

Mechanical Properties of Alkali Treated Casein Films

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ABSTRACT: Casein was treated with triethanolamine and made into films. The mechanical properties of the alkali treated casein films were studied under uniaxial and biaxial stress conditions. A reduction in longitudinal stress and elongation at break was observed with the simultaneous application of lateral stress.

KEY WORDS Casein / Triethanol Amine / Uniaxial / Biaxial / Stress
Relaxation /

Casein, a milk protein, is used as a surface coating material in leather, paper and textile industries. There are many advantages in using casein films; however, casein films has two major draw backs. It forms into hard, brittle and discontinuous films and the film is hydrophilic in nature. Due to this, the wet rub resistance of the film is poor which needs modification.

Addition of plasticisers to casein can alter physical properties such as flexibility, hardness, tensile strength elasticity etc. In leather finishing, turkey red oil (TRO) humectants like glycol,¹ sulphonamide² were used for this purpose. But these external plasticisers migrate into the surface in course of time, making the film brittle. Triethanolamine can also be advantageously used as a plasticiser.³

Molecular weight of casein⁴ is between 33600 to 375000. Most properties of the polymer changes with molecular weight.^{5,6} Properties that increase in value as the molecular weight increases include tensile strength, melting point, and glass transition temperature. The impact strength, breaking strength and abrasion has got a direct relationship with the increase of molecular weight.⁷ Solubility and

thermal conductivity^{8,9} decreases with increase of molecular weight.

It was reported^{10,11} that for amorphous polymers large changes in viscoelastic behaviour may be brought about by changing the molecular weight, which controls the degree of molecular entanglement. Bersted and Anderson¹² reported the influences of molecular weight distribution on the tensile strength of amorphous polymers. Above glass transition temperature, the loss tangent ($\tan \delta$) values decreases with the increase of molecular weight.^{13,14} The literatures sited above shows that the change in molecular weight could result in serious deteriorations of mechanical properties. It was thought, that if this molecular weight of casein was slightly reduced, then the stretchability can be improved and casein may form a continuous film.

By partially hydrolysing casein, the molecular weight can be reduced. For this purpose, triethanolamine can be used as a base. The hydrolysis and the molecular weight of hydrolysed product depends upon the temperature of reaction and on the amount of base used. Triethanolamine, when used in excess and if the temperature is raised to 180°C thermal

condensation^{15,16} and *trans* amidification reactions occur in proteins and in this reaction the molecular weight of the hydrolysate depends upon the amount of the base used. So care should be taken in controlling the molecular weight. The advantage of using triethanolamine over other base is that triethanolamine itself acts as a plasticiser.³

In the present investigation, casein was dissolved and partially hydrolysed, using triethanolamine as the base. The hydrolysed casein was cast into films and the mechanical properties were studied. Experiments were performed separately to study the effect of triethanolamine as a plasticising agent. Since the casein is hydrophilic, the moisture absorbed by casein films can also act like a plasticiser. Therefore, the role played by the absorbed water on mechanical properties of alkali treated films were studied.

EXPERIMENTAL

Preparation of Alkali Treated Casein Films

Casein (5 g) soaked overnight in water (50 ml) was heated in a bath at 60°C for 30 min and then treated with various quantities of triethanolamine. This mixture was heated at 60°C for 30 min and then immediately cooled.

For the molecular weight determination, the sample was prepared as follows: the solution obtained after alkali treatment was solidified using liquid nitrogen and then totally dried under vacuum. The dried alkali treated casein sample was again dried in a vacuum desiccator at 50°C for 3 h. Molecular weight of the alkali treated casein samples were measured by gel permeation chromatography in a buffer solution having pH of 11.2 using Waters 150-C ALC/GPC instrument. Buffer solution was prepared by dissolving 3.75 g of glycerin and 2 g of NaOH in 1 liter of water. The chromatograms were recorded at a flow rate of 1 ml min⁻¹. Average molecular weights of alkali treated casein were calculated from a calibration curve of polyethyleneoxide stan-

dards.

