The Different States of Polymers Based on Their Thermomechanical Properties

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I. INTRODUCTION

The different states of polymers have been determined by the use of thermal, mechanical, and electrical methods of following the change of characteristics as a function of temperature.[1a–k]

In this work we present diagrams giving the breaking or yield stress of certain materials as a function of temperature, and also their transition temperatures. These graphs, which show the results of our experiments and those of other authors, seem to be fundamental for the various thermomechanical applications.

The possibility of the three states—rigid, plastoelastic, and rubbery—is examined with respect to the basic structure of the polymers. As polymers are viscoelastic solids, special attention has been given to the change of characteristics as a function of time.

Regular Polymers

Linear macromolecules of such regular or crystalline polymers as polyethylene, polyamide, isotactic polypropylene, and isotactic polystyrene (PSi), are composed of segments that are repeated according to a definite periodicity. One may consider that, after the rigid state characterized by general inertia and the breaking of the solid by brittle fracture, these segments move at characteristic temperatures, called transition points, up to the melting point. The transition points may also indicate the melting of amorphous areas in which the crystallites are embedded. In the crystallites aligned chain segments exist which present laterally higher attractive forces.

Irregular Polymers

Linear macromolecules of irregular polymers may be composed of identical, but inverse, segments. This is the case with polyvinyl chloride (PVC), polymethyl methacrylate (PMM), and atactic

polystyrene (PSa). In the case of such copolymers as polyvinyl chloride acetate (PVCAc) the segments alternate in number and presentation. On this basis, one may assume that the rigid state is separated from the plastoelastic one by a transition point and that a rubbery state succeeds this plastoelastic one after another transition point, since there must be a pasty melt because of the lack of periodicity of the segments.

Crosslinked Polymers

Crosslinked polymers are, in fact, copolymers resulting from the crosslinking of medium-sized molecules, such as polyethylene maleate, the link being, for instance, styrene between the segments of two adjoining molecules. Or they may result from crosslinking between the ends of molecules, such as polyepoxides, by means of short molecules, such as diamines. As we shall see later, the characteristics of the crosslinked networks are rather similar to those of irregular polymers.

Multibranched Polymers

These polymers, which derive from basic molecules of functionality greater than 2, at least for one of the two considered categories (melamine 3 and formaldehyde 2, for instance), present only a rigid state. As a matter of fact, the structure comprises meshes that enclose numerous branches and seems not to be easily distorted.

II. EXPERIMENTAL

A. Tensile Elongation at Various Constant Temperatures but for Increasing Stress as a Function of Time

At a given temperature the stress–strain diagram may be established, under the best defined conditions, by linearly changing either stress or elongation as a function of time. The slope of the fairly

linear parts of this diagram as well as the shape of the curved parts depends, as already mentioned, on the constancy of either stress or strain.

1. Typical Curves

(a) *Regular or crystalline polymers.* According to the speed, v, the temperature, θ, or the orientation, O, the general behavior of the curves varies according to the direction of the arrows in Figure 1 as a function of temperature, speed, or orientation. The upper curve is representative of an oriented material.

Examples of particular curves are given in Figure 2 for low density polyethylene[2] (bPE) and in Figure 3 for polyamide 6.6 (Pa 6.6).

(b) *Irregular linear polymers.* The stress–strain diagrams as a function of speed, temperature, and orientation show the general behavior of regular polymers. Examples are given for PMM (Fig. 4) and PVC (Fig. 5).
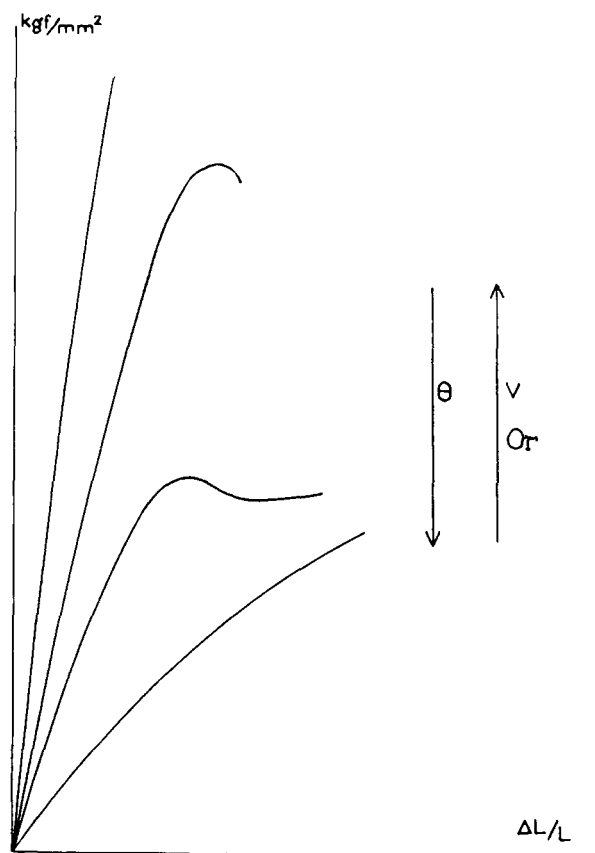
(c) *Crosslinked polymers.* The stress–strain diagrams are similar to those of irregular polymers and, when taken at room temperature, to those of multibranched polymers. An example is given for polyepoxides (Fig. 6).

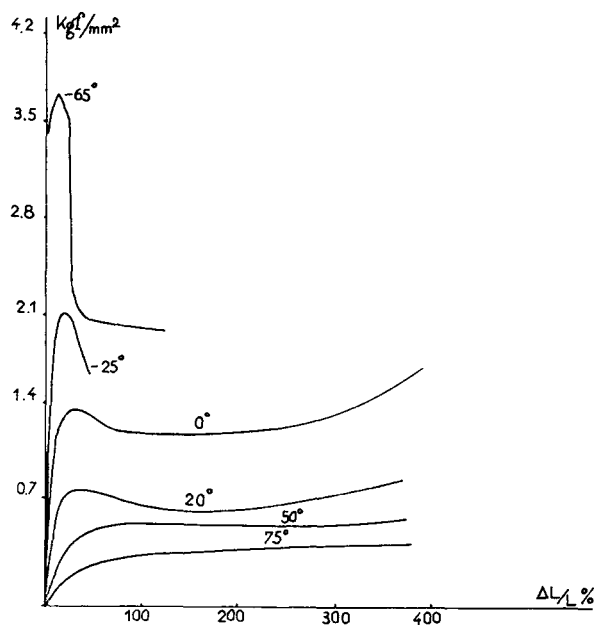(d) *Multibranched polymers.* The tensile curves

Fig. 2. Stress-strain diagram obtained with bPE at different temperatures.

