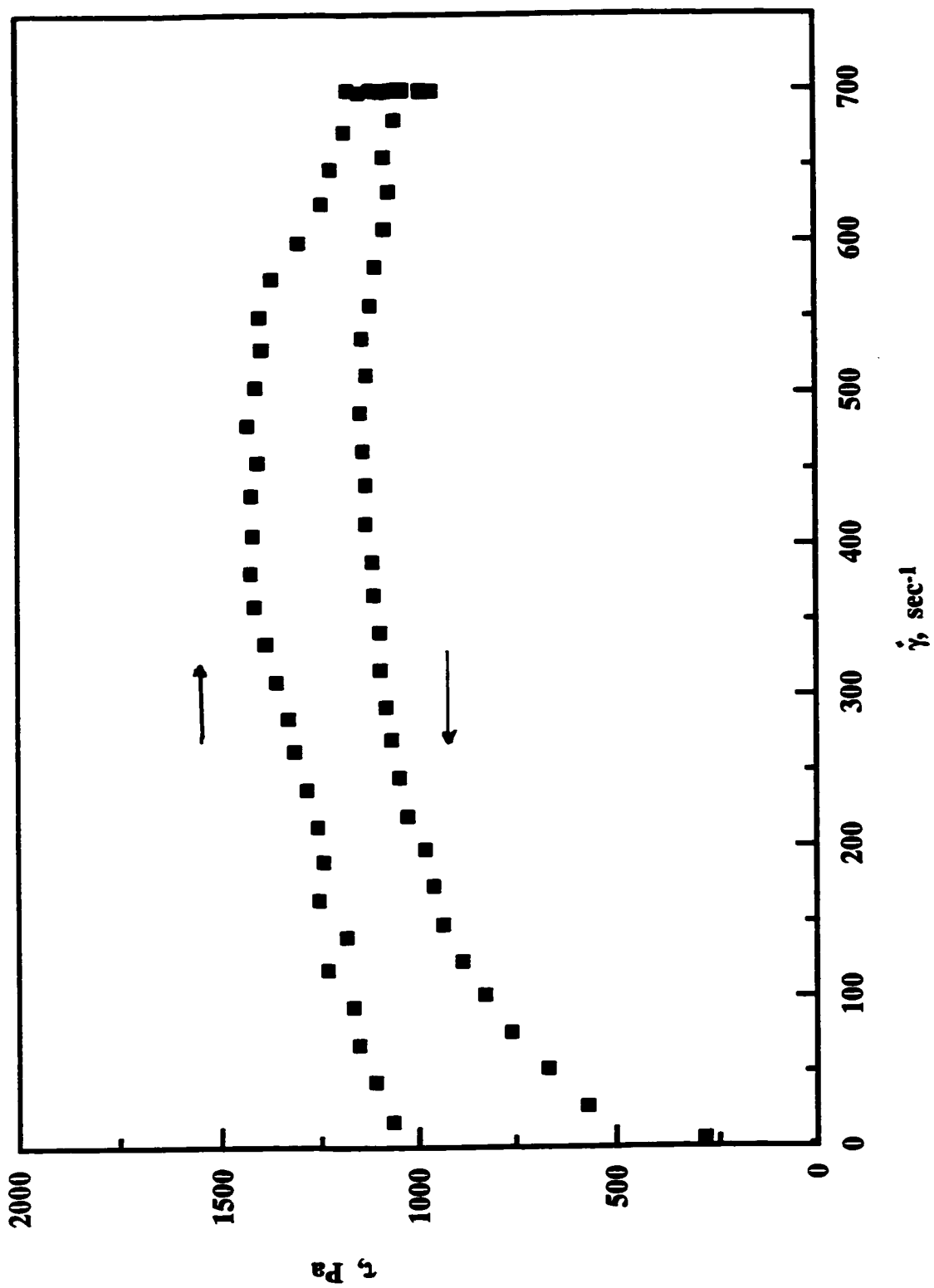
**Figure (4-12) : Thixotropy - First technique at 200 sec for 6 % CMC.**



**Figure (4-13) : Thixotropy curve - first technique at 200 seconds for 7 % CMC**



**Figure (4-14) : Thixotropy - First technique at 200 sec for 8 % CMC.**



**Figure (4-15) : Thixotropy - Second technique at 200 sec for 6 % CMC.**

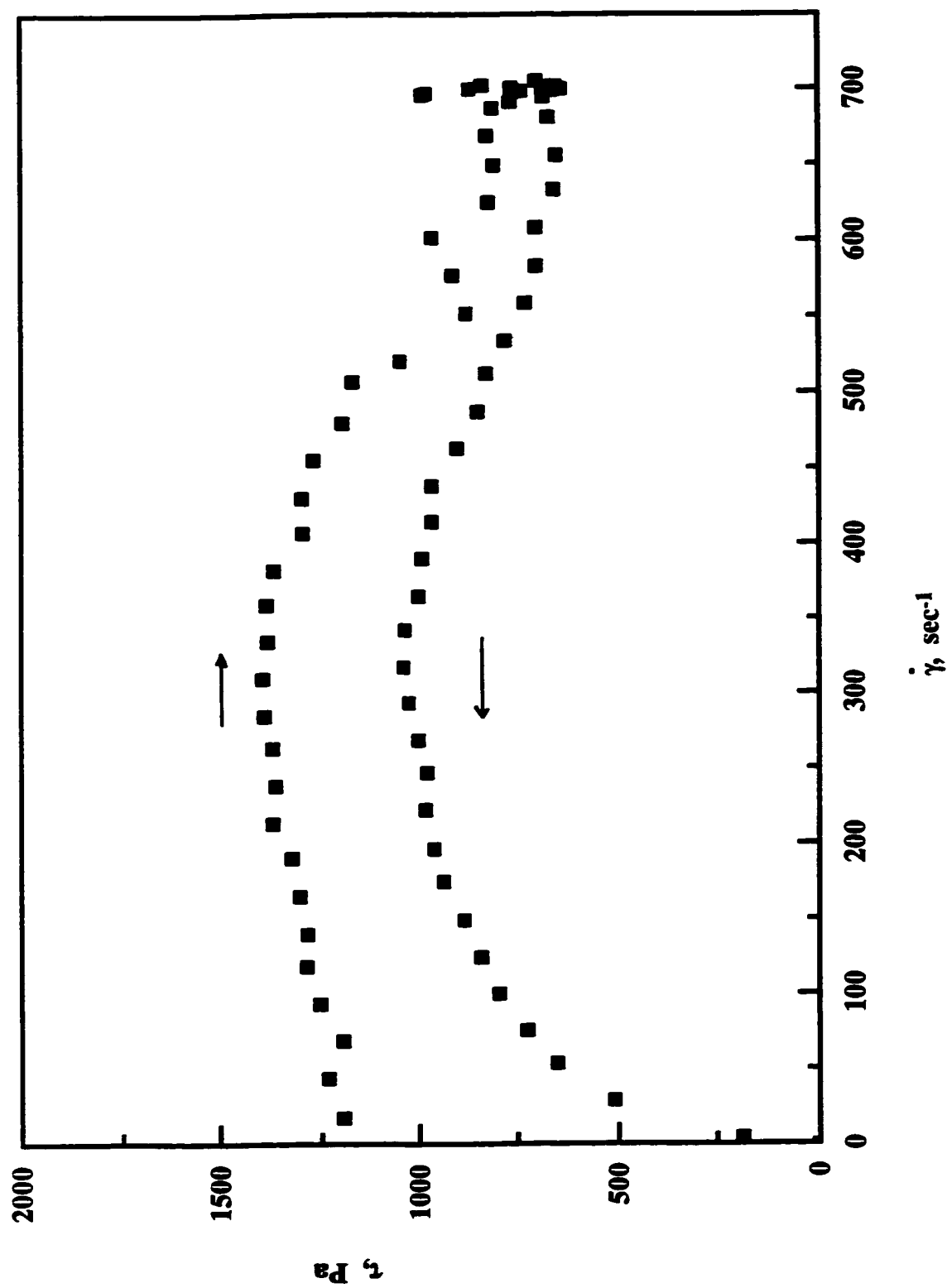
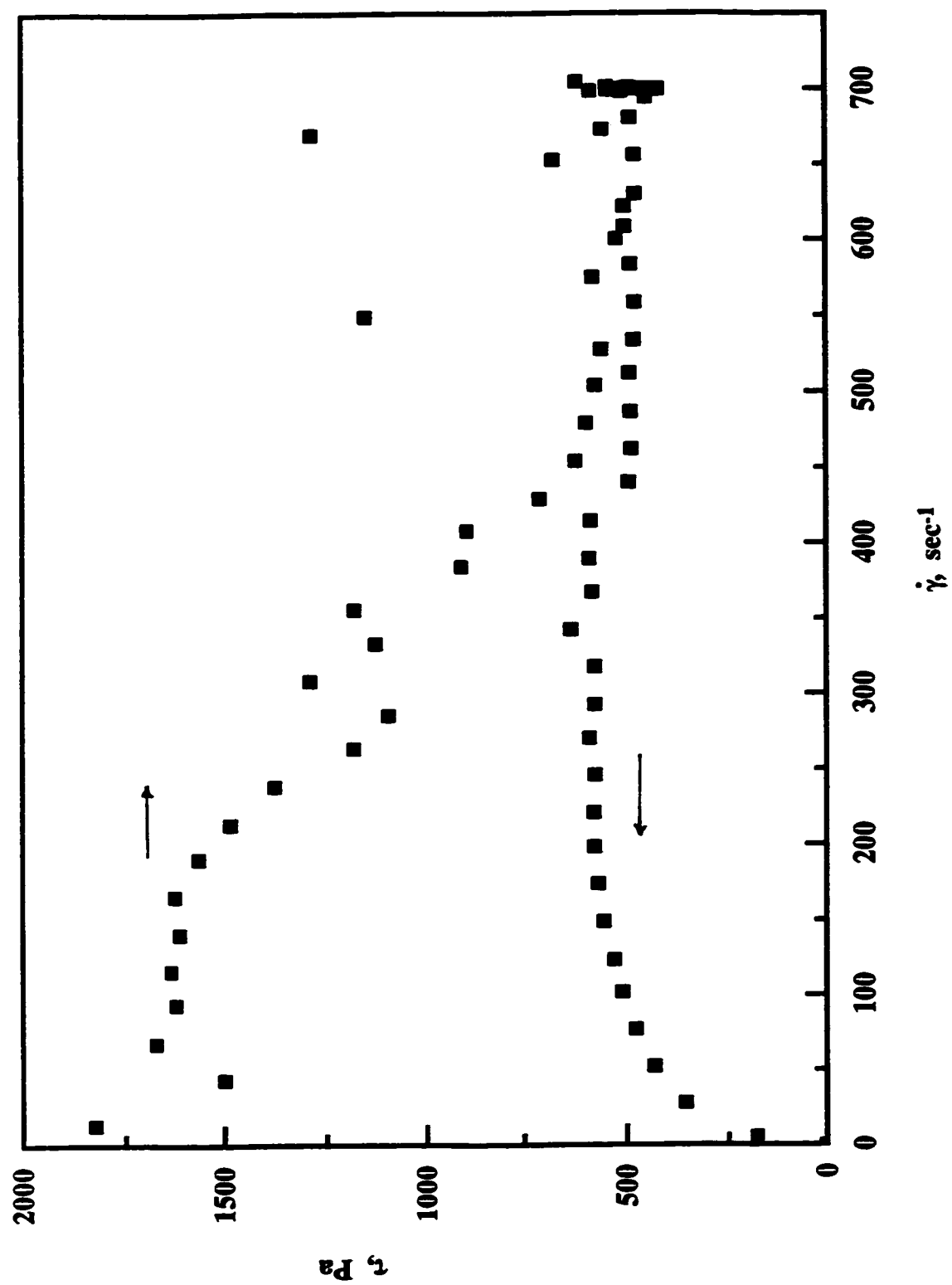


Figure (4-16) : Thixotropy - Second technique at 200 sec for 7 % CMC.