Preparation of Polymer Films

Films were cast on a mercury surface from a solution of alkali treated casein. The concentration of the solution corresponded to 15% solid content on drying. The films were cast at 65% RH and 25°C. The films thus obtained were removed from the mercury bed, dried in vacuum and conditioned for 7 days at 25°C and 65 ± 2 RH in a desiccator.

Pure casein film was prepared as follows: 1 g of casein was soaked overnight in water (10 ml). The contents were heated in a bath at 60°C for 30 min. Ammonia solution (≈ 1 ml of 25% w/w) was added drop by drop to casein in order to make casein into solution (pH of the solution is 7.8). In this publication, this solution was referred as pure casein solution and films were made from this solution.

For studying the physical plasticisation effect of TEA, known quantities of triethanolamine (TEA) was added to the pure casein solution at room temperature, stirred and immediately made into film over the mercury surface as mentioned above. The dried films were tested for mechanical properties after conditioning the samples at 65 ± 2 RH and at 25 ± 2°C.

Testing of the Films

Mechanical properties such as tensile strength, elongation at break etc. of the films are normally studied only uniaxially, by stretching the specimen in one direction (longitudinal direction). While testing these films uniaxially, it was found that these films contract perpendicular to the direction of stretch.¹⁷ Moreover, uniaxial testing of films has only limited application, since in practice, the films are rarely subjected to an unrestricted extension in one direction and in actual use, the film is ordinarily subjected to forces in several directions simultaneously. As a result, there is lateral contraction which cannot be studied in one dimensional test. Due to the lateral contraction, during uniaxial straining,

the value obtained may not reflect the exact property of the film. Therefore, it was thought essential to prevent the lateral contraction by applying a load (lateral stress) in the lateral direction.

For uniaxial testing, dumb-bell shaped specimens were cut as per ASTM standards.¹⁸ The thickness of the specimens were measured using a thickness guage having a sensitivity of the order of a mil (Mitutoyo). Samples were tested using an Instron universal tensile testing machine (model 1112). Regarding the biaxial testing and the sample shape, details were given in our previous publication.¹⁹ In biaxial testing, a constant load was suspended in the lateral direction (Figure 1) and the stress-strain characteristics in the longitudinal axis was studied. The applied stress in the lateral direction was varied up to 40 kg cm^{-2} .

For stress-strain measurements, the samples were continuously stretched up to break and from the data, stress-strain curves were plotted. The lateral constant load would however, result in creep in that direction and in this present investigation, this creep effect has not been taken into account.

In the case of stress relaxation experiments, the samples were stretched to a level of 20% strain and the stress decay was studied. In the

case of biaxial testing, the lateral stress was varied up to 30 kg cm^{-2} and the decay patterns were studied. All these experiments were carried out at $65 \pm 2\%$ RH.

To study the role of humidity, the dumb-bell shaped specimens were kept in a desiccator containing saturated solutions of different salts²⁰ to condition the films at the required humidity for 7 days at $25 \pm 2^\circ\text{C}$. After 7 days the stress-strain characteristics were measured. A simple procedure to test these samples in the humidity at which they were conditioned is as follows: the samples were immediately wrapped in polyethene sheets and the gripping area was not covered by the polyethene sheet and it was tightly gripped in an Instron tester and the experiment was performed quickly to prevent any alteration in the testing condition of RH. Care was taken to see that the externally covered polyethene did not interfere in the mechanical testing conditions, other than to maintain the specimen in the testing humidity conditions.

RESULTS AND DISCUSSION

The stress-strain curve of pure casein film is given in Figure 2a for comparison. The films formed from the pure casein gave a very small extension and very high tensile strength. For a film forming material on the other hand, optimal extension is essential. From the figure, it can be understood that pure casein forms a hard brittle film. So casein is plasticised with TEA in order to improve elongation. Stress-strain curves of plasticised films were given in Figures 2a and 2b.