Fig. 1. Theoretical diagram showing the influence of speed V, temperature θ, and orientation on stress-strain curve: R = breaking stress for rigid state; P = yield stress for photoelastic state; $\Delta L/L$ = elongation; ordinate, kg./mm.[2].
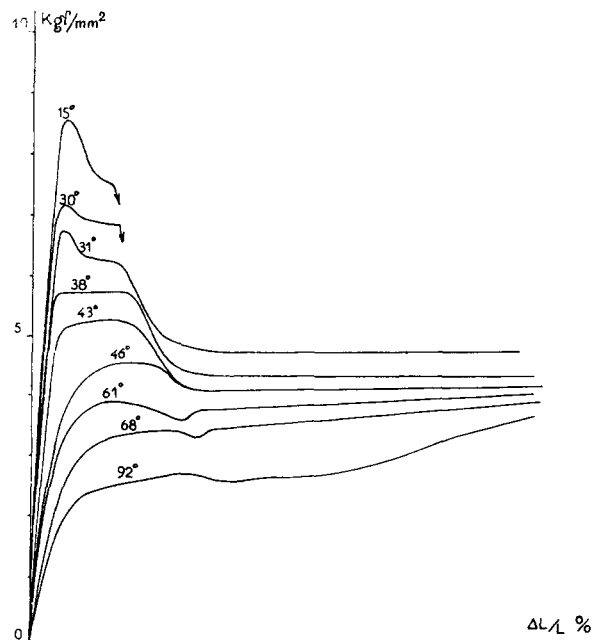

Fig. 3. Stress-strain diagrams obtained with PA 6.6 at different temperatures.
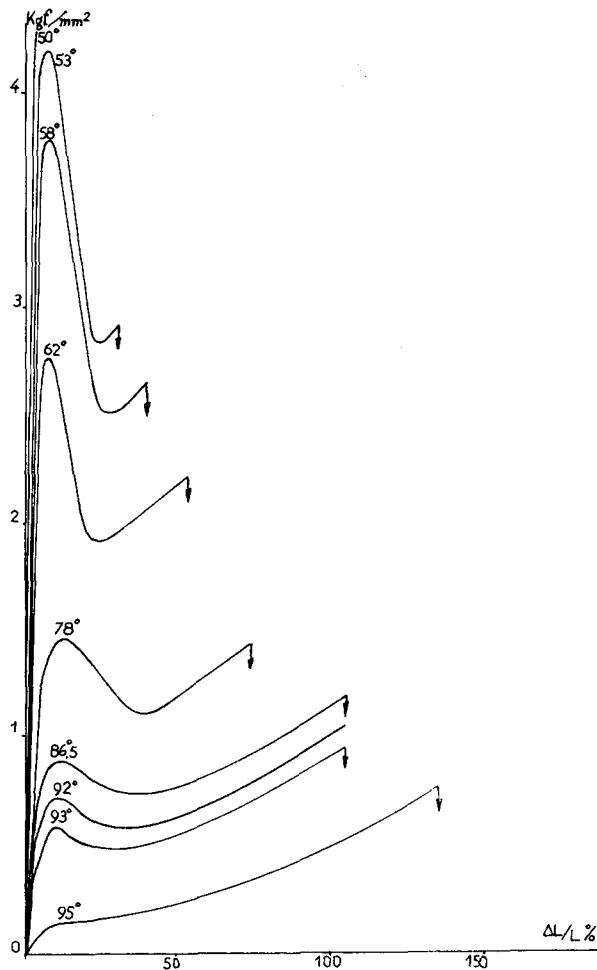
Fig. 4. Stress-strain curves for PMM at different temperatures, °C.

Of course, this orientation disappears as the injection temperature increases. Therefore, polyamide 6.6 (melting point about 250°C.) is almost not oriented, whereas polyamide 11 (melting point about 175°C.) presents a rather noticeable orientation. Furthermore, the tensile specimens obtained by injection of this material from a large gate usually break at the fillet opposite this gate, whereas in polyamide 6.6 the ruptures occur at random in the gate section. Another example, similar to the case of polyethylene, has recently been given by Kargin:[4] polypropylene, Figure 9.

Orientation may be due also to stretching which, when multiaxial, seems to reduce the crazing tendency as in the case of PMM, as shown by Kline and his co-workers.[5] It should be noted that, for two

of these polymers are fairly linear (Fig. 7). The small elongation (a few per cent) increases slightly with the temperature, whereas the breaking stress appreciably decreases. This stress is not very different from the elastic limit.

(e) *Characteristic points.* As will be shown in the discussion of results (Section III), there exist a characteristic breaking stress R for the rigid state and a characteristic yield stress P for the plastoelastic state (Fig. 1).

2. Effect of Various Factors on Shape of Stress–Strain Curve

(a) *Orientation of the linear polymers.* In the case of regular polymers such as polyethylene (bPE), an orientation sheath results from injection in a large-gated mould. The tensile curves according to the direction parallel or perpendicular to injection show a different behavior (Fig. 8).[3]
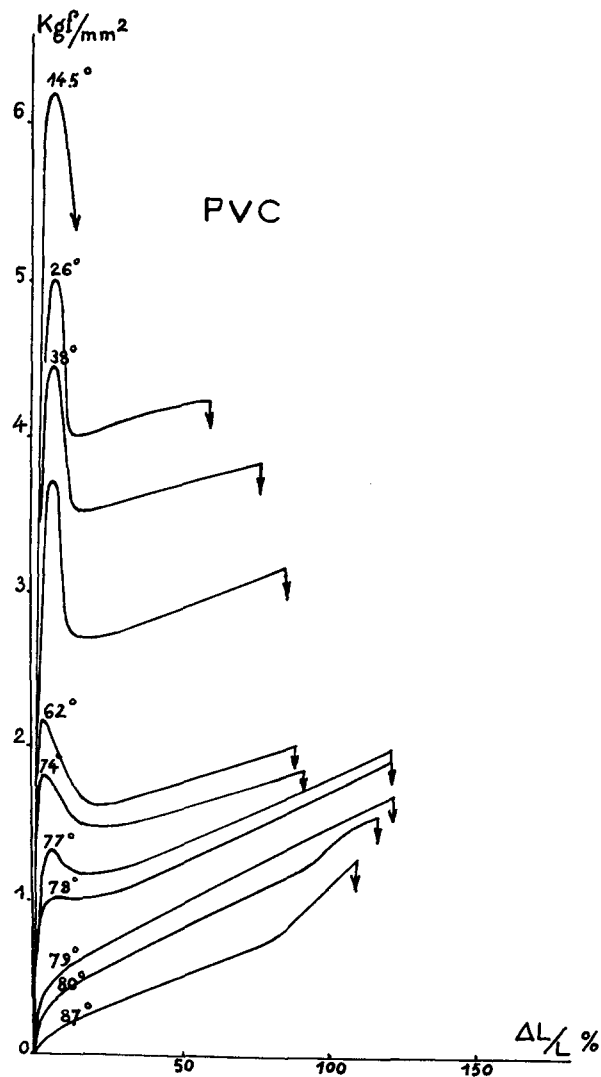

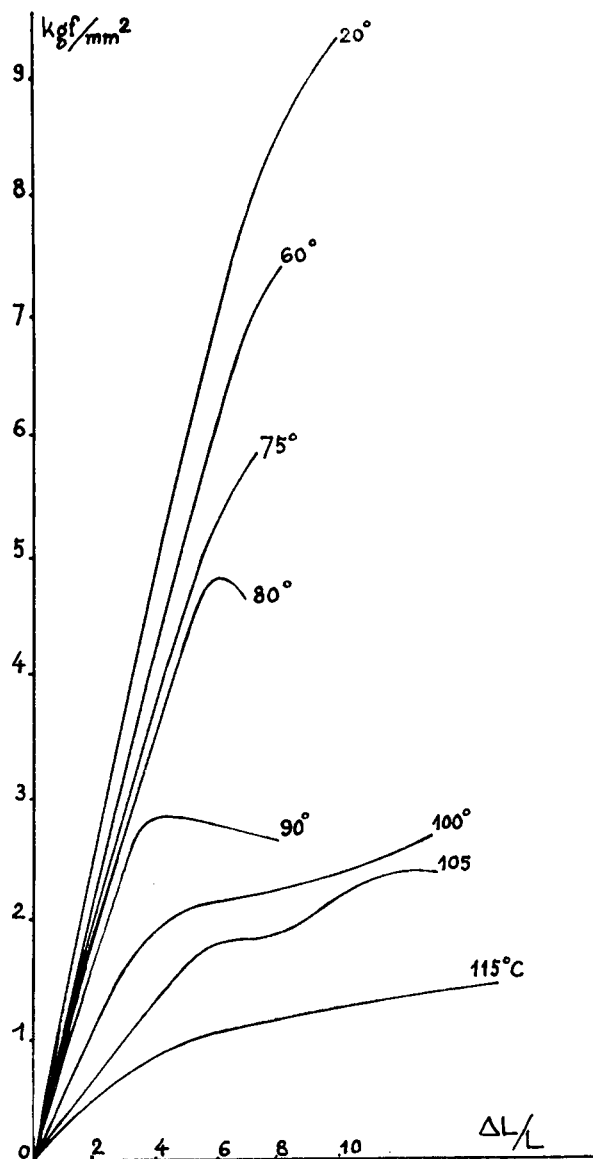Fig. 5. Stress-strain curves for PVC at different temperatures, °C.