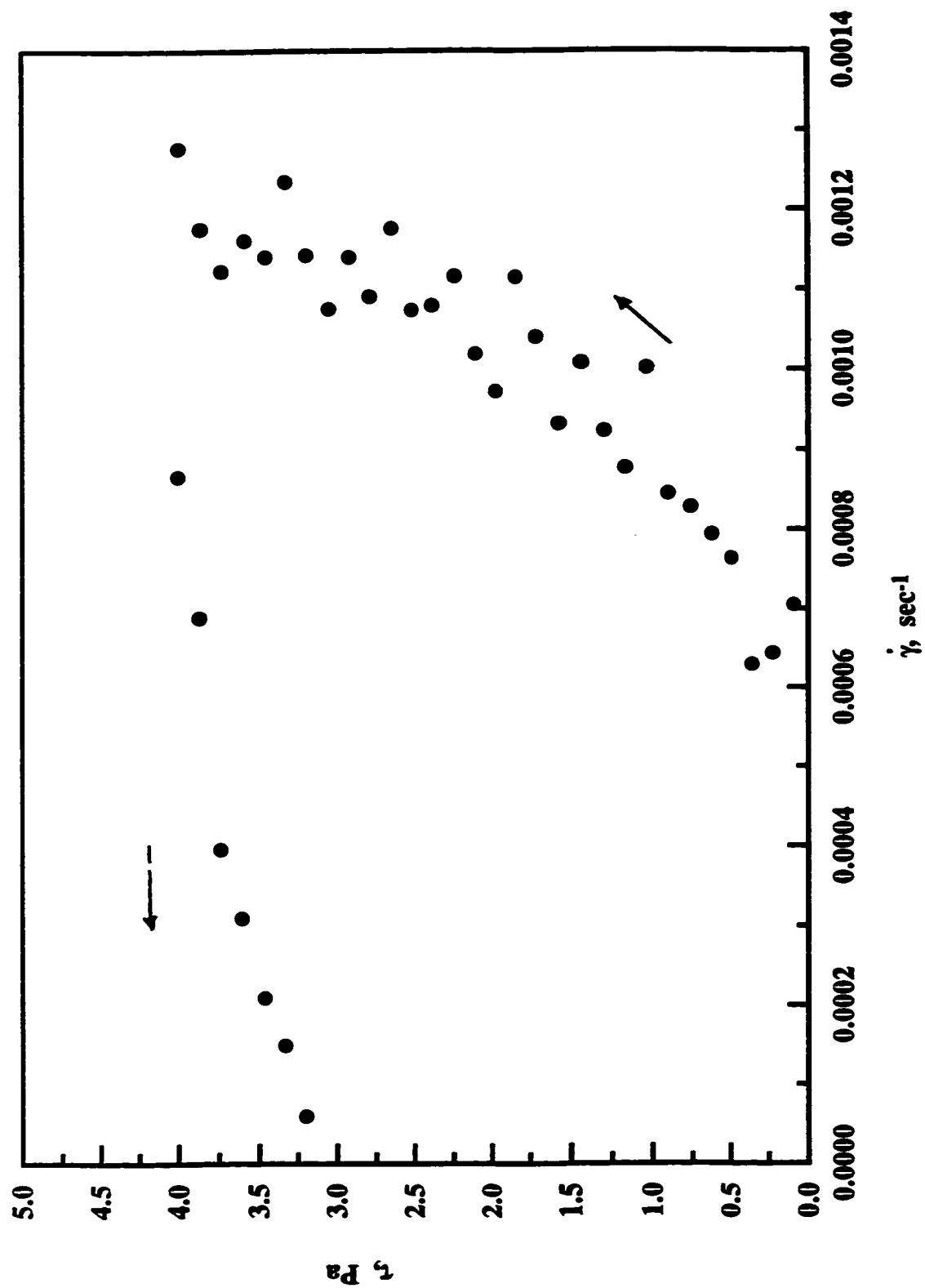
**Figure (4-17) : Thixotropy - Second technique at 200 sec for 8 % CMC.**

As a conclusion of the thixotropy test carried out on the CMC samples, there is an obvious build-up of areas of hysteresis when an increase of concentration is made. Large thixotropic areas were obtained due to a large increase in CMC viscosity with the increase of concentrations. Also, transient test results confirmed those of the thixotropy test that the CMC material is time-dependent and pseudoplastic.

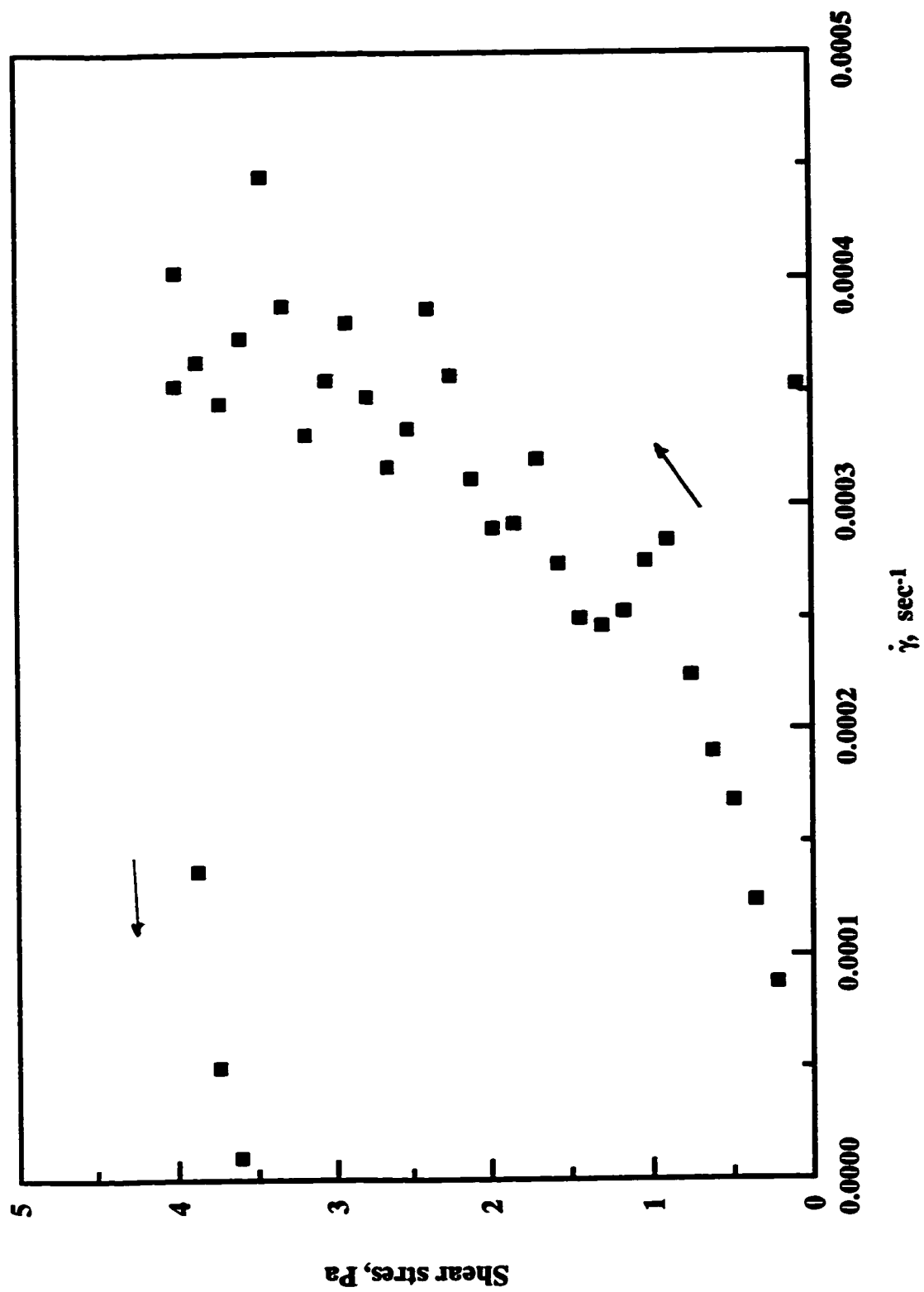
## 4.4 Yield Stress

Yield stress is the stress corresponding to the transition from elastic to plastic deformation  $\tau_y$  (Pa), or the limiting stress below which sample behaves as a solid. Also, it can be defined as the elastic deformation that disappears when the applied stress is released. In general, the yield point is the stress applied that causes unlimited deformation where the sample starts to flow. In this study, the yield test was performed using the RS100 rheometer in a controlled shear stress mode, and stress ramp option with 180 seconds per segment. The test shows the relationship of  $\tau = f(\dot{\gamma})$ , by applying two segments of gradual increase and follows that with an immediate decrease in shear stresses in three different tests. These segments were (0.09 Pa - 4 Pa - 0.09 Pa), (0.09 Pa - 50 Pa - 0.09 Pa), and (0.09 Pa - 100 Pa - 0.09 Pa) in 180 sec for each segment. These three separate tests were performed in order to detect any possible deformation behavior for the concentrations of CMC 5 - 8%. Yield stress has to be analyzed on the result plots of  $\tau$  -vs.-  $\dot{\gamma}$ , which are defined by conclusions from the literature [7-9]. Figure (4-21) shows the yield stress response for all the concentrations used. The test shows that higher concentrations of CMC produce a higher resistance to flow even though the solutions showed no yield stress. This result is in agreement with the conclusion of the same test response for the low range of CMC concentrations as stated in figures 6, and 7 in Ghannam and Esmail [1]. The samples exhibit thixotropic behavior as they are sheared from (4 Pa - 0.09 Pa), or

(50 Pa - 0.09 Pa), or (100 Pa - 0.09 Pa) as illustrated in figures (4-18) to (4-21)  
and show yield point  $\tau_{o2}$ .



**Figure (4-18) : Yield stress response of 6 % CMC at (.09 Pa - 4 Pa - .09 Pa) segments.**



**Figure (4-19) : Yield stress response of 7 % CMC at (.09 Pa - 4 Pa - .09 Pa) segments.**

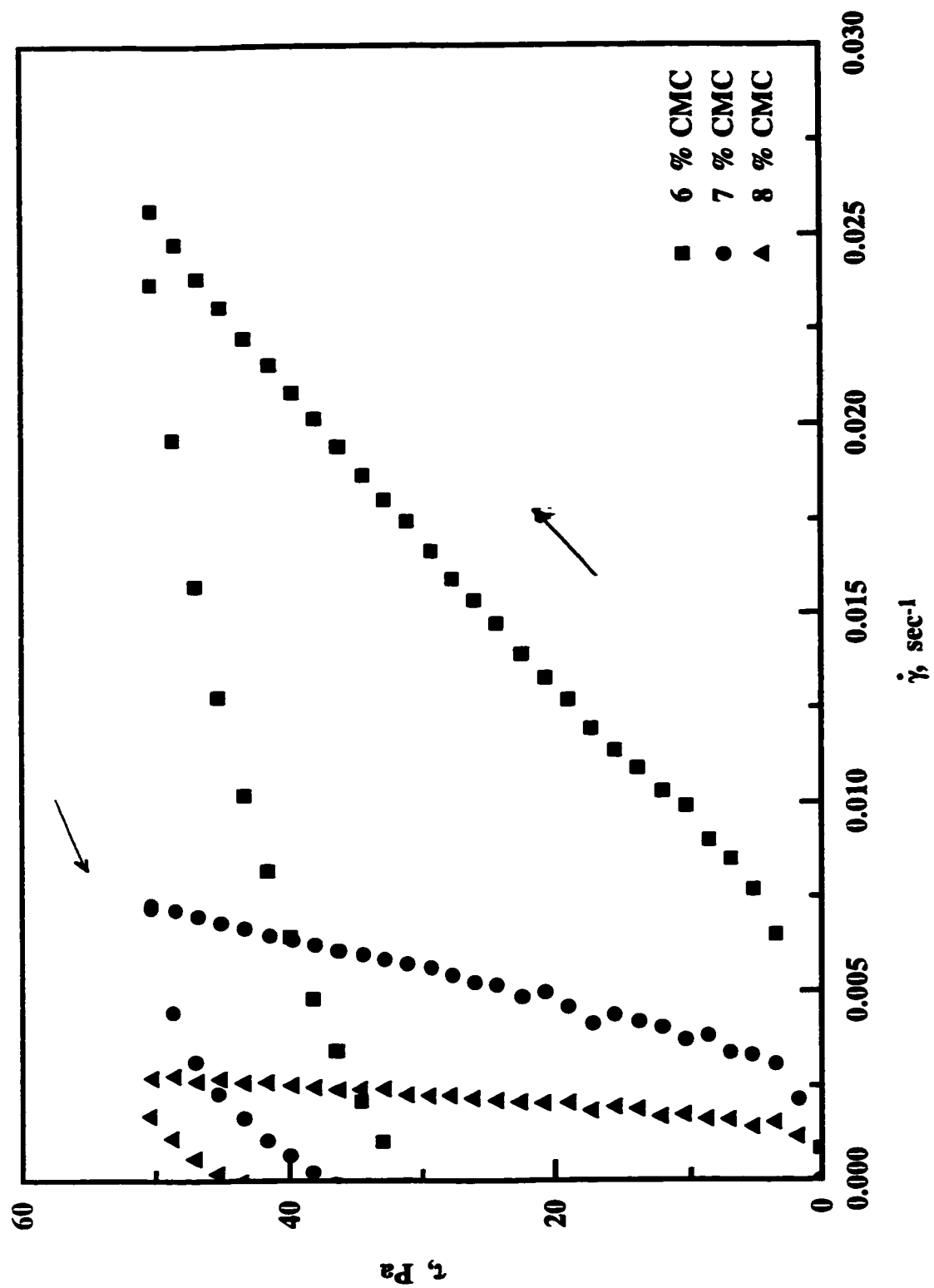


Figure (4-20) : Yield stress response of CMC at (.09 Pa - 50 Pa - .09 Pa) segments.