For pure casein films, load raises continuously until the specimen breaks, with the increase of strain, which is characteristic of brittle fracture. The fracture occurs in the sample before the average stress reaches yield point. With 0.2 ml of plasticiser per gram of dry casein, the stress decreases considerably, whereas there is only a marginal change in strain at break. When the concentration of

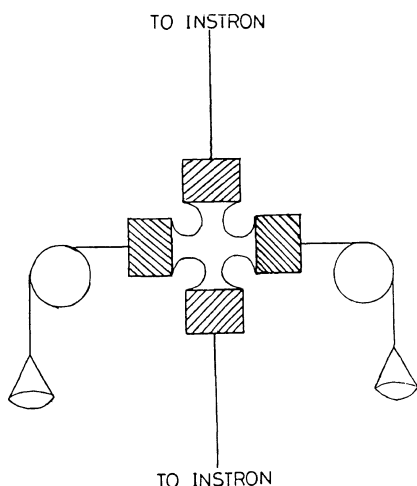
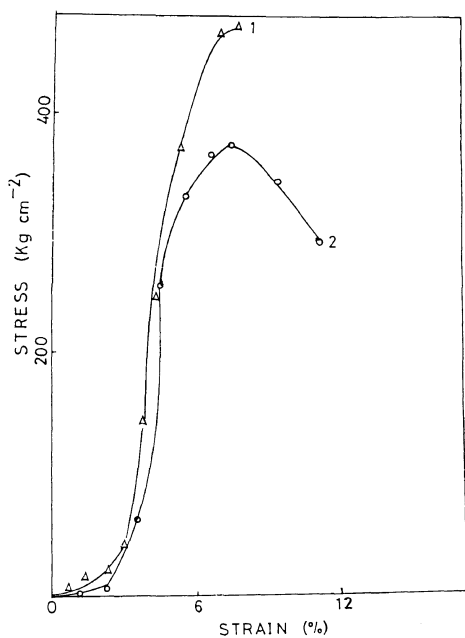
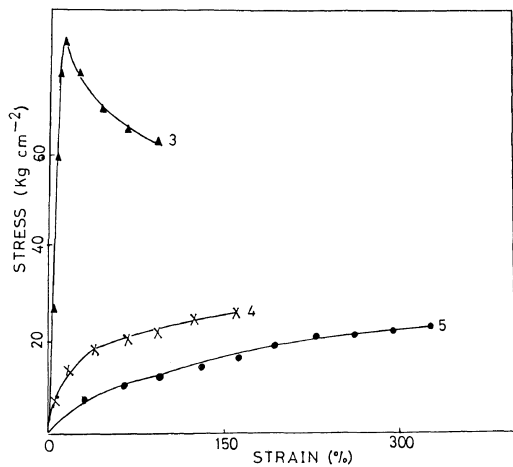


Figure 1. Diagram showing the plan of biaxial testing.



(a)



(b)

Figures 2a and 2b. Stress-strain curves of casein with different level of plasticisation. 1, control casein; 2, 0.2 ml; 3, 0.5 ml; 4, 1.0 ml; 5, 2.0 ml of TEA per gram of dry casein.

plasticiser is increased, the stress decreases to an optimum value, whereas the strain increases to a very great extent (Figure 3). The addition of plasticisers to polymeric materials produces an effect similar to an increase in temperature.^{21,22} This is so, because the properties of

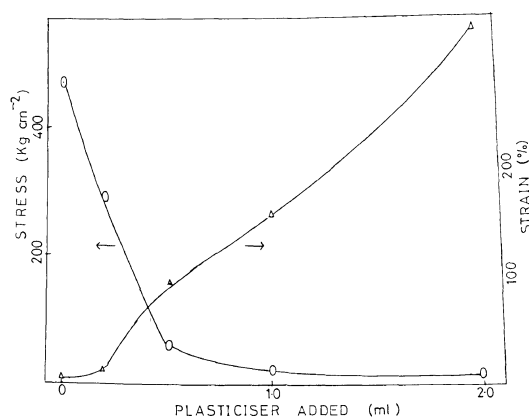


Figure 3. Effect of plasticiser on stress and strain, at break.