Fig. 6. Stress-strain curves obtained at different temperatures, °C., with epoxydes.

different grades of this material—regular, 1, and heat-resistant, 2 (Fig. 10)—the strain as a function of temperature presents a transition point at 50°C.

(b) *Effect of speed.* The curves of Figure 11 show the effect of speed on regular polymers; those of Figure 12, the effect on irregular polymers.[6] It is evident that, if the rate of strain is greater than that of relaxation, the latter has no time to occur and the strain is strictly elastic.

For multibranched polymers, it was established that the breaking stress is proportional to the logarithm of speed.[7] As the curves of Figure 13 will show, even for these materials the small

possibility exists of an elastoviscous strain as a function of speed.

B. Tensile Elongation for Various Constant Stresses and at Linearly Increasing Temperature as a Function of Time

The curves of Figure 14 are related to phenol-formaldehyde (wood-flour-filled, P 21), PMM, and polyundecanamide (Pa 11). These curves were obtained[8] by exerting in each case a constant stress and recording the progressive elongation due to the increase of temperature as a function of time. The case of irregular polymers seems the most interesting, since they are theoretically able to present the three different states: rigid, plastoelastic, and rubbery. Curves of Figure 15 present the tension and compression results obtained with PMM. Those of Figure 16 show the effect of speed.

These curves are frequently used for studying creep. Figure 17 shows the curves obtained for PMM.

III. DISCUSSION OF RESULTS

The various diagrams are obtained by plotting, on the ordinates, the breaking stresses or the yield stresses and, on the abscissas, the temperature, when elongation is effected according to the conditions given above.

A. Multibranched Polymers

The breaking stress decreases fairly linearly as a function of temperature (Fig. 18). If the polycondensation were complete, thermal expansion alone should probably provoke the rupture. In this case, a breaking temperature, θ_r, at which rupture would occur without any external mechanical stress, could be observed. However, the situation is complicated by the presence of internal stresses that may affect the phenomenon. In any case, the plastoelastic state when it happens is fugitive. Therefore, the multibranched polymers must be considered as presenting only the rigid state, rather close to the elastic state. As a matter of fact, as shown by the stress–elongation diagram (inset in Fig. 18), strain up to the breaking point practically does not leave any permanent set.

B. Irregular and Crosslinked Polymers

Under the associated effect of a mechanical stress and of the increasing temperature, a transition point, which may be called the plastoelastic temperature, θ_p, is observed (Fig. 19). This point separates the rigid state in which brittle fracture
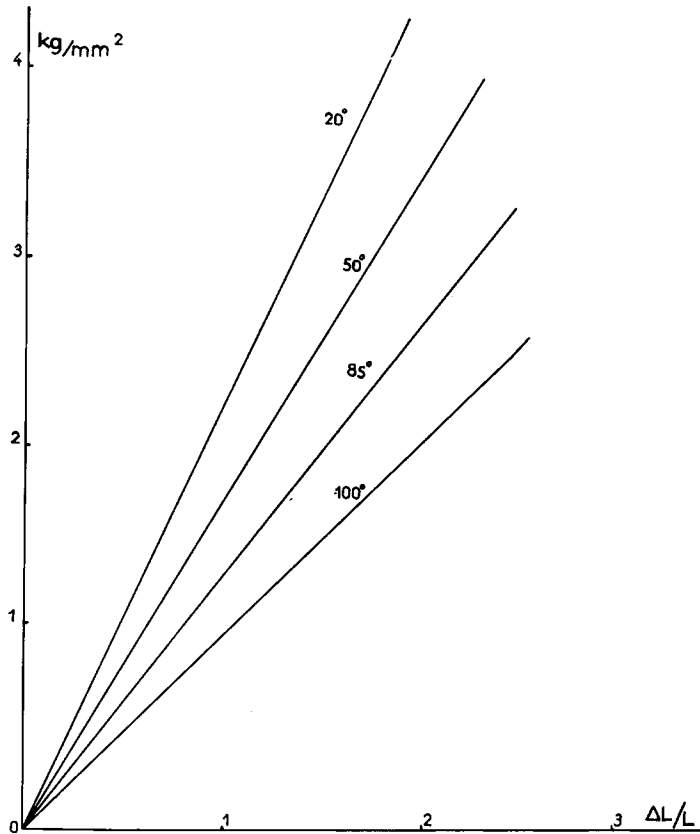
Fig. 7. Stress-strain curves at different temperatures for wood-flour-filled
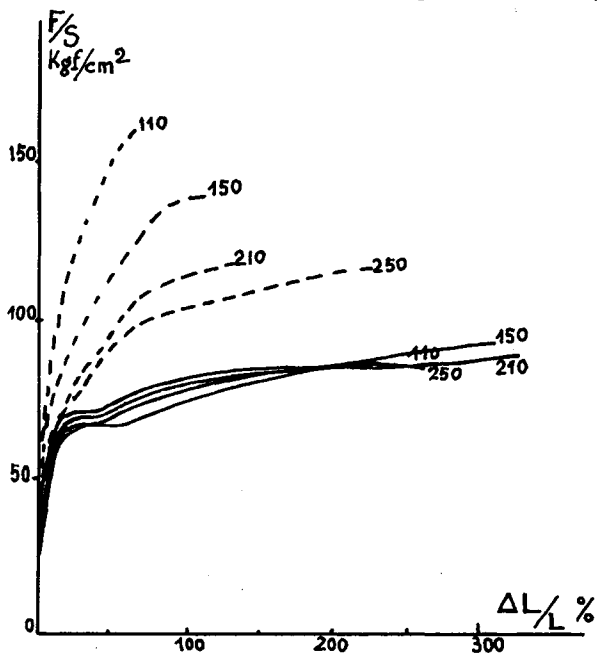phenol–formaldehyde incompletely cured.

Fig. 8. Stress-strain diagrams for different injection tem-
peratures, °C.: (- -) direction of injection; (——) direction
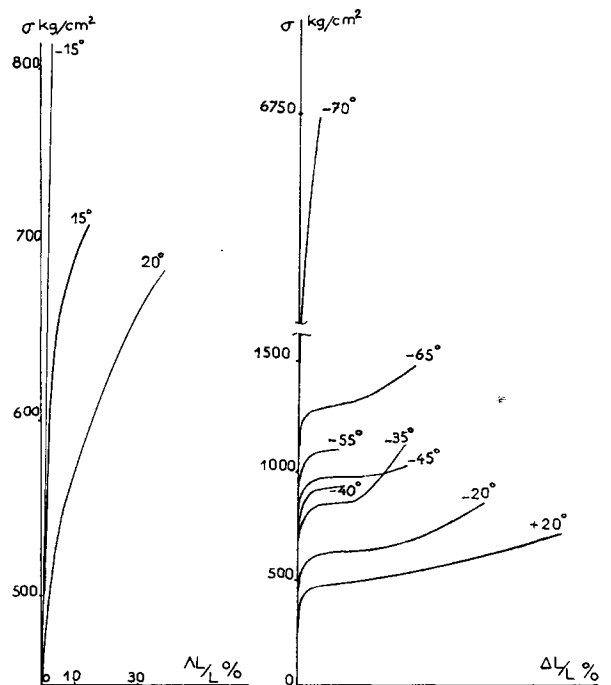perpendicular to injection.