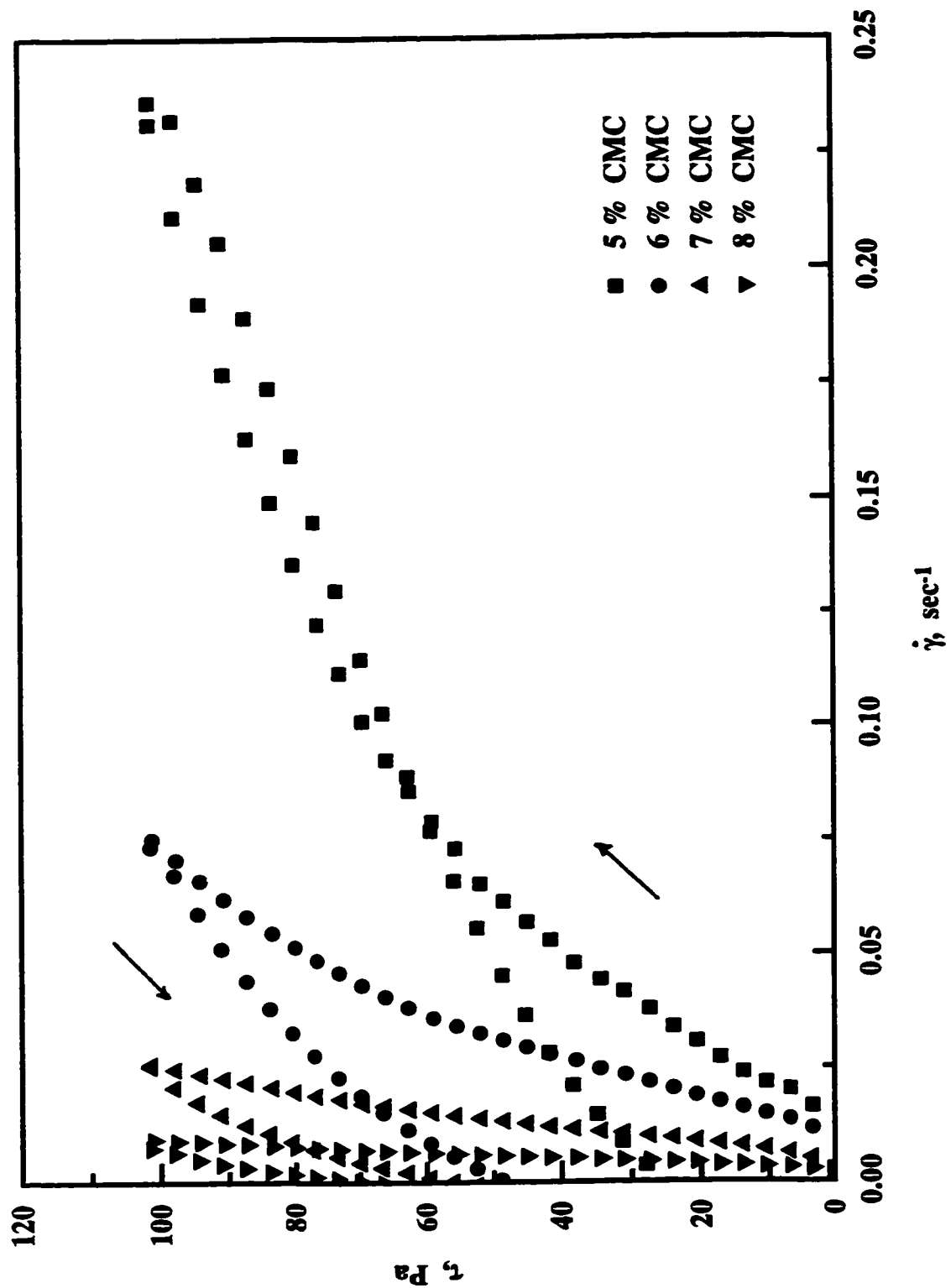


Figure (4-21) : Yield stress response of CMC at (.09 Pa - 100 Pa - .09 Pa) segments.

## 4.5 Creep Recovery Test

Another important aspect of the rheological characterization of carboxymethyl cellulose solutions in higher concentrations is the creep-recovery property. Creep is the test where a constant stress is applied on a sample and the resulting strain is obtained. It is also defined as a slow development of deformations,  $\gamma(t)$  at that applied constant stress. Time dependent compliance,  $J(t)$  is introduced as the material constant in the Creep Equation:

$$\gamma(t) = \tau \cdot J(t) \quad (4-5)$$

For the given applied stress, the higher the material compliance the easier it can be deformed. The recovery part of the test is a measure of the decline of the material deformation when the stress is removed. Recovery effects can strongly enhance the material quality. A slow recovery is an indication of the ability of the material to store the residual stress.

Creep and recovery experiments were carried out using Rheometer RS100 at controlled stress mode at various stress levels ranging from 0.02 Pa to 150 Pa. The test had two main parts - creep and recovery. These parts were performed on the same sample for a period of 300 sec each. The objective of the test was to distinguish between the linear and nonlinear viscoelasticity of the material under study. In the linear viscoelastic region, the compliance of the material is independent of the applied stress. Moreover, the material network structure is

elastically deformed and it can recover only when the stress is removed. On the other hand, higher stress values lead to the nonlinear viscoelasticity and the material is continuously deforming, i.e. it flows.

In a previous study by Ghannam and Esmail [1], it was shown that CMC at low concentrations has a viscoelastic characterization. Ghannam et Esmail [1] found that for a concentration of 3%, the linear viscoelastic range has a limit of 10 Pa of stress and the response was nonlinear for 15 Pa as shown in figure 8 of their paper.

In this work the creep recovery results of the solutions 5 - 8 % CMC are plotted in figures (4-22) to (4-29). The results indicate that CMC solutions at high concentrations continue to behave as viscoelastic materials. Elasticity is seen to be lower for all the solutions with increased stress. This is due to the structural breakdown that occurs. The recovery part of the samples showed the strain has less recovery for increased values of shear stress. This can be clearly seen in the plots of 8% CMC concentration at stress values 1 Pa, 50 Pa, and 150 Pa. Viscoelastic properties of the solutions can be better analyzed at lower values of stress where the deformation is happening with insignificant or little breakdown in the material structure. Generally, all the results of this test can be categorized in two ways. An instantaneous shear stress is constantly maintained for 300 seconds, and the responding action is the instantaneous increase of the strain or deformation. When the stress is removed, an instantaneous component

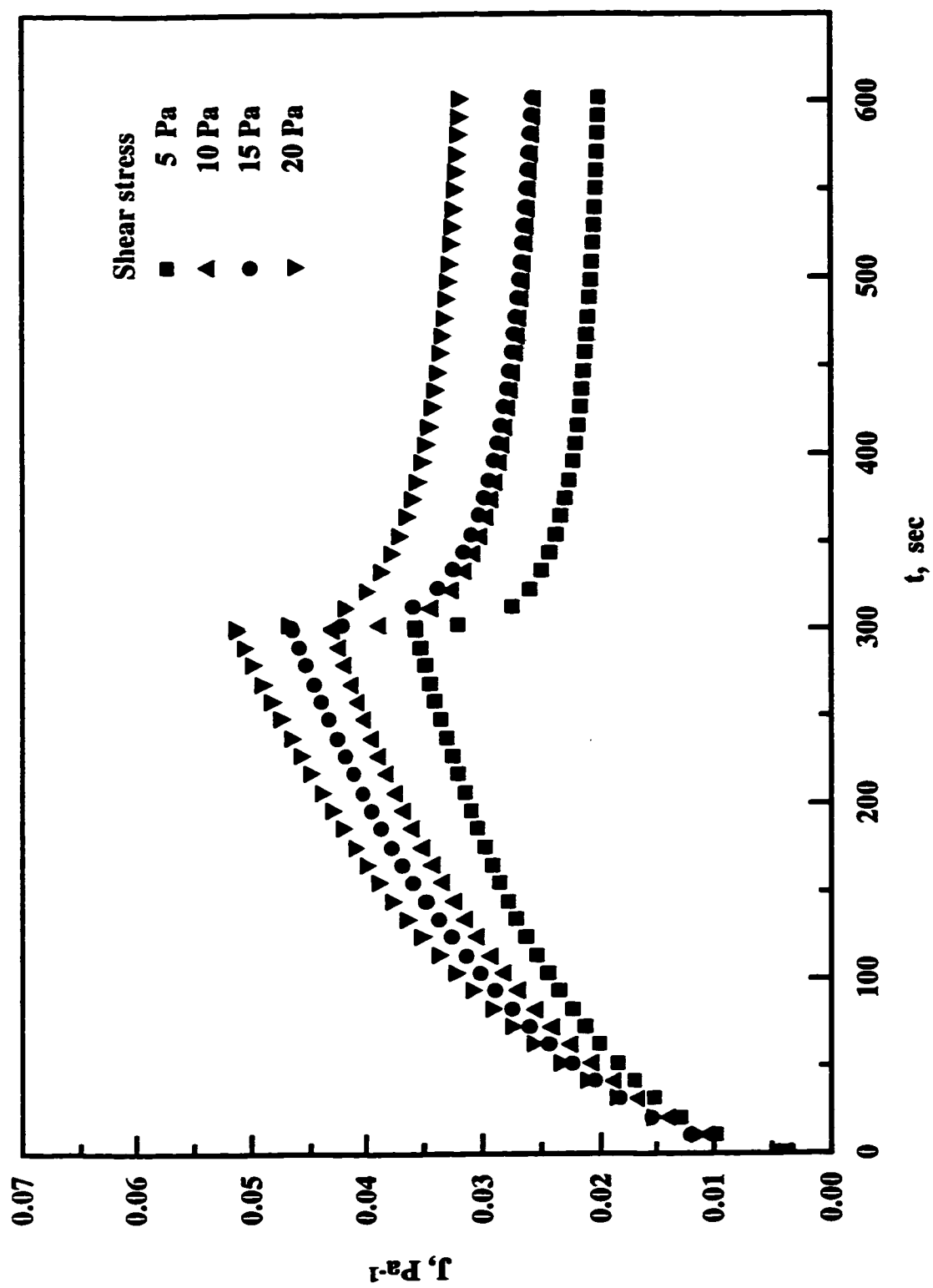
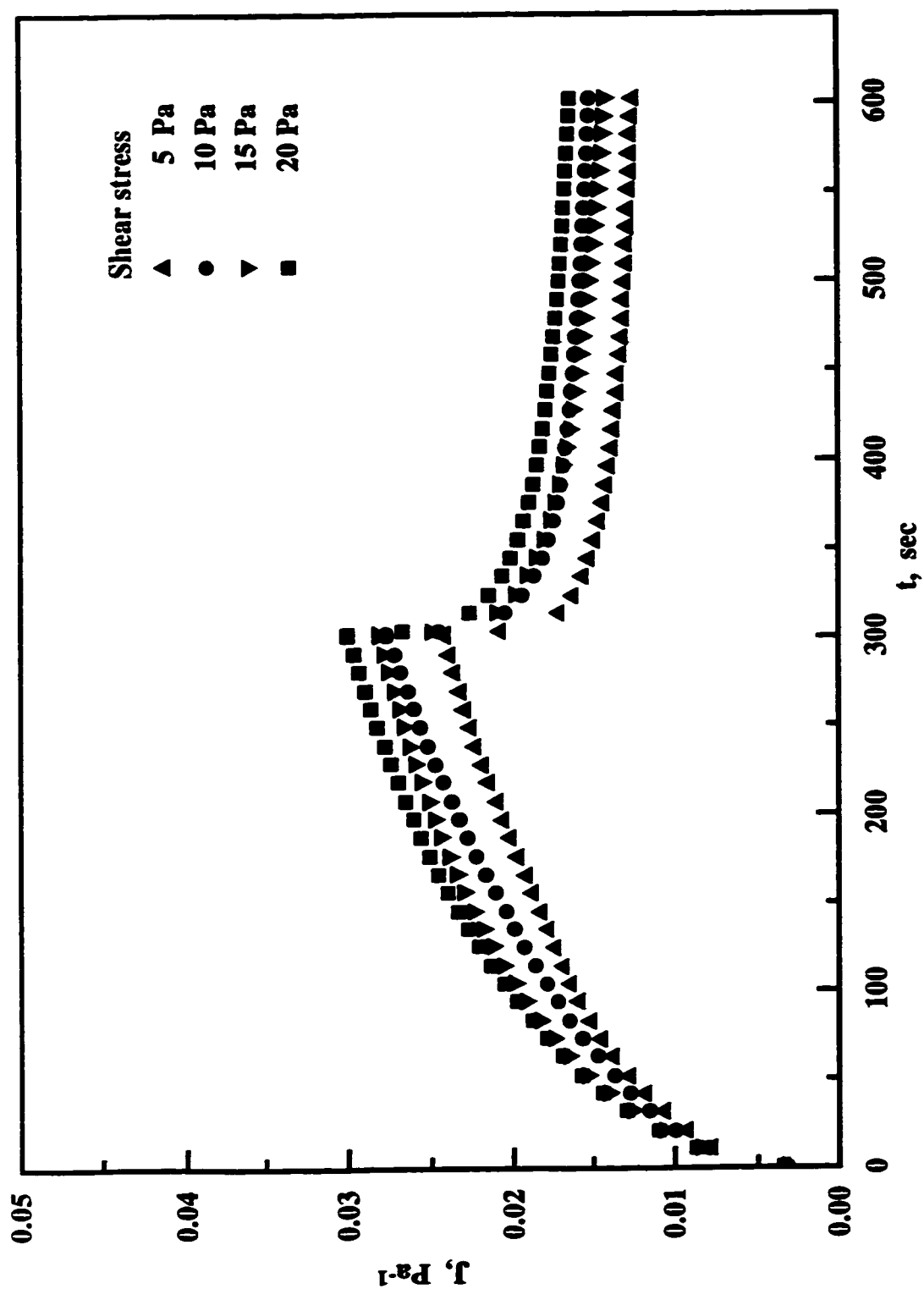
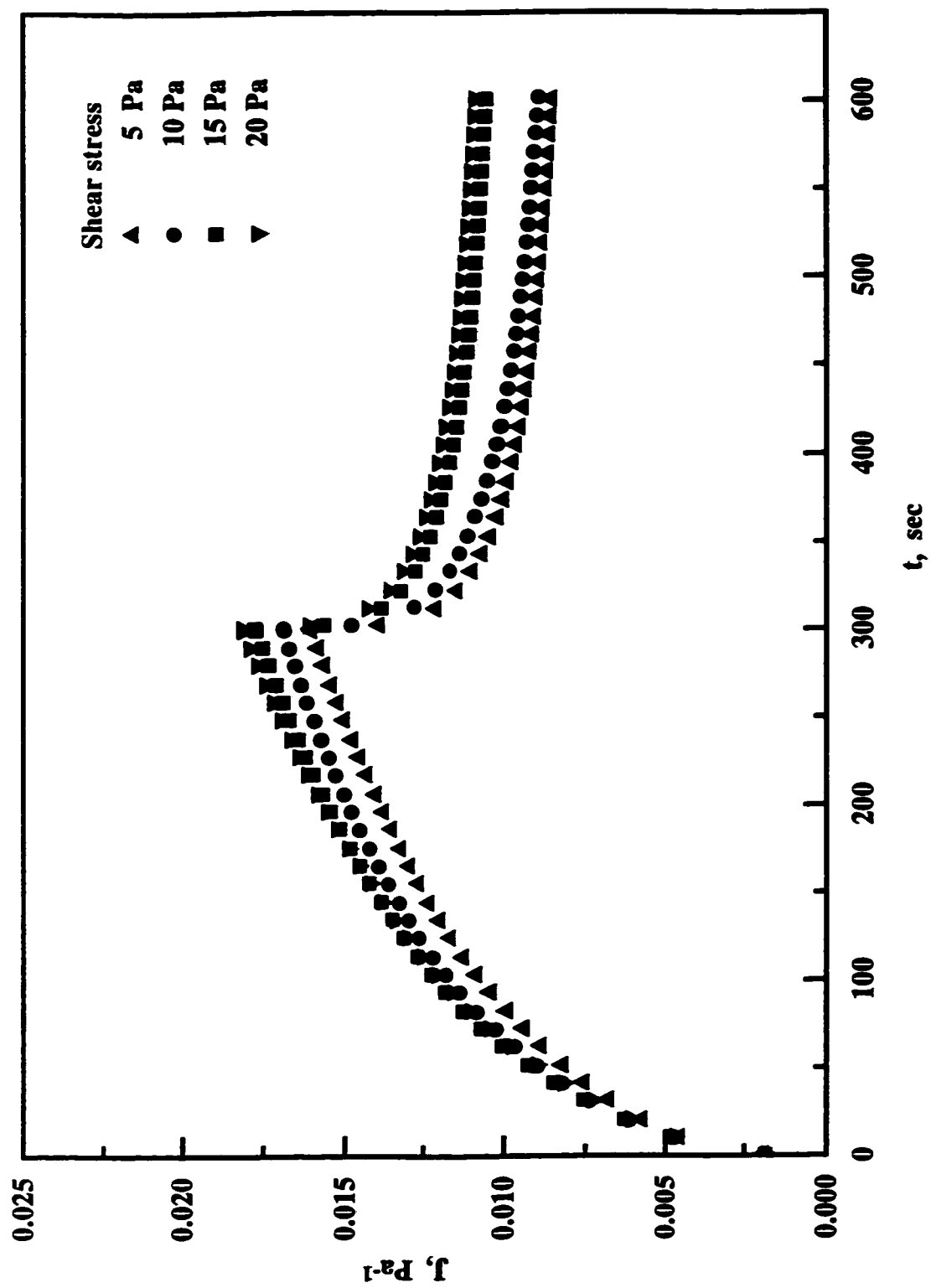