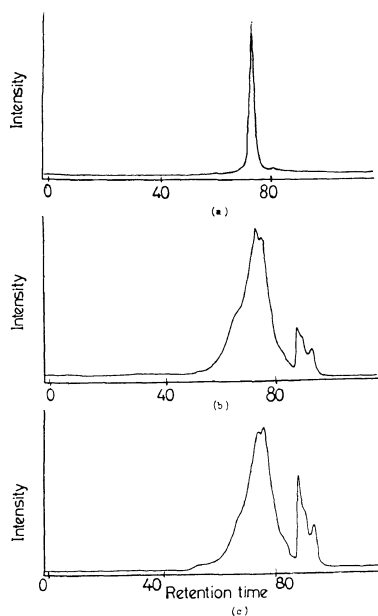


Figure 4. GPC curves of casein treated with TEA. a, pure casein; b, 0.2 ml of TEA; c, 0.6 ml of TEA per gram of dry casein.

the materials are dependent on the difference between the testing temperature and the glass transition temperature.

In the next stage, instead of physically plasticising casein, with TEA, the casein was treated with the same amount of TEA at 60°C for 30 min and molecular weight was calculated using GPC. Figure 4 (a, b, and c) shows the

GPC of the pure casein and casein treated with 0.2 ml and 0.6 ml of TEA per gram of casein. Molecular weights for caseins were presented in Table I.

GPC of control casein has \bar{M}_n of 18591 and \bar{M}_w of 23277 having a very narrow dispersity of 1.25. The GPC curve of control casein shows that the polymer has got narrow unimodal distribution. But on the other hand, alkali treated casein has got a bimodal distribution and the polydispersity increases with the increases of alkali added. The \bar{M}_n decreases from 18591 in the case of pure casein to 1885 for the casein treated with 0.2 ml of TEA per gram of dry casein. It further decreases with the increase of alkali to 1214 for the sample treated with 0.6 ml of alkali. However a weak shoulder with shorter retention time indicating the possible formation of some higher

molecular weight fragments on TEA treatment was also observed in the GPC (Figures 4a and c). This observation may suggest some restructuring of proteins in casein which implicate probably crosslinking, after treatment with TEA. The nucleophilicity of the amine may induce nucleophilic reactions at or near side chains bearing sulphur and phenolic hydroxyl groups. However on the basis of the experimental evidence obtained in the present study, it is difficult to draw meaningful conclusions on the possible crosslinking processes induced by TEA on casein.

In Table II, tensile parameters of casein, treated with various amounts of TEA is presented. In the case of casein treated with 0.05 ml of TEA per gram of dry casein, the stress at break decreases to 227 kg cm^{-2} , whereas there is only a marginal change in the strain at break values. With the increase of alkali treatment, the stress decreases, whereas the strain at break increases as is seen from Table II.

Fracture behaviour changes considerably with the increase of alkali treatment. From brittle rupture, it changes to necking followed by cold drawing and the sample uniformly extends till break without forming a neck.

These results show that decreasing the molecular weight improves stretchability of casein films. Since an optimum extension is needed for casein films used for leather finishing, casein treated with 0.2 ml of TEA per

Table I. Molecular weight data of treated casein obtained from gel permeation chromatography

	Pure casein	Casein +0.2 ml g ⁻¹ of dry casein	Casein +0.6 ml g ⁻¹ of dry casein
Number-average molecular weight	18591	1885	1214
Weight-average molecular weight	23277	98392	108977
z Average molecular weight	27286	1474403	2525782
Dispersity	1.25	52.2	89.8

Table II. Tensile parameters of alkali treated casein films treated with different concentrations of TEA