Fig. 9. Stress-strain curves obtained by Kargin and Mart-
chenko with polypropylene: left, direction of orientation;
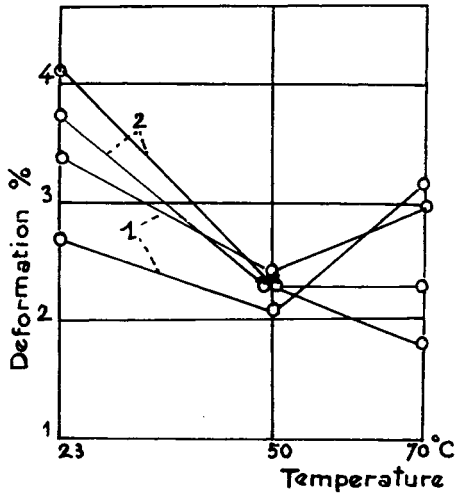right, direction perpendicular to orientation.

Fig. 10. Strain-temperature curves, for two different grades of PMM.[5]

occurs, from the plastoelastic state, in which a progressive flow of the material is caused by the unrolling of the coils and by the slipping of the linear entangled macromolecules that exist in the non-oriented rigid state. In this state, the rupture is of the "ductile" type.

Temperature of plastoelasticity, θ_p, is the minimal temperature at which a minimal mechanical stress provokes the flow of the material without brittle fracture. Above this temperature the mechanical stress necessary to initiate flow decreases with the temperature.

Minimal yield stress is the minimal mechanical stress (in kg./mm.²), for which the yield temperature of the material is lowest. A diagram for PMM obtained by the IIA method (Fig. 20) and another by the IIB method (Fig. 21) are given as examples. In both cases, the temperatures of
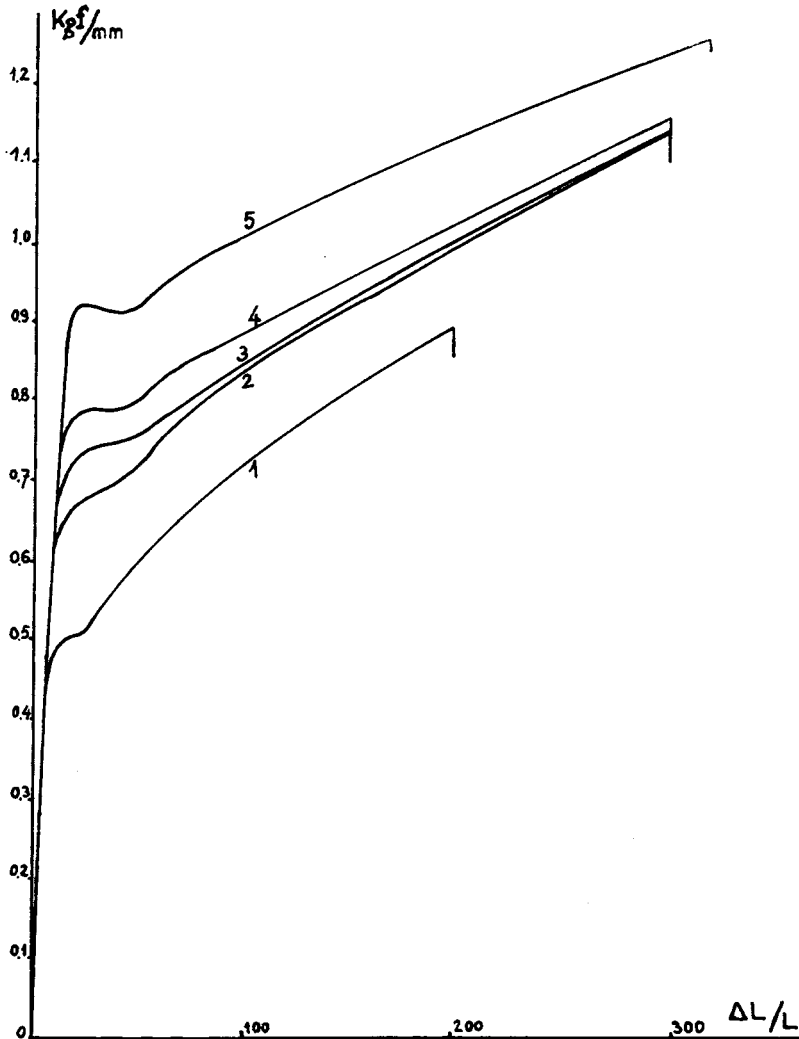

Fig. 11. Influence of speed on a low-density polyethylene: stress-strain diagrams for speed varying from 0.5 to 590 mm./min.

plastoelasticity and minimal yield stress are approximately the same. These characteristics are essential for the use of materials that must withstand mechanical stress at various temperatures. As a matter of fact, if the creep is determined under

Fig. 12. Influence of speed on stress-strain diagrams obtained with PMM.

constant stress and temperature above the temperature of plastoelasticity, a rapid flow occurs.

Rubbery temperature, θ_0, is the minimal temperature (Fig. 19) at which a minimal mechanical stress provokes strain of the elastic type. As the stress-elongation curve shows, there is either an instantaneous or a retarded return to the origin when one removes a stress approaching the rupture point.

Rubbery mechanical minimal stress is the minimal mechanical stress which, at the rubbery temperature, provokes elastic strain. It is interesting to observe that annealing of a highly contracted tensile specimen, if done below this temperature, causes only a partial return to the origin, whereas the return is complete when annealing is done at a temperature higher than the rubbery one, even for a specimen broken into two parts.