Figure (4-22) : Creep-Recovery curves of 6% CMC



**Figure (4-23) : Creep-Recovery curves of 7 % CMC**



Figure(4-24) : Creep-Recovery curves of 8 % CMC

of the strain recovery is shown in the plot. This is followed by an elastic response or time-dependent recovery in 300 seconds. It has been found that a period of 10 minutes divided between the creep and the recovery parts is sufficient for analyzing the linear viscoelastic behavior of the given samples.

A high stress applied to the sample led to a breakdown in structure and a material flow. A decrease in the curvature of the creep curve indicates a strong decline in viscosity, and recovery is slowed or absent at these stresses. An absence of recovery shows that the sample is in a viscous flow and that no elastic effects remain active.

The results in figures (4-22), (4-23), and (4-24) show a comparison between the linear viscoelastic ranges for the concentrations 6, 7, and 8 % CMC at several constant shear stresses. The shear stresses chosen were 5Pa, 10Pa, 15Pa, 20 Pa as plotted in the three graphs. The linear viscoelastic range for the creep curves at constant stresses converges with the increase in solution concentration. On the other hand, when a higher stress such as 50 Pa is applied as shown in figures (4-25) and (4-26) for the solutions 5% and 6% CMC; the compliance curves indicate a non-linear viscoelastic effect. Moreover, figures (4-27), (4-28), and (4-29) illustrate the interesting behavior of solutions 7% and 8% CMC where the compliance changes from a steady state to an almost straight line at 150 Pa shear stress. This explains the transition of the solution from a viscoelastic state to a viscous state. Besides this, deformation ' $\gamma$ ' of the

solution grows by increasing the stresses exerted until the structure is broken-down. This is shown in figure (4-29) where the compliance and deformation curves have high values and the recovery rate is lower.

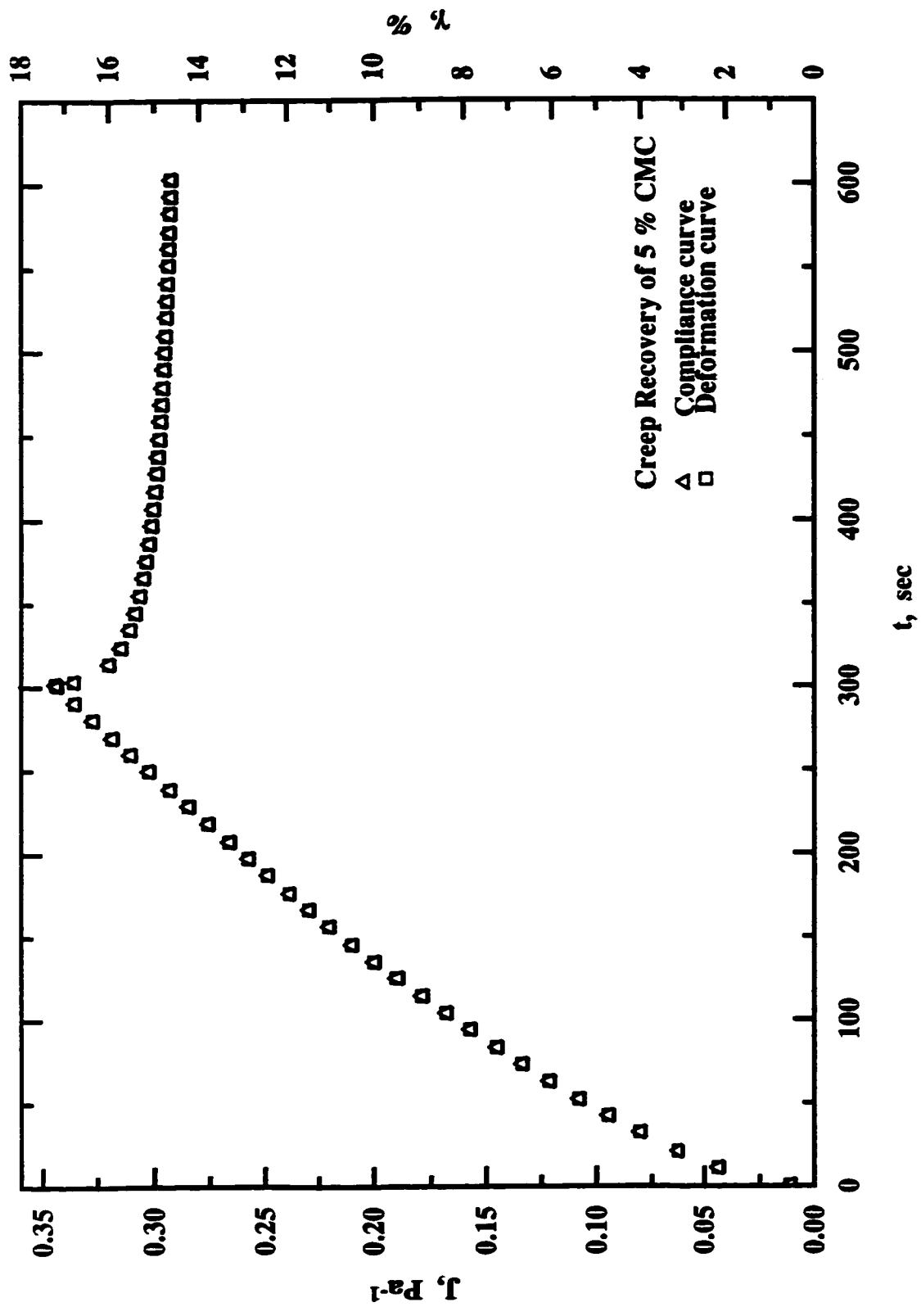


Figure (4-25) : Creep Recovery curves for 5 % CMC at 50 Pa.

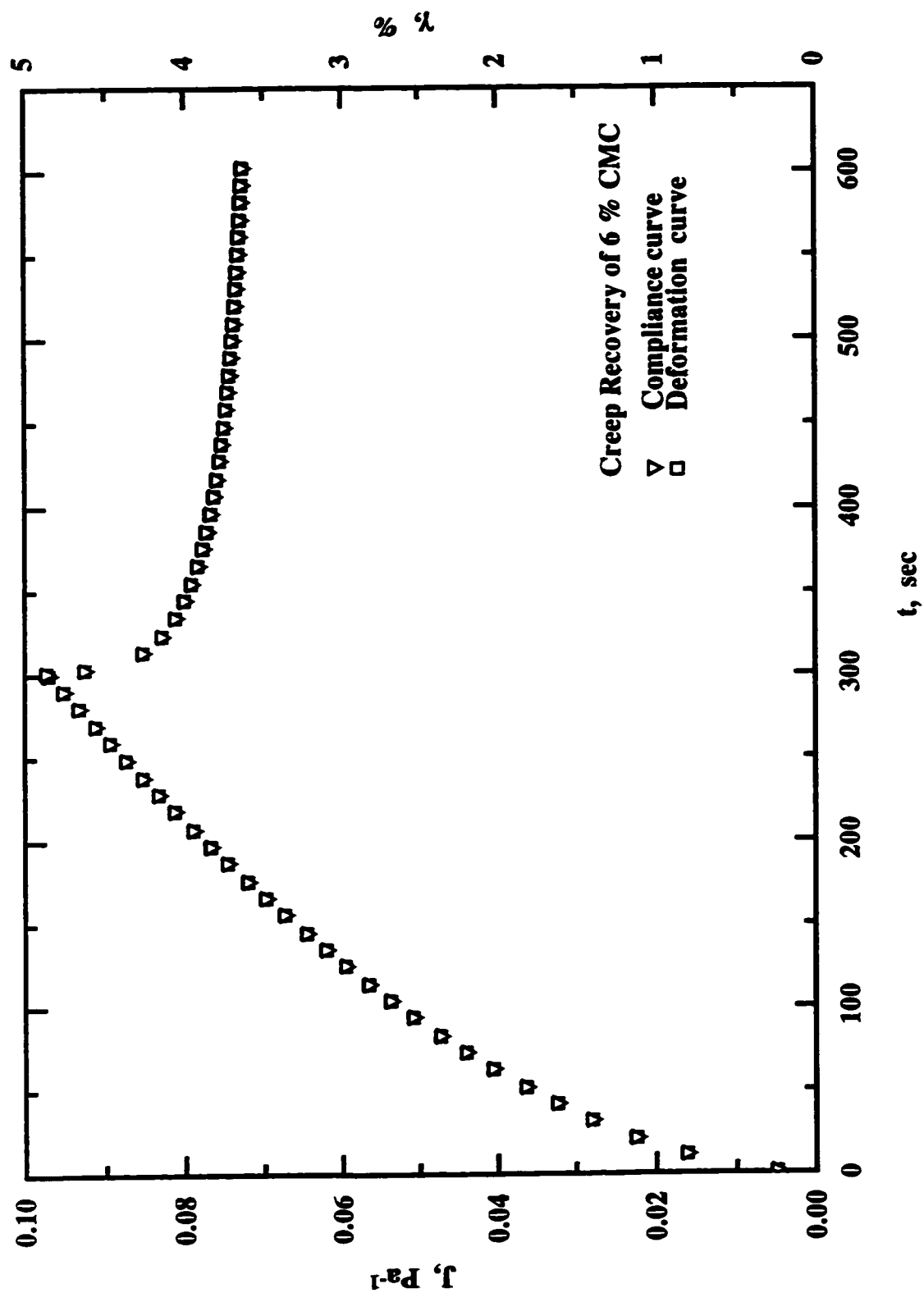


Figure (4-26) : Creep Recovery curves of 6 % CMC at 50 Pa.

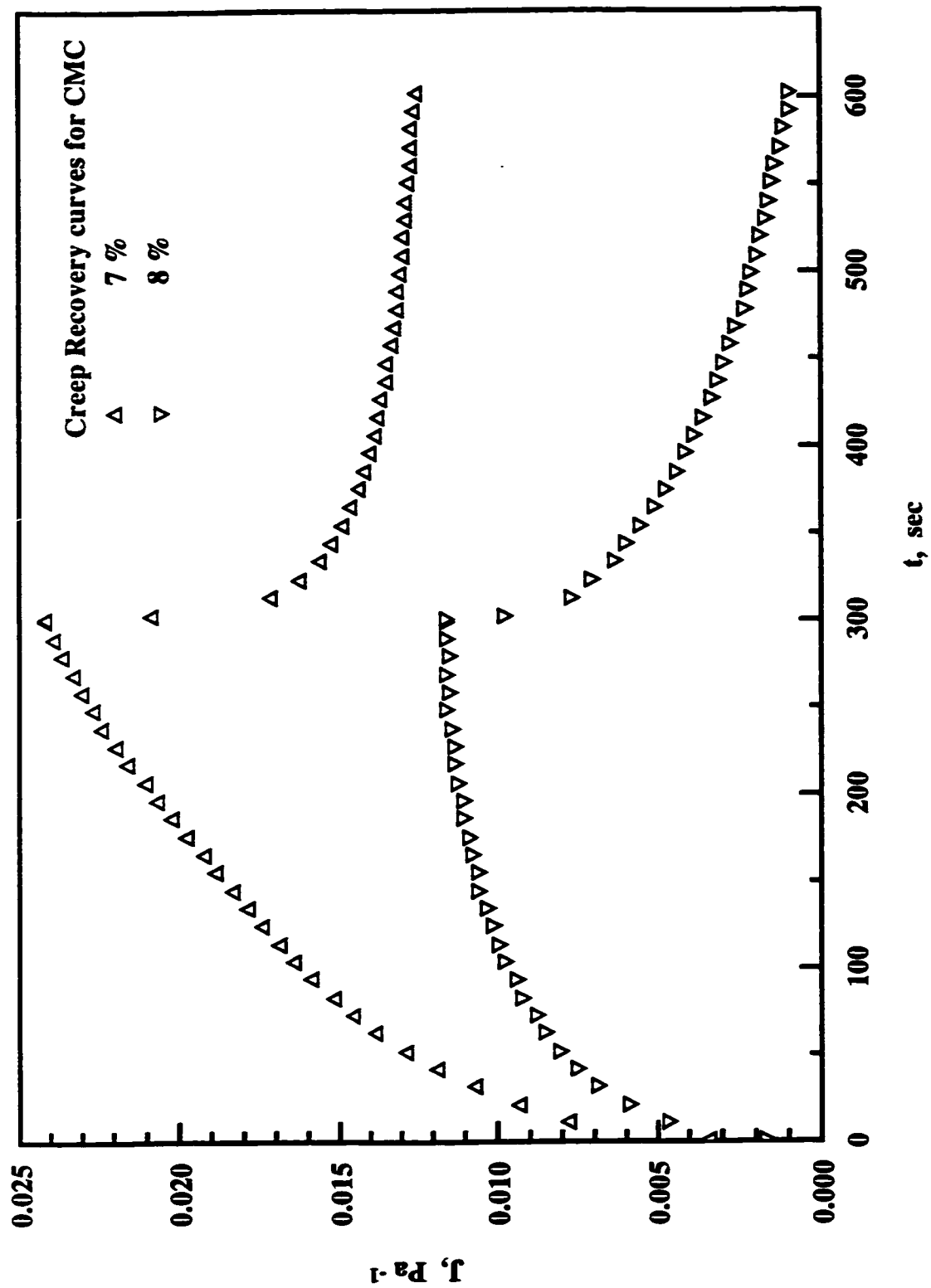


Figure (4-27) : Creep Recovery curve for 7, 8 % CMC at 1 Pa.