Volume of TEA added	Stress at yield	Strain at yield	Stress at break	Strain at break	Energy to break
ml g ⁻¹	kg cm ⁻²	%	kg cm ⁻²	%	MJ m ³
0	—	—	469.0 ± 60.0	7.72 ± 0.8	1.593
0.05	270.0 ± 12.3	4.5 ± 0.4	227.0 ± 2.8	10.10 ± 0.5	1.880
0.1	174.3 ± 12.0	4.7 ± 0.2	135.0 ± 11.7	33.80 ± 3.4	4.160
0.2	56.3 ± —	21.6 ± 2.4	64.0 ± 5.0	107.80 ± 12.0	5.780
0.5	—	—	26.8 ± 1.9	120.40 ± 6.0	2.040
1.0			Forms tacky film		
2.0			Forms tacky film		

gram of dry casein films were used for other studies like biaxial testing, effect of humidity etc.

The stress and strain, at break of the samples treated with 0.2 ml of TEA per gram of dry casein is compared with the properties of the samples plasticised with the same amount of alkali (Figures 2 and 6). These figures show that treatment of alkali decreases the stress at break (about 5 times), where there is an appreciable increase in strain (10 times). This shows that by partially hydrolysing casein properties can be changed to an optimum level.

Stress-strain characteristics of alkali treated casein films tested uniaxially is presented in

Figure 5. The stress initially increases, but the yield point is not very much pronounced. After the yield point, the stress is not appreciably changed with the increase of strain. These graphs show that, when casein is treated with alkali, the behaviour changes from hard brittle to hard tough.

Biaxial stress-strain characteristics of alkali treated film (0.2 ml of casein TEA per gram of dry casein) under various applied lateral stress levels *viz.* 2.5 to 40 kg cm⁻² is presented in Figure 6. The effect of applied lateral stress on the stress and strain, at break is presented in Figure 7. It is clearly seen from these figures, that the strain in the longitudinal direction is

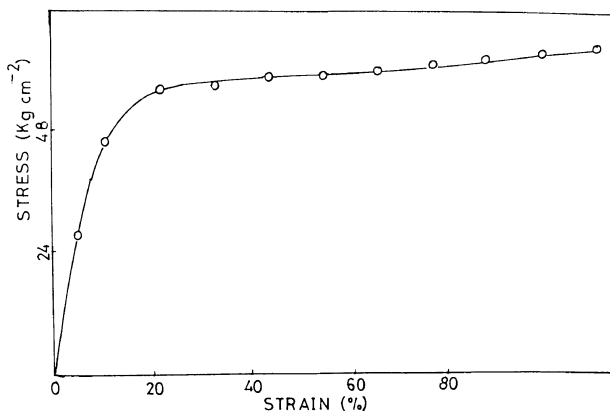


Figure 5. Stress-strain curves of alkali treated casein films at (uniaxial).

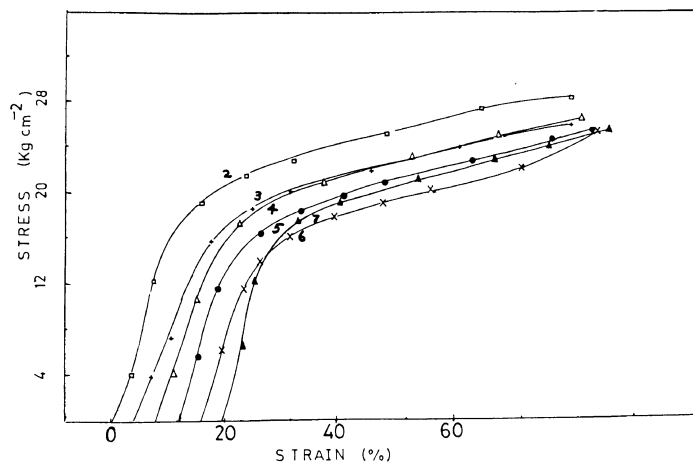


Figure 6. Stress-strain curves of alkali treated casein films at different applied lateral stress (kg cm⁻²).

very much affected by the applied lateral stress. The longitudinal stress at break shows a steep decrease as soon as lateral stress is applied and shows practically no change beyond an applied lateral stress of 5 kg cm^{-2} .