Evolution of the yield temperature in the case of PMM, for instance, the apparent rubbery temperature (Fig. 22) is generally higher in compression than in tension, but the difference decreases as the stress is lowered. The middle curve, *m*, between the compression, *c*, and tension, *t*, curves for low stress represents the curve of linear expansion. When linear expansion is measured with the dilatometer C.E.M.P. model, involving compression stresses of a few g./mm.², these stresses are sufficient to influence the yield temperature since the experimental curve, *d*, is close to the compression one. This explains the many different points of view concerning the glass transition temperature determined by dilatometry for inorganic glasses.
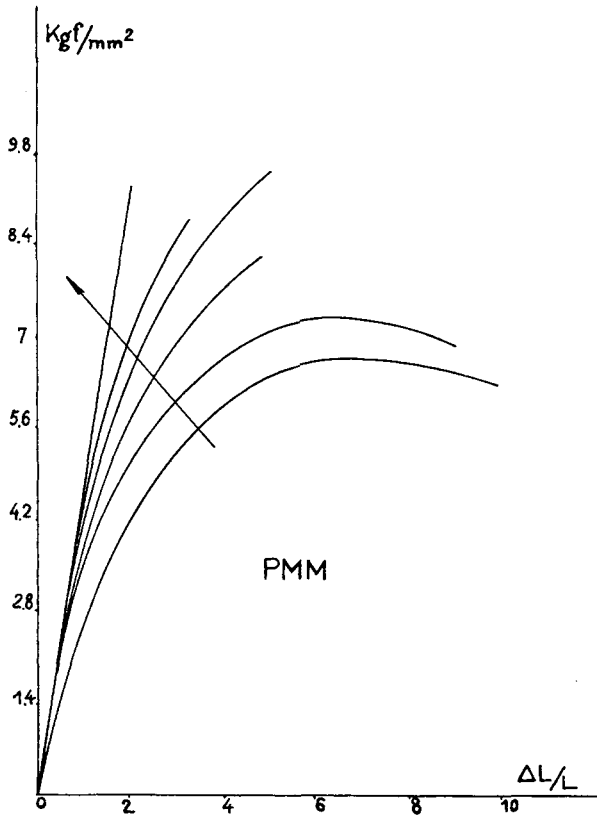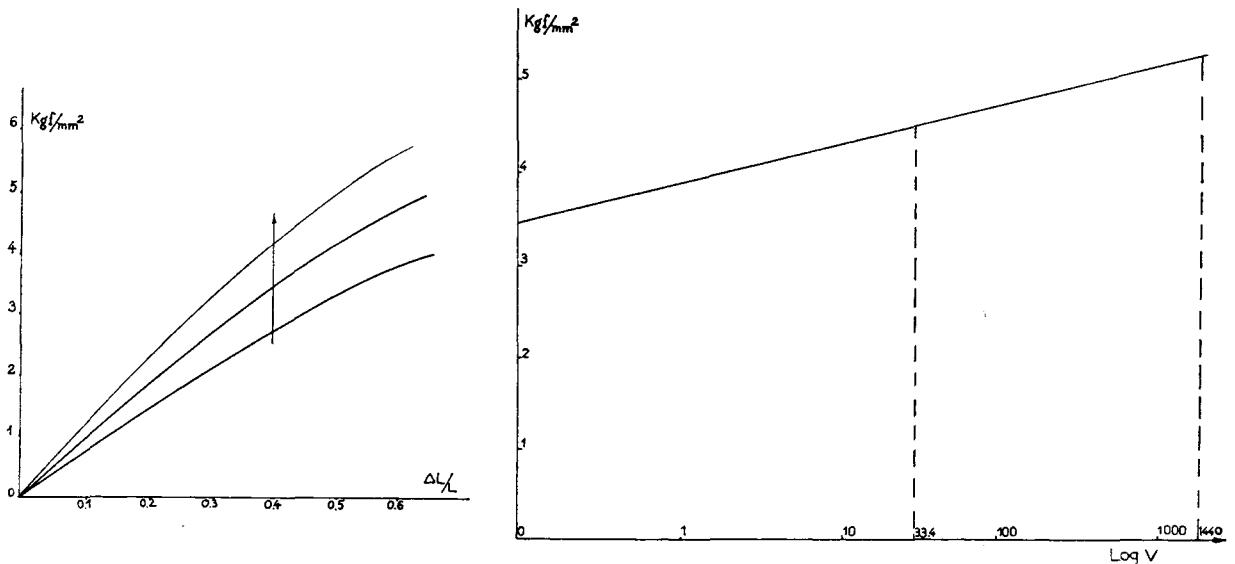
The inflection of curve *d* (Figs. 20–21) may be

Fig. 13. Influence of speed on stress-strain diagrams obtained with phenol–formaldehyde; curves, by day: 1440% (top); 33.4% (middle), 0.1% (bottom).
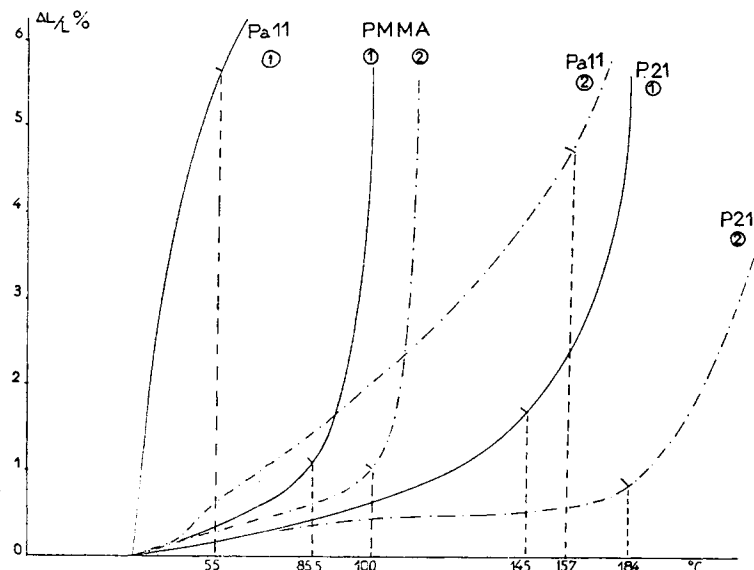
Fig. 14. IIB method applied to different materials with two different stresses.
P21 (phenol–formaldehyde): *(1)* 2 kg./mm.²; *(2)* 1 kg./mm.². PMM:
(1) 2 kg./mm.²; *(2)* 1 kg./mm.². PA11: *(1)* 2 kg./mm.²; *(2)* 1 kg./mm.².

compared to the above-mentioned temperature of plastoelasticity. Thus, in a number of thermomechanical experiments, a transition point may be found around 50°C. This temperature has been determined by measuring the loss angle tan δ and the permittivity[1d] ϵ (Fig. 23), the vibrating modulus of elasticity and, more clearly, the damping coefficient from mechanical losses (Fig. 24).

One may assume that, after the rubbery temperature (Fig. 19), the curve meets asymptotically

the abscissa axis, but the values have not been plotted. Figure 25 presents data for PMM, PVC, and atactic polystyrene.

C. Regular or Crystalline Polymers

The rubbery temperature seems to be slightly lower than the melting point at which generally the weight of the material is sufficient to provoke flow, whereas an additional stress is necessary for irregular polymers. Example of curves are given in Figure 26.

A primary temperature of plastoelasticity, θ_p, often occurs in a region of ±20°C. around room temperature. It is probably the manifestation of
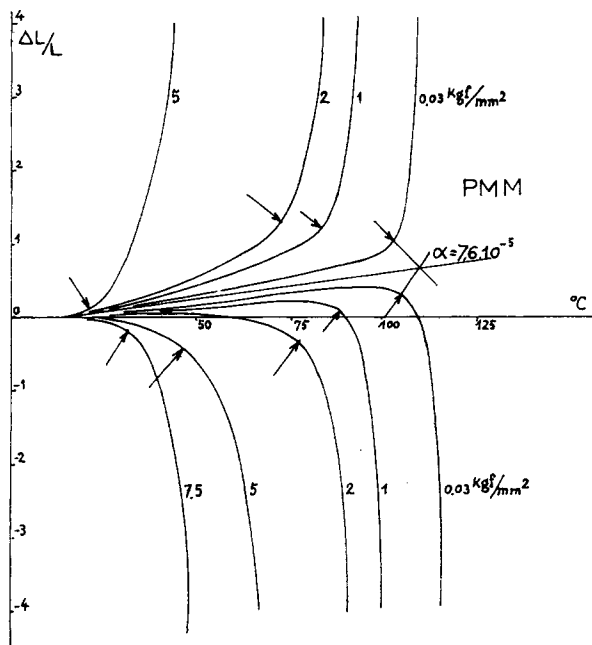

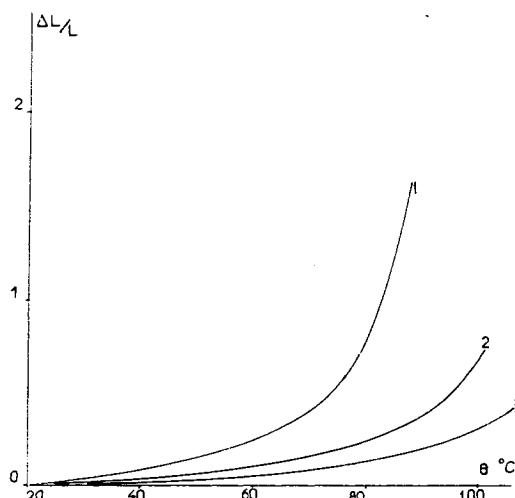Fig. 15. Results given by IIB method applied to PMM: Upper curves, tension; lower curves, compression.