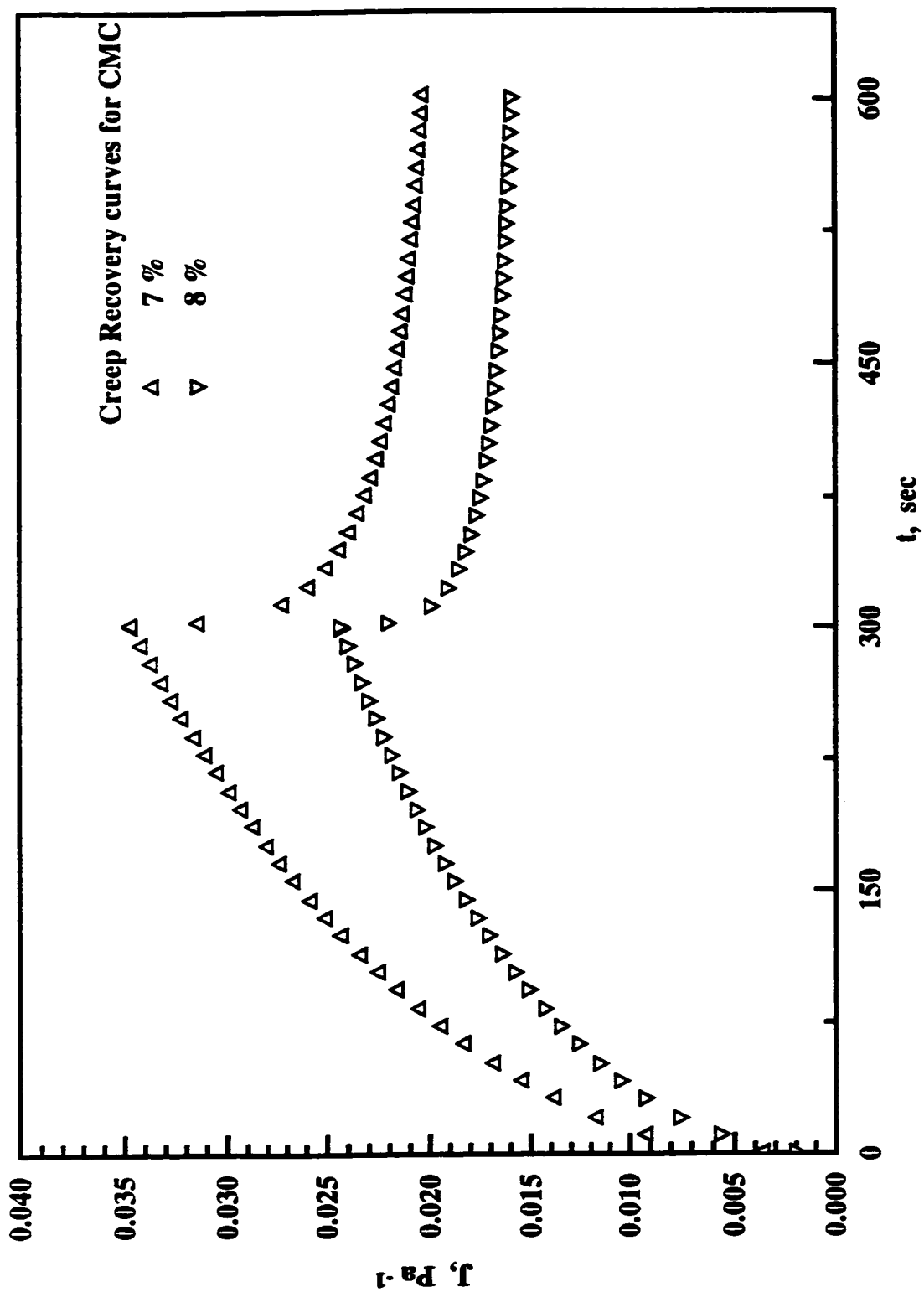


Figure (4-28) : Creep Recovery curves for 7 , 8 % CMC at 50 Pa.

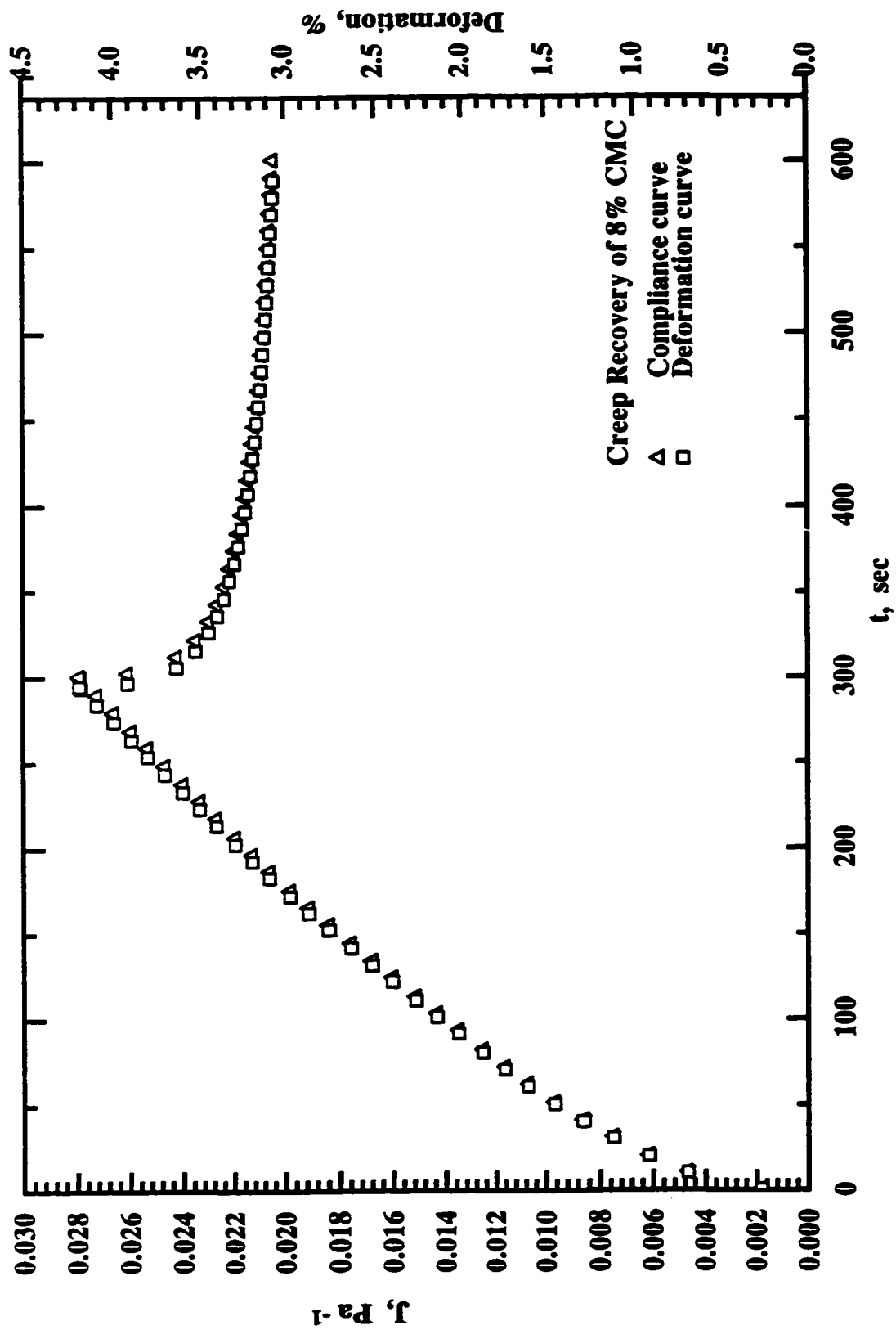


Figure (4-29) : Creep Recovery curves for 8 % CMC at 150 Pa.

## 4.6 Dynamic Test

Dynamic tests are extremely useful tool to study and evaluate the visco-elastic behavior of polymeric materials. The test is carried out by using the rheometer RS100 in the Oscillating mode. Two important tests were performed on the CMC solutions in this work, the stress sweep test and the frequency sweep test. The dynamic tests were used in this study to detect some aspects of visco-elasticity of CMC solutions that can not be described in the creep recovery tests.

Linear viscoelasticity prevails for small amplitude oscillatory shear, in which the polymeric structure is not significantly disturbed from its equilibrium state, and the material functions are independent of the amplitude of deformation. The strain and the resultant stress can be expressed as follows:

$$\gamma = \gamma_o \sin \omega t \quad (4-6)$$

$$\tau = \tau_o \sin (\omega t + \delta) \quad (4-7)$$

where:  $\gamma_o$  = Strain amplitude

$\tau_o$  = Stress amplitude

$\delta$  = Phase angle

$\omega$  = Angular velocity =  $2 \pi f$

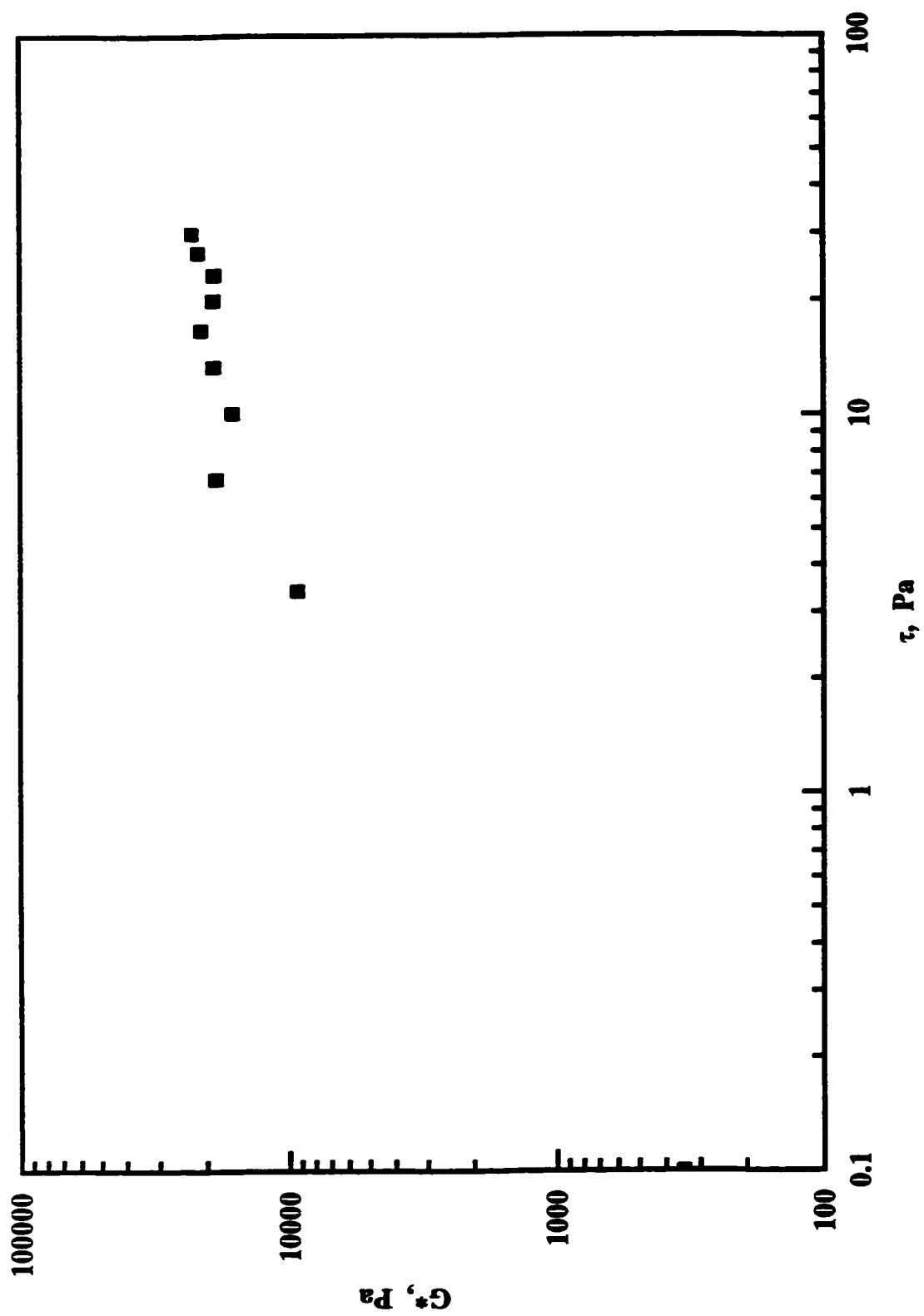
The amplitude ratio,  $\tau / \gamma$  ( $G^*$ ) which is the total resistance of a substance against the applied strain will be dependent on the strain amplitude in the case of high levels of applying the strain amplitude. Also, the linear viscoelastic

material functions cannot be determined.