Effect of RH on Stress-Strain Characteristics

In amorphous polymers presence of water can induce a substantial reduction of T_g , which

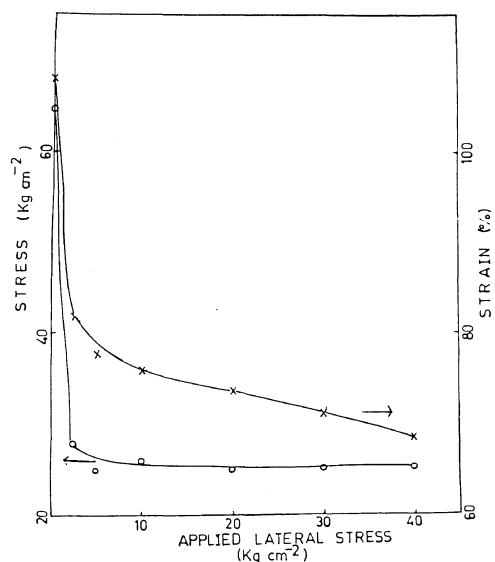


Figure 7. Effect of applied lateral stress on longitudinal stress and strain, at break.

in turn affects the properties. Recent literature shows the continued interest in the interaction of hydrophilic polymers with water.²³⁻²⁹ Stress-strain curves of alkali treated casein films at various RH are given in Figure 8. The tensile strength decreases, while the extension at yield and at break gradually increases with the increase of RH as is seen from Table III. The amount of moisture absorbed by the sample at various RH are also presented in Table III. The xerofilm initially absorbs moisture at a very slow rate and the absorption increases less markedly with increase in humidity and finally absorption increases very markedly as saturation is approached.

At lower humidities, the sample yields initially and cold draws. During the first rise in stress, the specimen deforms uniformly. The deformation is localized, near the narrowest section neck formation takes place and then the load starts increasing. When the humidity is increased, the yield point is not predominantly seen (a pseudo yield point) and the strain increases with, very little increase of stress. At saturation ($\approx 97\%$) the stress is very little and the strain enormously increases and the slope value is very less when compared to the slope value at 17%.

In general, plasticisers has similar effect like

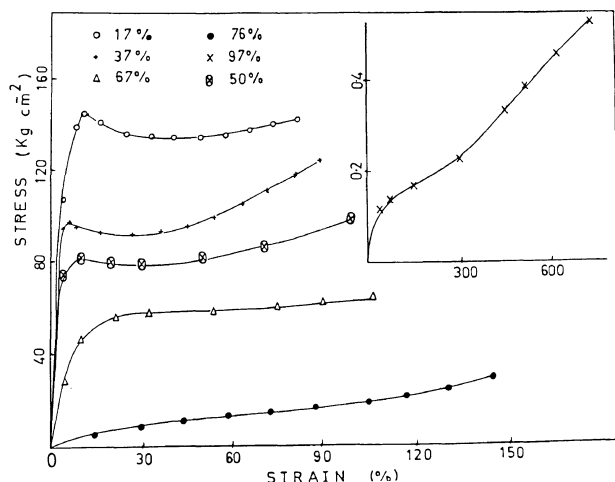


Figure 8. Stress-strain curves of alkali treated casein films at different RH levels.