Fig. 16. Influence of the rising speed of temperature with PMM in the IIB method, 1 kg./mm.²: *(1)* 120°C./hr.; *(2)* 60°C./hr.; *(3)* 30°C./hr.
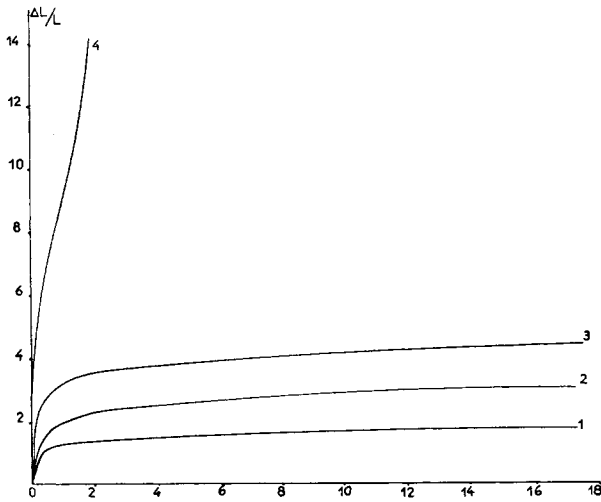
Fig. 17. Classic strain-time diagrams obtained with PMM: At 40°C.: (1) kg./mm.²; (3) 2 kg./mm.². At 55°C.: (2) 1 kg./mm²; (4) 2 kg./mm.².
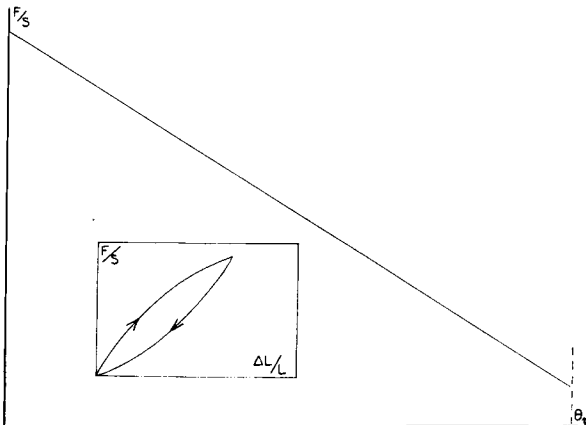

Fig. 18. Theoretical diagram showing rupture stress-temperature variations for thermosets.

the initial melting of the crystallites that are embedded in the amorphous mass. However, the plastoelasticity exists under this primary temperature of plastoelasticity until a lower temperature, which may be called the secondary temperature of plasticity, θ_s, marks the passage to the rigid state.

This simplified view of the transition temperatures is expressed by the diagram of Figure 27.

D. Heat Distortion Temperature under Load (ISO Standard)

The temperature at which rapid creep begins is conventionally determined by applying a load of 0.046 or 0.196 kg./mm.² in flexure between supports. The temperature is raised linearly at the rate of about one degree per minute until the deflection of the specimen reaches a conventional value of 0.25 mm. Thus, there are two different values for the heat distortion point under load, the higher one being obtained with the lower stress.

The distortion temperatures so determined do not agree with the definitions given for the rubbery temperature and the temperature of plastoelasticity, which characterize changes in state under stress. Therefore, one may assume that the use of distortion temperatures under stress leads, in many cases, to very serious misuse in the applications of polymers if the user does not know that he can apply at these temperatures only stresses lower than those mentioned above.

IV. CONCLUSION

This work shows the effects of associated mechanical and thermal stresses on the determination of transition temperatures, of interest particularly
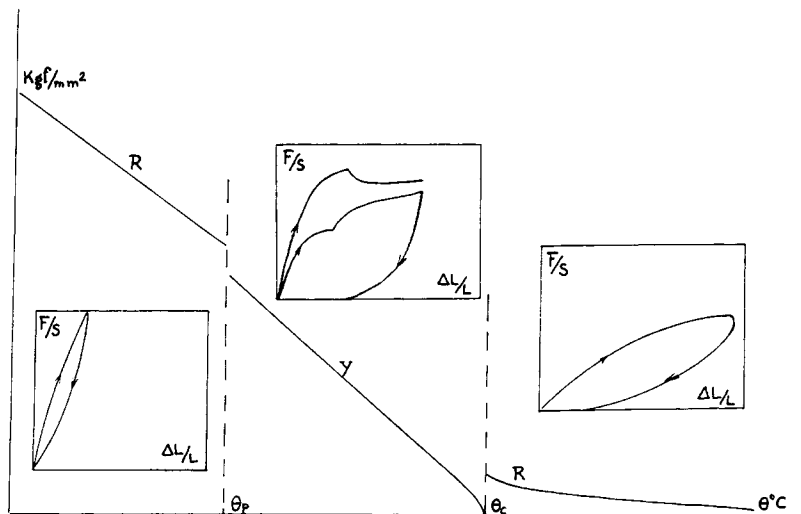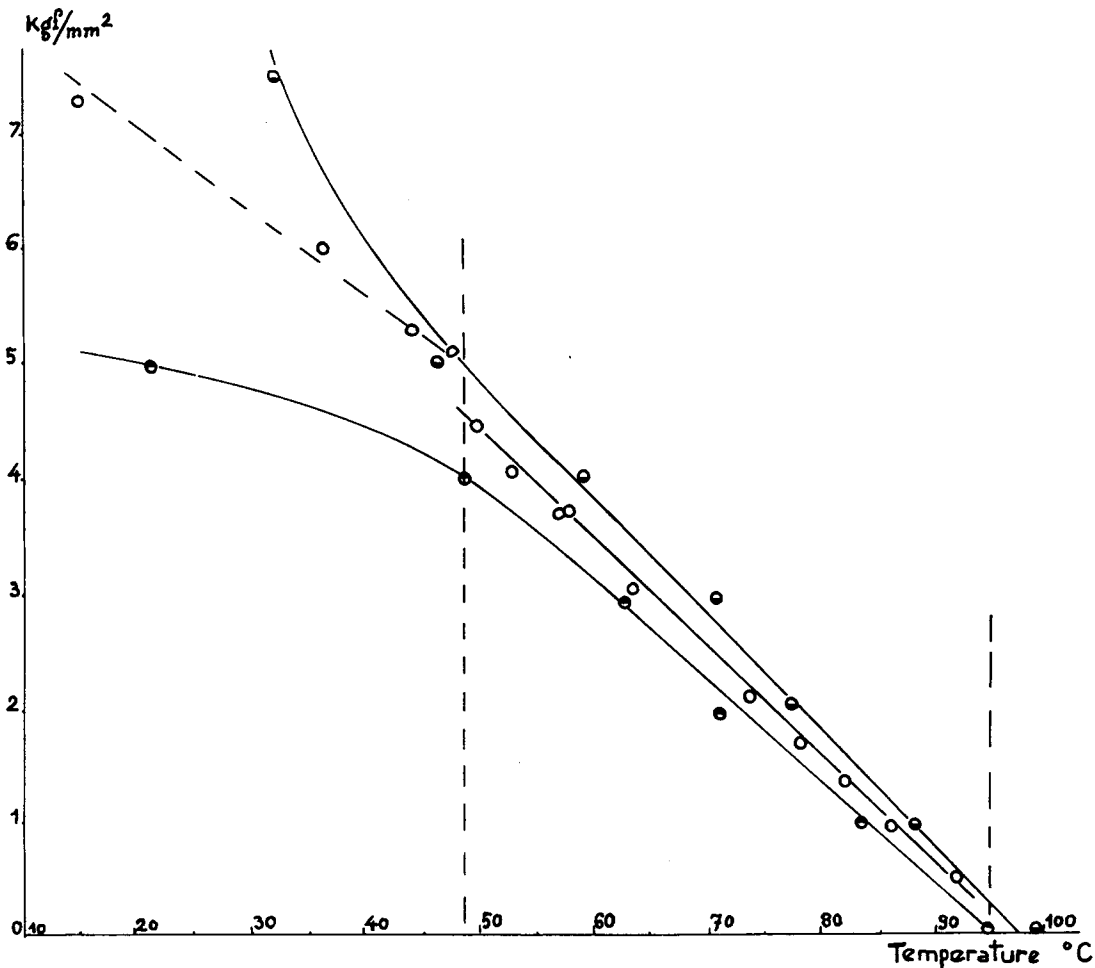

Fig. 19. Theoretical diagram showing the variation of the rupture stress R and the yield stress Y, with temperature for irregular polymers.