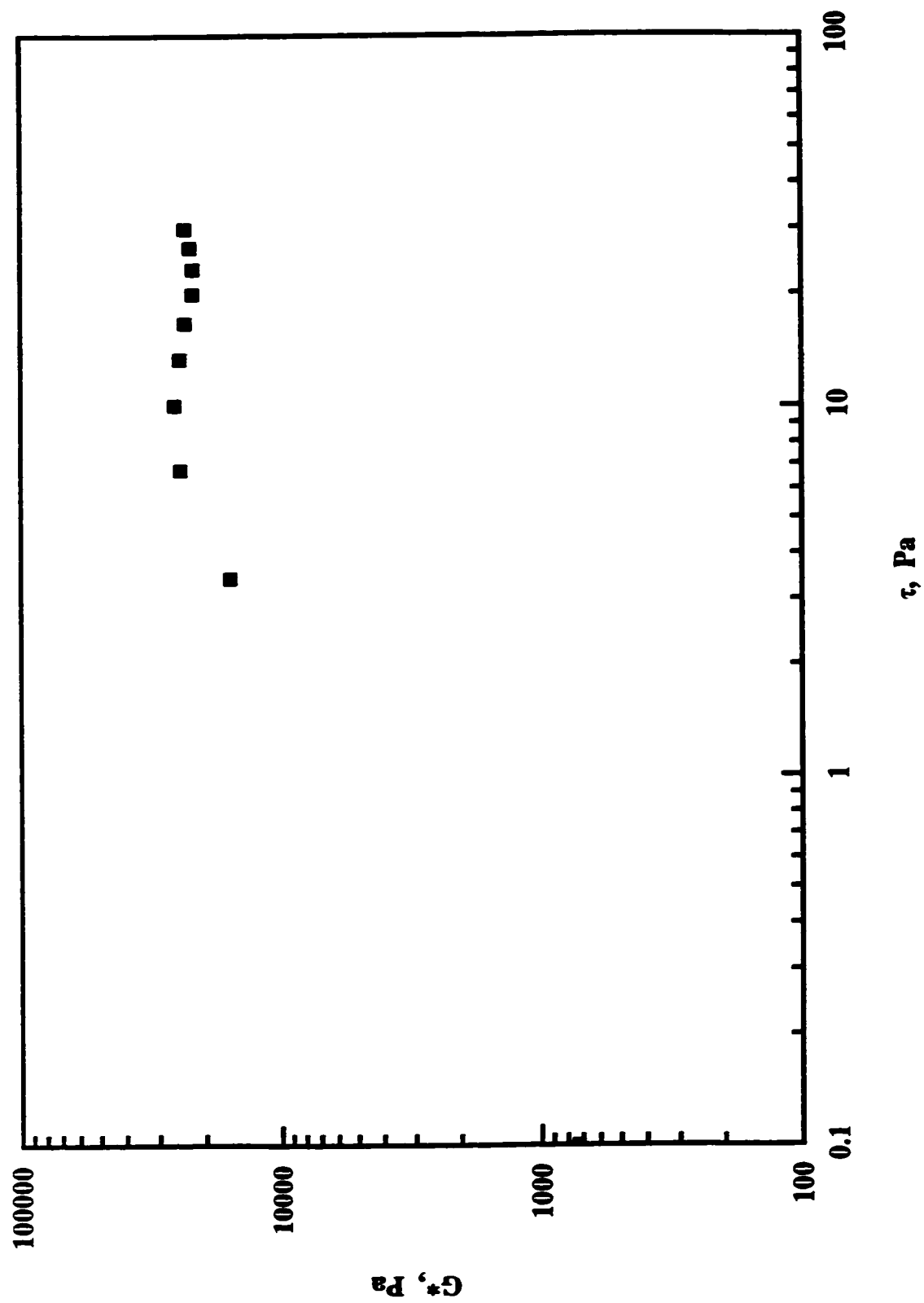
Stress sweep is the dynamic test used to determine the linear visco-elastic range. In the test, the limit between the linear and the non-linear visco-elasticity is plotted as complex modulus,  $G^*$  versus applied stress. Fixed frequency of 0.1 Hz is used in the stress ramp mode in three different tests. In the first test, a stress ramp of 0.1 - 5 Pa is applied on all the solutions. Another two stress ramps of 0.1 - 30 Pa and 0.1 - 100Pa are performed to cover the possible visco-elastic linearity responses in three regions of stresses low, medium, and high. The linear visco-elasticity is detected when the  $G^*$  appears constant in a certain stress range. The non-linearity is found to exist at high stresses where the sample could be deformed enough to destroy the internal temporary bonds of molecules. Sweep test is considered due to its importance to be the key dynamic test in finding out the limits of the linear visco-elastic region of the sample prior to performing the frequency test. Figures (4-30) to (4-32) show that the linear visco-elastic range for the 5 - 8 % CMC samples is detected in the neighborhood of 15 Pa.

In the Frequency sweep, the frequency ramp mode of 0.01 - 10 rad/sec was applied to reveal the storage modulus,  $G'$  and loss modulus,  $G''$  responses of the CMC samples within the linear visco-elastic range as plotted in figures (4-33) to (4-35).

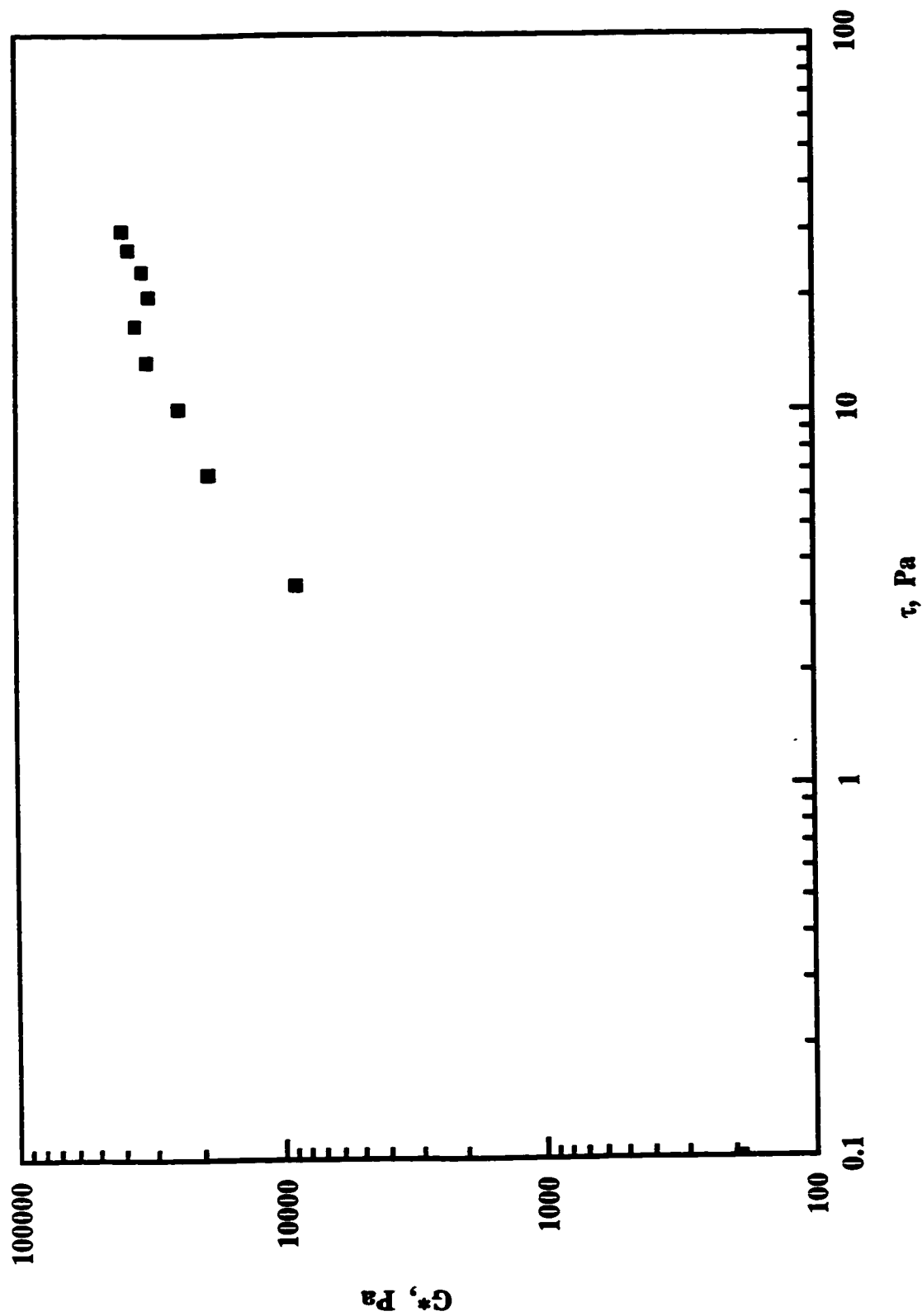
The storage or elastic modulus, and the loss or viscous modulus can be



**Figure (4-30) : Stress sweep [0.1-30 Pa] for 6% CMC.**



**Figure (4-31) : Stress sweep at (0.1 - 30 Pa) for 7% CMC.**



**Figure (4-32) : Stress sweep at (0.1 - 30 Pa) for 8% CMC.**

defined according to equation

$$G^* = G' + i. G'' \quad (4-8)$$

Where  $G^*$ , the complex modulus that is used in the stress sweep to determine the range of viscoelasticity. The results of frequency sweep in figures (4-33) to (4-35) showed that the elastic behavior was higher than the viscous one over the entire range of applied frequencies. In addition, the elastic modulus increases with increasing the concentration of CMC solutions as can be interpreted from figure (4-36). The difference in viscous modulus for CMC solutions described in figure (4-37) is insignificant compared to the case of the elastic modulus. Also, the results of figures (4-36) and (4-37) indicating that  $G'$  of CMC samples is less sensitive than  $G''$  which can be an indication that the CMC material at these concentrations is more elastic.

The complex viscosity  $\eta^*$ , Pa.S is also obtained from the frequency sweep test. Figure (4-38) illustrates the complex viscosity behavior of the CMC samples versus the frequency that has been assigned in the test. Both dynamic viscosity and steady shear viscosity are known to be good characterization tools in studying the rheology of some polymeric solutions. It is also known that they could have identical behavior. The shear and dynamic viscosities were not similar in the results of this work. This can be due to some intermolecular structure of this high range of concentrations of CMC. Dynamic viscosity according to figure (4-38) decreases with the frequency for all CMC solutions

confirming the conclusion of the shear thinning effect detected in steady shear viscosity test. Moreover, complex viscosity  $\eta^*$  is influenced significantly by the increase in the concentration of CMC. Shear viscosity for all concentrations is less than their dynamic viscosity as can be interpreted from both figures (4-2) and (4-38).