Table III. Effect of relative humidity on the various tensile parameters of alkali treated casein

RH	Moisture absorbed	Stress at break	Strain at break	Energy to break
%	%	kg cm ⁻²	%	MJ m ⁻³
17	1.38	142.7 ± 10.0	82.4 ± 2.6	10.78
37	3.80	125.2 ± 11.0	90.2 ± 6.0	8.53
50	4.13	100.2 ± 8.2	101.4 ± 10.0	8.01
67	19.51	64.0 ± 6.4	107.8 ± 1.2	5.85
76	28.52	28.4 ± 3.1	145.8 ± 15.0	2.15
97	105.96	0.5 ± 0.03	740.0 ± 15.0	0.21

increase in temperature.^{21,22} As the concentration of the plasticiser is increased, the T_g moves to lower temperatures and consequently the moduli and yield stress at normal ambient temperatures are decreased. As the plasticiser concentration increases, the yield stress decreases and the type of failure changes from brittle fracture to necking rupture, cold drawing and then to uniform extension. These effects are clearly seen in the figure (Figure 8).

So in the case of alkali treated casein films, water acts as a plasticiser and affects the mechanical properties as mentioned above. It was reported³⁰ that in general, in amorphous polymer, the probable site for water penetration in the molecular structure would be the -OH groups present in the molecule. The fact that water will loosen interchain interactions by competing for the interchain hydrogen bonds may induce the failure by chain slipping and thus reduce the tensile strength.

Table III shows the variation of RH (absorbed moisture) changes the stress at break and reduces to half, when RH was changed from 17 to 67. It also changes the fracture pattern. But in the case of strain at break, the effect is not very much pronounced and increases from 82.4% to 108 only. Comparing these results with pure casein and casein plasticised with 0.2 ml of TEA per gram of dry casein (Figures 2a, 6, and 8) it can be concluded that the reduction of molecular weight play a dominant role in mechanical properties of these

Table IV. Tensile parameters at break for alkali treated casein films

	Normal	After long term storage
Stress/kg cm ⁻²	64.0	22.4
Strain/%	107.8	93.7

films.

Effect of Ageing

TEA treated casein films were stored at 65 ± 2 RH and 25 ± 2°C for one year. The films, on storage becomes brown in colour. Stress-strain characteristics of these films were studied and presented in Table IV. Table IV shows that there is not much change in strain on ageing, whereas there is a considerable change in stress at break values.

Stress Relaxation

The uniaxial stress relaxation was studied at 20% strain level and the stress ratio (σ/σ_0) is plotted against time. Similarly, biaxial stress relaxation values were also plotted and from these graphs, (using σ/σ_0 vs. time) σ/σ_0 is plotted against applied lateral stress at various time levels (Figure 9). Application of lateral stress, affects the stress relaxation and the σ/σ_0 is more for those systems, showing the viscous component is affected by the application of lateral stress.

With the application of lateral stress, the σ/σ_0 increases initially, (*i.e.*, relaxation is less

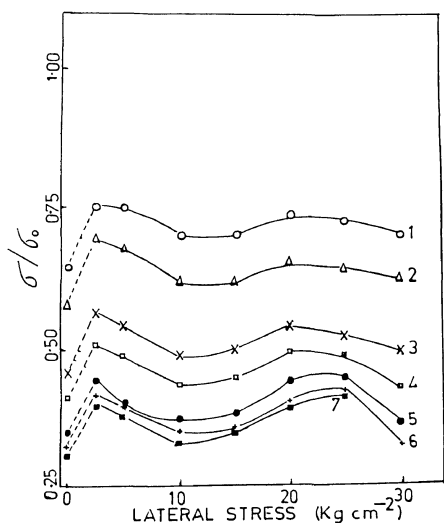


Figure 9. Effect of applied lateral stress on stress decay (σ/σ_0) at various time levels (s). 1, 20; 2, 40; 3, 120; 4, 200; 5, 400; 6, 800.

when compared to uniaxial relaxation) decreases and then increases with the increase of applied lateral stress. The increase in values is due to the effect of creep in the lateral direction which is predominant, compared to relaxation. This trend is observed at all the time intervals.

In conclusion, these studies give a clear picture of the stretchability of the casein systems, after the alkali treatment. The biaxial stress study, leads to conclusions on the importance of the lateral stress.

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