Figs. 20–21. Two diagrams plotted on the same figure: (O) Figure 20, rupture and yields tress-temperature following method of page 20; (◐) Figure 21, results obtained with method IIB in a compression test method of page 22; Figure 21, ◖ results obtained with method IIB in a tension test.
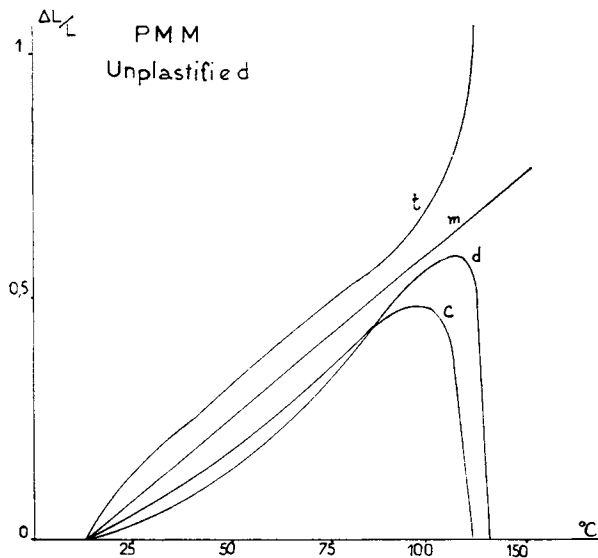

Fig. 22. Curves corresponding to IIB test with PMM and very small stress (0.03 kg./mm.²) in tension t and compression c. The curve m represents the curve of linear expansion; the curve d has been obtained with a linear dilatometric method.
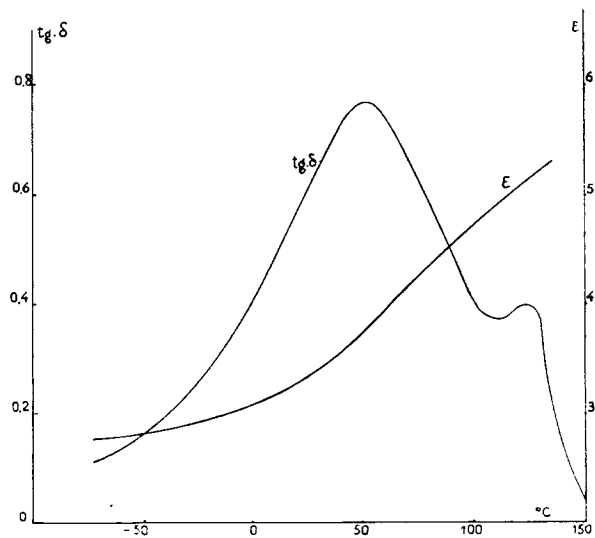

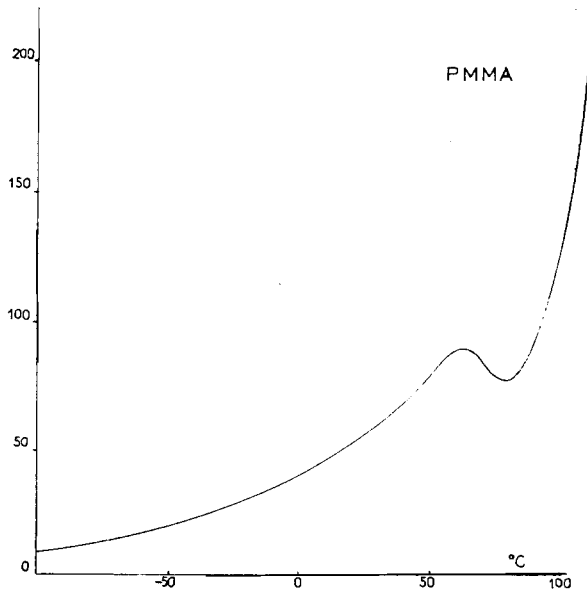Fig. 23. Variations of the loss angle tan δ and the permittivity ϵ according to temperature.

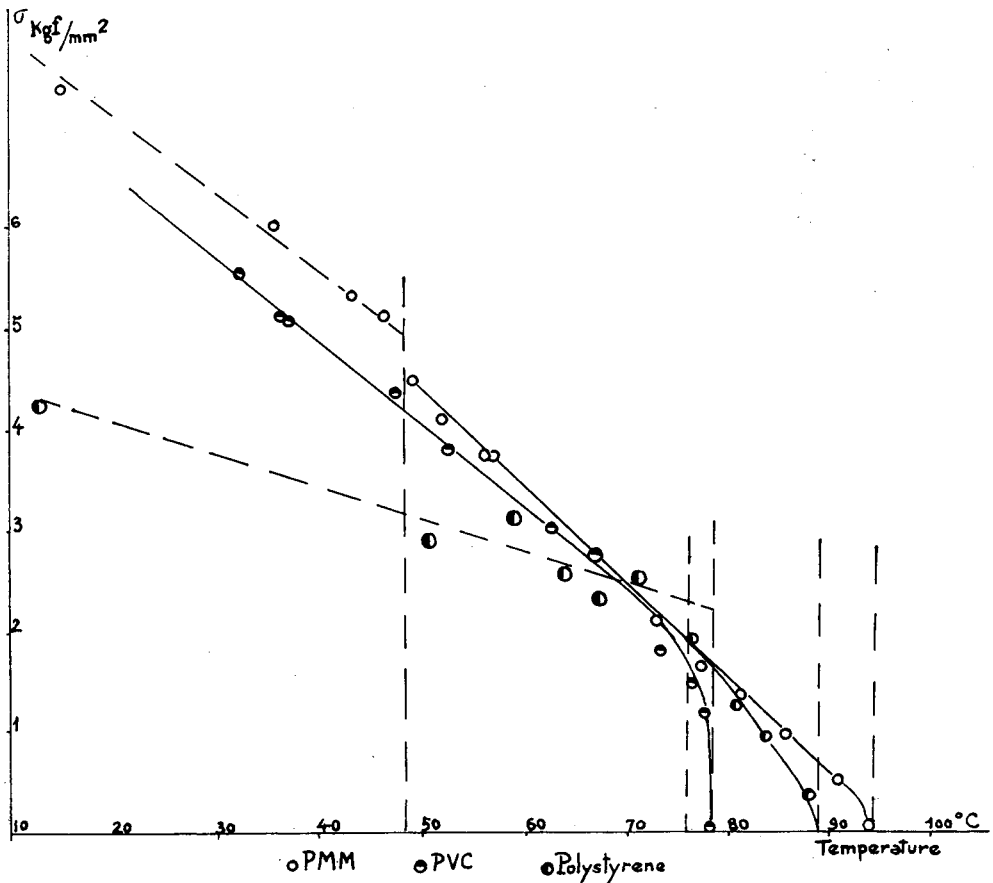Fig. 24. Variations of the mechanical losses according to
temperature.