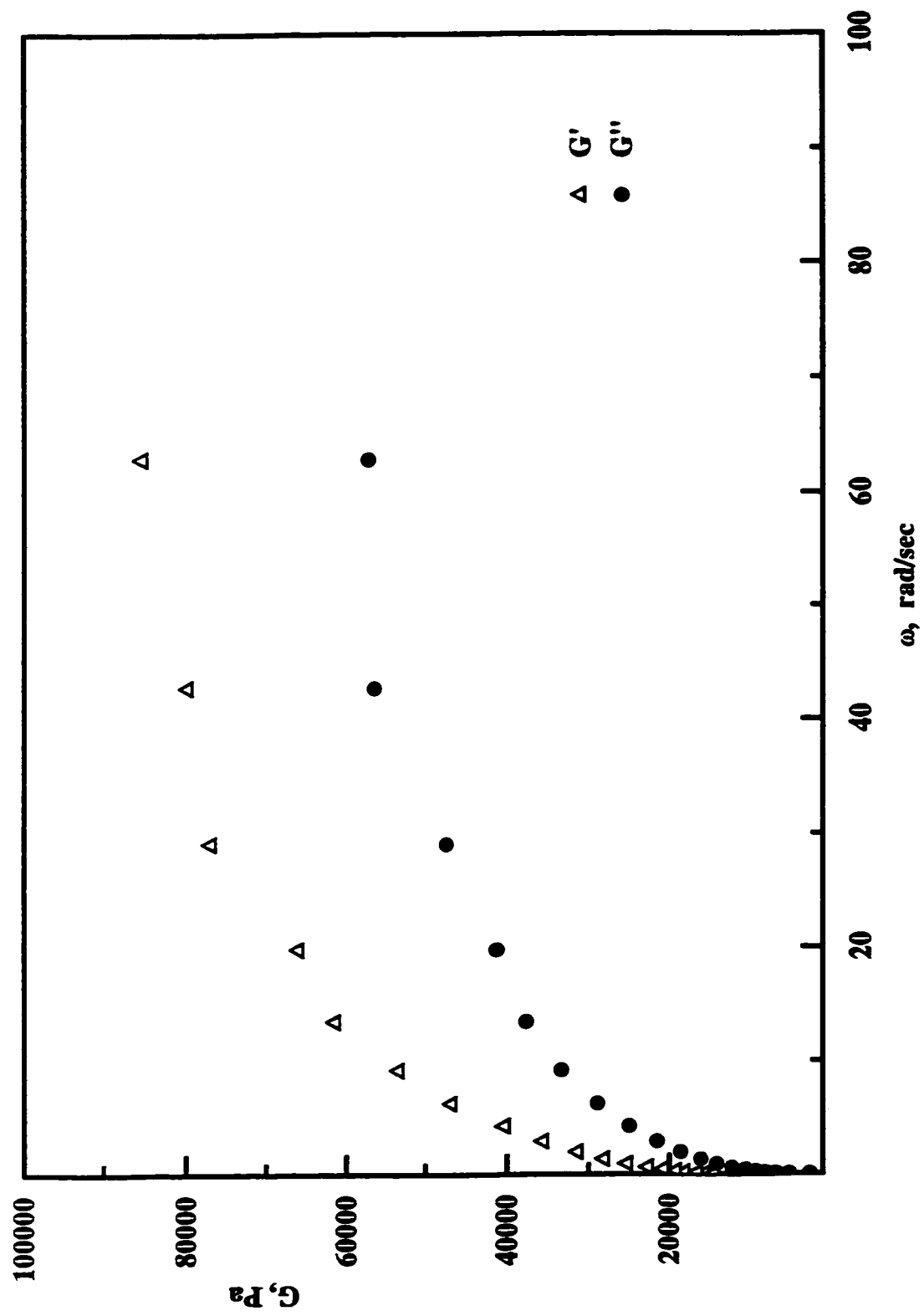
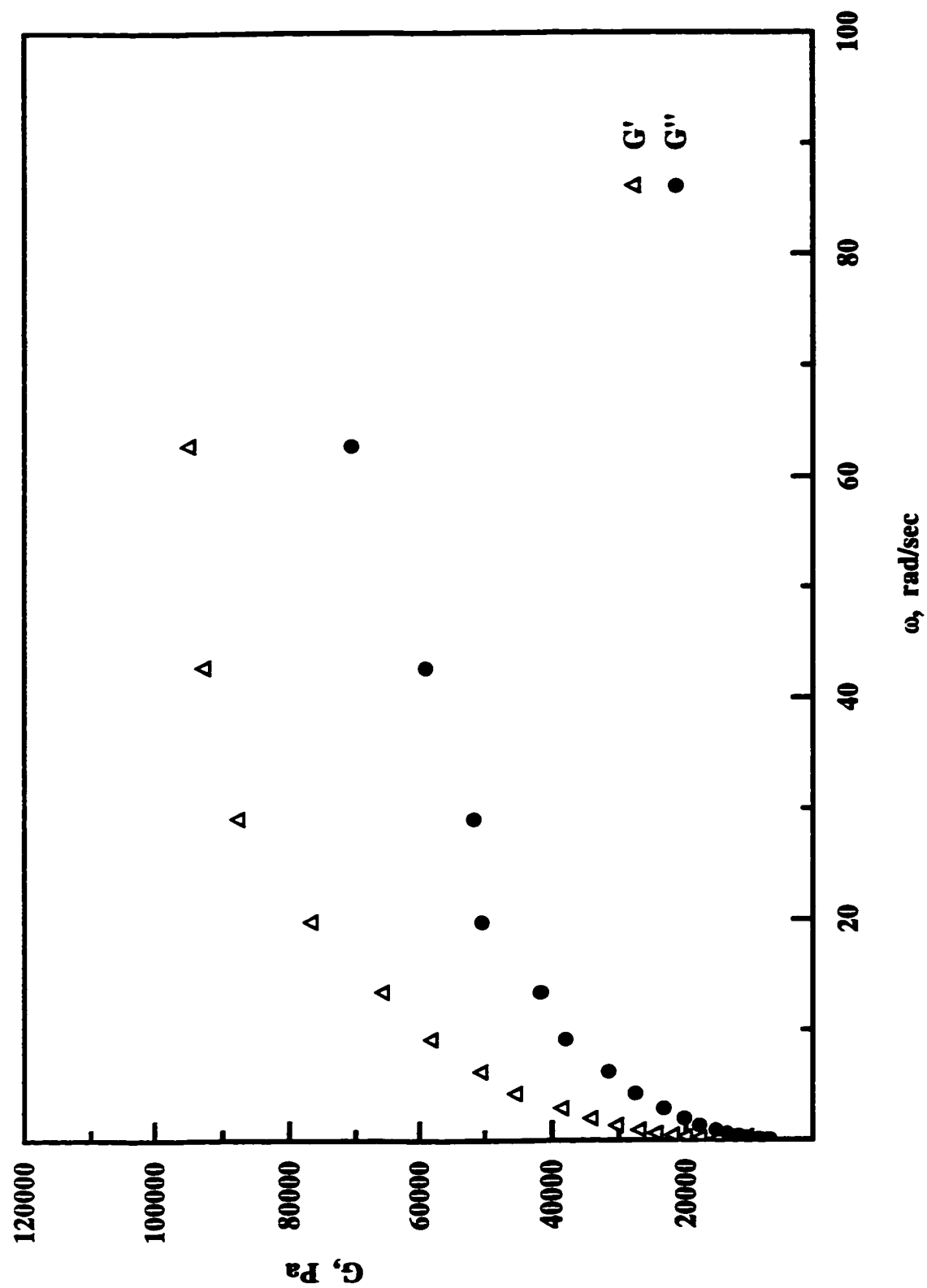


Figure (4-33) : Elastic,  $G'$  and viscous,  $G''$  modulus for 6% CMC.



**Figure (4-34) : Elastic,  $G'$  and viscous,  $G''$  modulus for 7% CMC.**

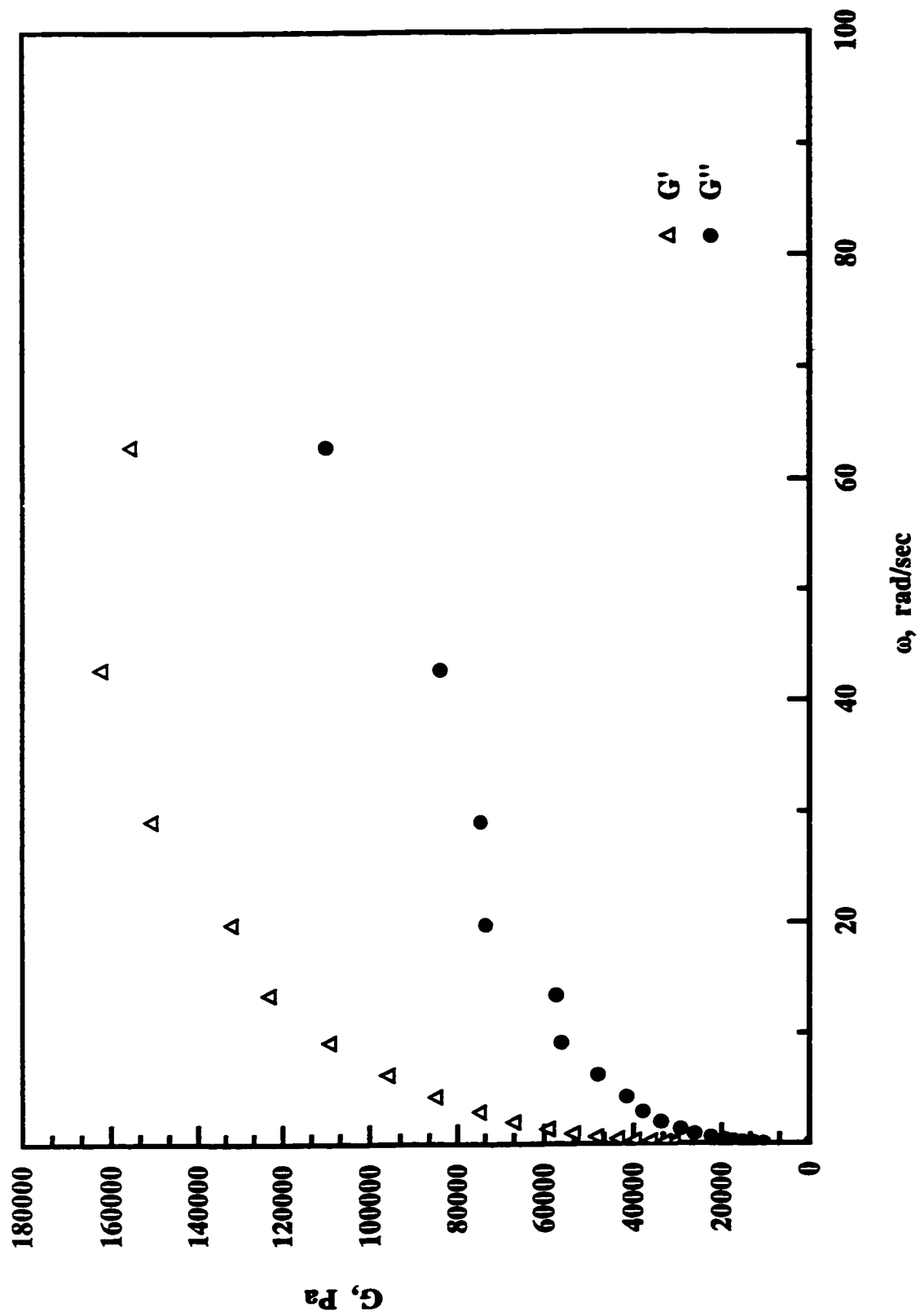


Figure (4-35) : Elastic,  $G'$  and viscous,  $G''$  modulus for 8% CMC.