Fig. 25. Field stress-temperature diagram: (O) PMM; (◒) PVC; (◉) Polystyrene.
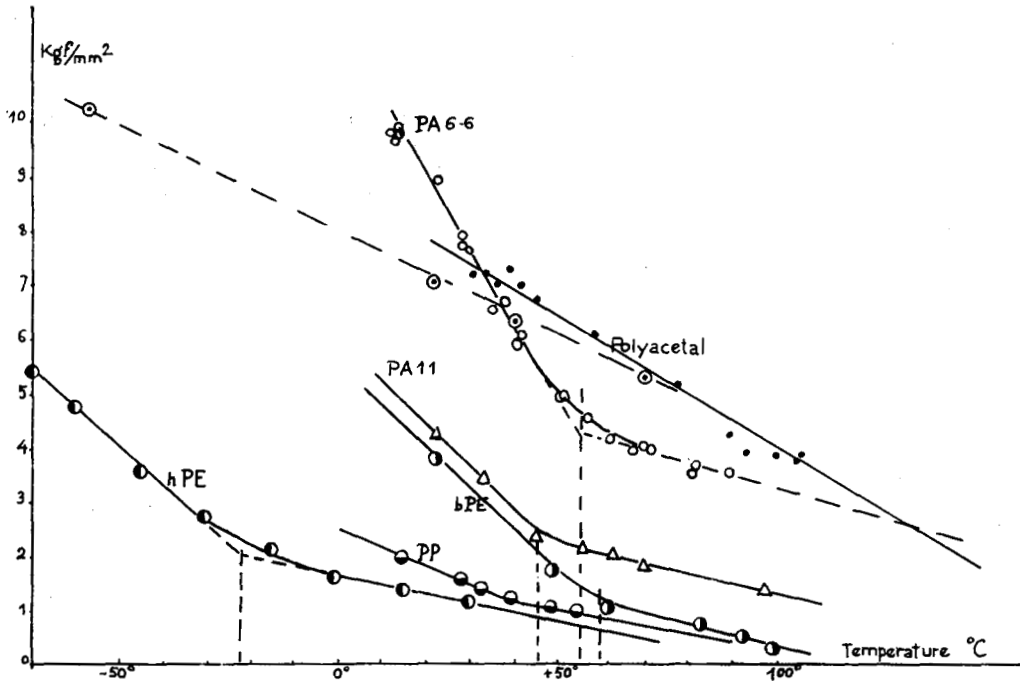
Fig. 26. Field stress-temperature diagrams obtained with regular polymers: (O) nylon 6.6 = PA 6.6; (△) polyamide 11 = PA 11; (◑) high density polyethylene = hPE; (◒) polypropylene = PP; (◐) low-density polyethylene = bPE; (●) polyacetal; (⊙) data given by the manufacturer of polyacetal.
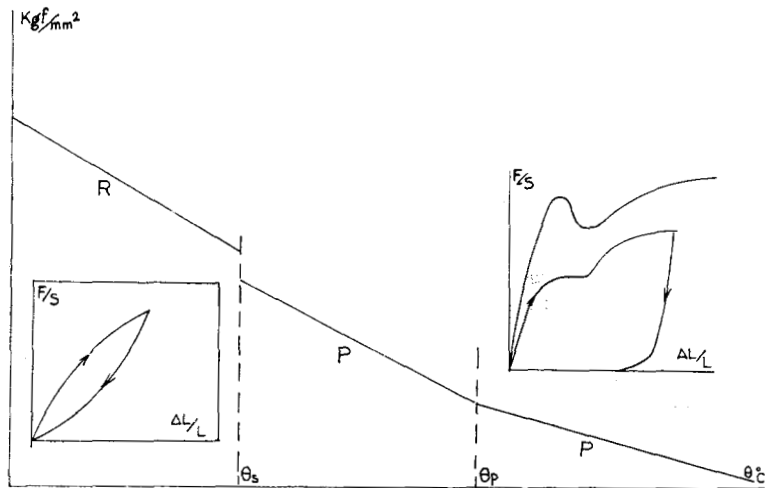
Fig. 27. Theoretical diagram concerning regular polymers.

when thermomechanical applications of the polymers are concerned. So, with such associations, the existence around 50°C. of a temperature of plastoelasticity, separating the rigid and plastoelastic states of PMM, has been confirmed; the rubbery temperature is approximately 90°C.

However, the diagrams showing the passage from the rigid to the plastoelastic state and from the plastoelastic to the rubbery state as a function of mechanical stress and temperature have been determined for too small a number of materials to establish that they have a general significance.

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Synopsis

The different transition points which characterize eventually the three solid, plasto-elastic and rubbery states have been determined by several methods. The authors show nevertheless that good data can be obtained using very simple traction experiments, at different temperatures. These experiments were carried out in different conditions of mechanical strain and temperature; the corresponding characteristics of breaking load and flow strain were noticed. Thus thermomechanical diagrams were obtained, either of the breaking load either flow strain, in function of the temperature for the most important classes of polymers: thermoset, thermoplastics, including crystalline linear and regular polymers, linear irregular polymers and crosslinked polymers. These diagrams give an indication on the limiting strains from which the use must be excluded taking into account flow straining at a given temperature. These diagrams make also more precise the transition points determined at given mechanical strains, of which the effect is important on the temperature where they occur. It is interesting to notice the increasing thermosensitivity of the method for the multibranched, crosslinked, irregular and regular polymers.

Résumé

Alors que les différents points de transition qui distinguent éventuellement les trois états, rigide, plasto-élastique et "rubbery," ont été déterminés par différentes méthodes, les Auteurs montrent qu'on peut arriver à de bons résultats en utilisant simplement l'essai de traction, à différentes températures. Ils ont effectué cet essai dans diverses conditions de variation des contraintes mécaniques et de la température et noté les caractéristiques correspondantes de la charge à la rupture ou de la contrainte d'écoulement. Ils ont ainsi établi des diagrammes thermomécaniques, soit de la charge de rupture, soit de la contrainte d'écoulement, en fonction de la température, pour les catégories principales de polymères: thermodurcis, thermoplastes, comprenant les polymères linéaires cristallins ou réguliers, les polymères linéaires irréguliers et les polymères réticulés. Ces diagrammes donnent une indicationsur les contraintes limites dont il faut beaucoup s'écarter dans l'utilisation, en faison du fluage à une température déterminée. L'ensemble de ces diagrammes précise aussi les points de transition déterminés sous des contraintes mécaniques notables, dont l'effet est important sur la température à laquelle ils se présentent. Il semble intéressant de noter la thermosensibilité croissante dans l'ordre suivant: polymères: multibranches, réticulés, irréguliers, réguliers.

Zusammenfassung

Zur Bestimmung der Umwandlungspunkte, welche die drei Zustände, starr, plastoelastisch und kautschukartig, trennen, bestehen verschiedene Methoden; die Autoren zeigen, dass man mit der Durchführung eines einfachen Zugversuches bei verschiedenen Temperaturen gute Resultate erhalten kann. Dieser Versuch wurde bei verschiedener mechanischer Beanspruchung und bei verschiedenen Temperaturen ausgeführt und die für die Bruchbelastung oder Fliessgrenze charakteristischen Grössen ermittelt. So wurden thermomechanische Diagramme für die Bruchbelastung oder für die Fliessgrenze als Funktion der Temperatur für die Hauptkategorien der Polymeren: wärmehärtende und thermoplastische-einschliessend lineare, kristalline oder regelmässige Polymere, lineare unregelmässige Polymere und vernetzte Polymere-aufgestellt. Diese Diagramme lassen die wegen der Unbeständigkeit bei einer gegebenen Temperatur bestehenden Beanspruchungsgrenzen für den praktischen Gebrauch erkennen. Die Gesamtheit der Diagramme legt auch die unter beträchtlicher mechanischer Beanspruchung bestimmten Umwandlungspunkte fest, auf deren Temperaturlage diese Beanspruchung einen bedeutenden Einfluss hat. Die Wärmeabhängigkeit nimmt in folgender Reihefolge zu: mehrfach verzweigte, vernetzte, unregelmässige, regelmässige Polymere.