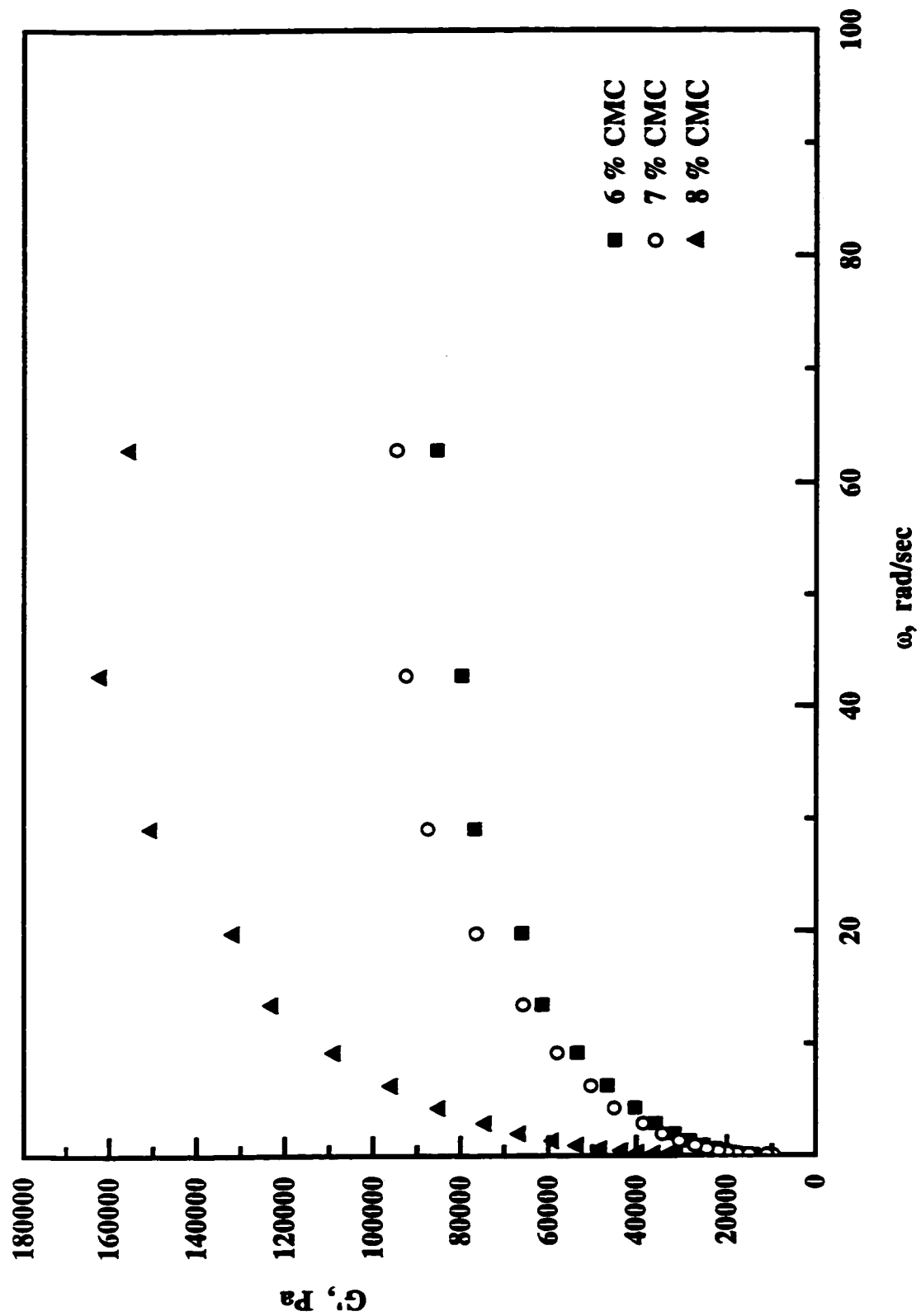


Figure (4-36) : Elastic modulus of CMC solution

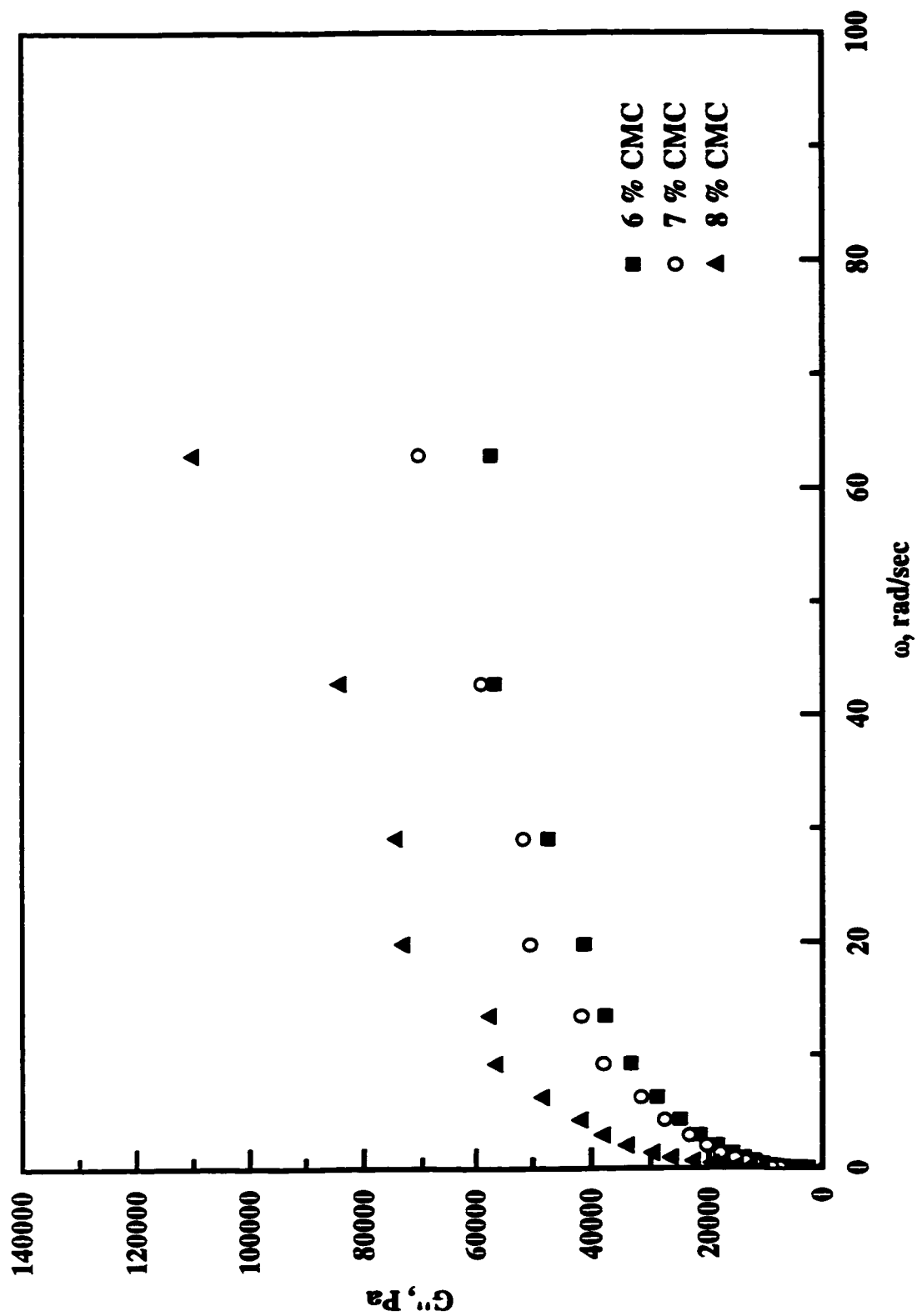
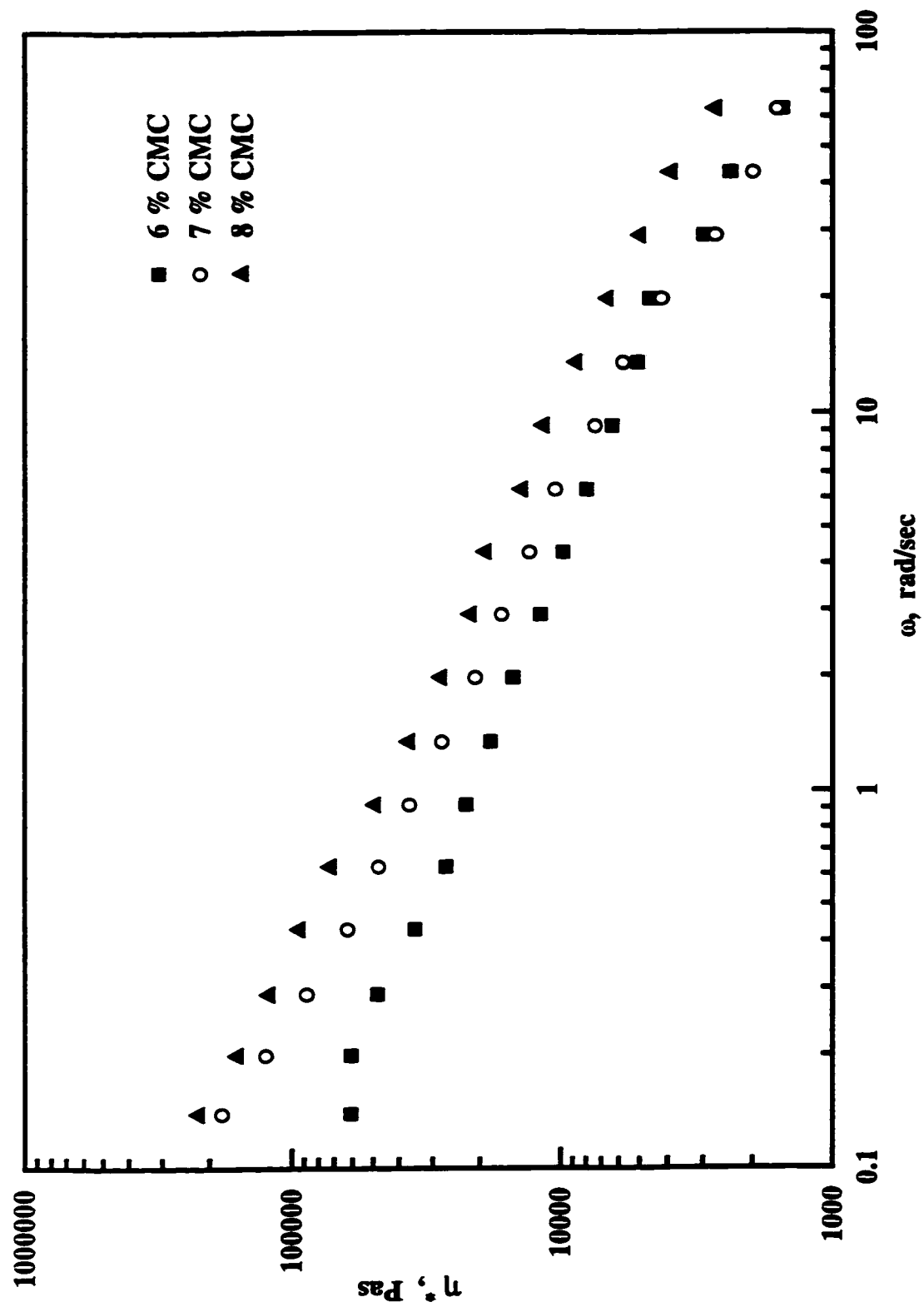


Figure (4-37) : Viscous modulus of CMC solutions



**Figure (4-38) : Complex viscosity for 6, 7, and 8 % of CMC solutions**

## **5.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH**

### **5.1 CONCLUSIONS**

The importance of CarboxyMethyl Cellulose with its wide range of applications in dairy food products, pharmaceuticals, detergents, paper industry, and petroleum industry underlines the need to have a full set of rheological studies for a high range of CMC concentrations. CMC solutions in the range of concentrations 5 - 8 % by weight were studied using a cone and plate Haake - RS100 rheometer.

CMC solutions starting from 5 % concentration showed a pseudoplastic or shear-thinning behavior for the entire shear rate range applied. Viscosity curves for 7% and 8% concentrations start to drop sharply at high shear rates of 500 sec and 300 sec respectively. It was found that the flow and viscosity curves mathematically follow the power law model and are represented by the rheological Ostwald-de-Waele model. However, at a concentration of 8 % CMC the viscosity curve is properly fitted to a hyperbolic mathematical model.

Transient shear stress response is a test to study the time effect characterization of CMC samples. Applying a various shear rates up to  $10 \text{ sec}^{-1}$  in CR and Time curve modes has determined that the solutions studied showed rheopexy behavior or time dependency of shear stress. Shear stress-overshooting behavior within the first 30 seconds of the test was found for the solutions

when shear rate of 100 sec was applied. Thixotropy test results seemed to show a confirmation for the ones that have been detected in the transient test. The thixotropy behavior test was carried out on the samples in CR mode by having a looped cycles of shear rates of 0.15 - 700 - 0.15 sec in different time intervals. Two techniques have been performed and the results revealed an existence of high thixotropic areas. The area decreases with the increase of the shearing time for all CMC concentrations and this decrease is getting sharper with the concentration increase. Also, the increase of CMC concentrations led to a build up of hysteresis areas due to the increase in CMC viscosity. The yield stress test of the solutions confirmed the existence of thixotropy behavior although no yield stress was detected which also was in agreement with the conclusion of the same test response in another publication [1] for the lower range of CMC concentrations.

Creep and Recovery test was carried out using Rheometer RS100 at controlled stress mode at various stress values ranging from 0.02 Pa to 150 Pa. The test was programmed to last 300 sec for each of the creep and the recovery parts in order to reveal the linear visco-elastic range for each concentration. The creep recovery results of the solutions 5 - 8 % CMC in this work indicated that CMC solutions at high concentrations continue to behave as a visco-elastic material. The linear visco-elastic regions for the samples were in the neighborhood of 15 Pa. Around this value of stress the creep curves are converging with the increase of the solution concentration. Dynamic tests including the stress sweep and frequency sweep parts were performed

using the same rheometer RS100 but under the oscillating mode. These tests were to give a better picture for the viscoelastic behavior for the solutions under study. In fact, the results came out with the same conclusion of the creep recovery test, a matter that gives confidence in the source. The frequency test with its ramp of 0.01 - 10 rad/sec was applied within the linear visco-elastic region. The results of the frequency sweep indicated that the elastic behavior is higher than the viscous behavior over the entire range of frequencies for all the solutions. In addition, dynamic viscosity was found to be dependent on the increase of concentration and to decrease by increasing the frequency for all CMC solutions. This confirmed the shear thinning effect detected in the steady state test.

## **5.2 RECOMMENDATIONS FOR FUTURE RESEARCH**

- 1) Studying the concentrations of CMC up to 10% due to the importance of their applications in pigment coats that are applied on the size press.
- 2) Temperature has a significant influence on viscosity, and the rheological behavior of a solution plays an important role in heat transfer operation. A heating circulator with powerful pumps can be connected to the Rheometer RS100 to provide a tool to study the temperature effect on the rheological properties of CMC solutions used in this thesis.

## REFERENCES

1. M. Ghannam, and M. N. Esmail, J. Appl. polym. sci., 64, 289 (1997).
2. K. Abdelrahim, H. Ramaswamy, G. Doyon, and C. Toupin, Int. J. Food Sci. Technol., 29, 243(1994).
3. S. Young, and C. Shoemaker, J. Appl. polym. Sci., 42, 2405( 1991).
4. D. Sikkema, and H. Janssen, Macromolecules, 22, 364(1989).
5. J. Westra , Macromolecules, 22, 367(1989).
6. M. Dolz-Planas, C. Ronald-Garcia, J. Herraiez-Dominguez, and R. Belda-Maximino, J. Pharma. sci., 80, 75(1991).
7. M. Dolz, J. Bugaj, J. Pellicer, M. Hernandez, and M. Gorecki, J. Pharma. Sci., 86, 1283(1997)
8. Y. Kawashima, T. Hino, H. Takeuchi, T. Niw, and K. Horibe, Int. J. Pharma. , 72, 65(1991).
9. M. Ghannam, and M. N. Esmail, Ind. & Engin. chem. Res. , 37, n4, 1335(1998).
10. P. Chaturani, and S. Narasimman, Acta Mech., 82, 197(1990).
11. E. Collins, C. Chen, and J. Padolewaski, J. Rheol., 36, 117(1992).
12. E. Collins, C. Chen, and J. Padolewaski, J. Rheol., 36, 131(1992).
13. A. Magnin, and J. Piau, J. Non-Newt. Fluid Mech., 36, 85(1990).
14. J. Hartnett, and R. Hu, J. Rheol., 33, 671(1989).
15. N. Pashias, D. Boger, and D. Glenister, J. Rheol., 40, 1179(1996).
16. P. Doremus, and J. Piau, J. Non- Newt. Fluid Mech., 39, 335(1990).

17. P. Cossot, S. Proust, and C. Ancey, *J. Non-Newt. Fluid Mech.*, **66**, 55(1996).
18. D. De Kee, and C. Chan Man Fong, *J. Rheol.*, **37**, i4, 775(1993).
19. R. Harden, and L. Burmeister, *J. Appl. polym. sci.*, **48**, 625(1993).
20. J. Zhang, D. Li, X. Zhang, *J. Appl. polym. Sci.*, **49**, n4, 741(1993)
21. M. Windholz, S. Budavari, R. Blumetti, and E. Otterbein, *An Encyclopedia of Chemicals, Drugs, and Biologicals*, Merck, Rahway, NJ, 1983.
22. C. Wiley, R. Kirk, D. Othmer, J. Kroschwitz, and M. Howe-Grant, *Encyclopedia of chemical technology*, fourth edition : index to volumes 1-25 ,.
23. F. Ullmann, W. Gerhartz, Y. Yamamoto, F. Campbell, R. Pfefferkorn, and J. Rounsaville, *Ullmann's Encyclopedia of industrial chemistry*, Weinheim, Federal Republic of Germany : VCH Verlagsgesellschaft ; Deerfield Beach, FL, USA : VCH Publishers, c1985- .
24. F. Snell, C. Hilton, and L. Etre, *Encyclopedia of industrial chemical analysis*, New York : Interscience Publishers, 1966 -74