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ΦΥΣΙΚΟΧΗΜΕΙΑ.—**The Influence of the Reaction Temperature to the Fracture Mode of Polyimide Membranes**, by *P. S. Theocaris - V. M. Starchev - N. F. Chugunova* *. 'Ανεκοινώθη ὑπὸ τοῦ 'Ακαδημαϊκοῦ κ. Περικλῆ Θεοχάρη.

ABSTRACT

The mechanical and optical properties of polyimides, which are used extensively as coatings of fibers in composite materials of heavy duty, were studied in this paper and the influence of the reaction-temperature on the physico-chemical properties of the polymers was evaluated at the end of the reaction process. In this way, the dependence of the stress-strain diagram, the stresses and strains at fracture, the load and elongation at failure, as well as of the refractive index of the polymer on the temperature of imidization was defined. Furthermore, and in order to find the behaviour of the polymers as thin membranes to fracture, simple tension tests with edge-cracked thin strips were executed. The method of caustics was used, with the specimens loaded at different stress-levels, to evaluate the stress intensity factor of the material at the yielding zone of loading in K_I -mode of deformation. This factor was evaluated by applying the simple Dugdale - Barenblatt model for the ductile materials, whereas for the cases of brittle behaviour of the material the elastic theory was used. Interesting results, concerning the physico-mechanical properties of these polymers, were derived.

* Π. Σ. ΘΕΟΧΑΡΗ - V. M. STARCHEV - N. F. CHUGUNOVA, 'Η επίδρασις τῆς θερμοκρασίας ἀντιδράσεως εἰς τὴν μορφήν τῆς θραύσεως πολυ-ιμιδικῶν μεμβρανῶν.

INTRODUCTION

Polyimide resins, which have been developed in the early seventies in the Soviet Union and the United States of America [1], consist of a rigid aromatic system, developed by polycondensation of an aromatic dianhydride (such as pyromellitic dianhydride [2]) and an aromatic diamine. In our tests we have used a 4:4'-diamino-diphenyl ether and dianhydride of benzophenoltetracarbic acid (pyromellitic acid) in a 10 percent solution. The polyimide was made by polycondensation of the aromatic dianhydride and the aromatic amine. The first step was a soluble polyamide-acid, which was then converted to polyimide by further condensation.

Polyimides retain their properties to high temperatures, exceeding 400°C, and may withstand exposures to temperatures of the order of 800°C for short periods of time. This property, together with their property of high thermal insulation, makes these polymers convenient for mesophase layers in multicomposite materials used in spacecrafts and other applications, where the interface boundary layers, between inclusions and matrix, must play the role of an adaptor to variable behaviour of the phases of the composite at a large spectrum of temperatures.

Since polyimides were introduced only recently, their mechanical, optical, physical and chemical properties are not up-to-now studied or disclosed, as it is also their exact chemical formulation in applications of different fields. These materials are opaque and may be cast into thin membranes, which are used as protective coatings of fibers in composites, for thermal insulation and as dumpers in shear forces between matrices and inclusions.

Their specific gravity is approximately 1.43 g/cm³ and the tensile strength at ambient temperature $\sigma_u = 72.5$ MPa, presenting normally an elongation at fracture of 5 to 7 percent. Their tensile modulus is 3,100 MPa and they present a rather high water absorption of 0.32 percent for 24 hours in bars of 0.0032 m thickness. The refractive index of the material and its Poisson's ratio remain still undetermined [2].

The purpose of this paper is to determine the mechanical and optical properties of polyimides in the range of temperatures between 20°C and 225°C, where the materials allow the highest degree of imidization and they pass through a transition zone. The mechanical and optical properties of

membranes, prepared according to the maximum degree of imidization, were tested in tension at the respective temperatures and their characteristic mechanical properties were evaluated. Furthermore, edge cracked thin plates were studied under mode-I deformation and their stress intensity factors were evaluated by using the optical method of caustics. Interesting results were derived, concerning the mechanical and optical behaviour of these polymers.

EXPERIMENTAL PROCEDURE

The purpose of this study is to evaluate the physicochemical properties of the final products of polyimides by regulating the reaction and curing temperature of the melt-fused salt. It has been already established [2] that the appropriate selection of the curing process for the preparation of polyimide membranes influences considerably their physicochemical and mechanical properties. The membranes in our tests were prepared from a solid precursor, prepared from a poly (amide-acid), and subsequently dehydrated to the respective polyimide by heating. The poly (amide-acid) was formed by reaction of a 10 percent solution of the dianhydride of the benzophenol-tetracarbic acid in dimethyl-formamide and diaminodiphenyl ether, which was subsequently dehydrated to the respective poly-imide.

By using differential thermal analysis and infrared spectroscopy of the initial poly (amide-acid) solution, a series of characteristic temperatures has been defined, varying between 20°C and 225°C, which allows to bound-in the optimum degree of poly-condensation (imidization). The final selection of the duration of the imidization-process for each particular reaction temperature was based on the study of the variation of the mechanical properties of the membranes. For this purpose, samples from each preparation were tested in simple tension, up to failure, and the stress-strain diagrams of the materials were plotted [2].

Fig. 1 presents the variation of the applied load P_f at the initiation of fracture, as well as the stress σ_f and strain ϵ_f at failure, versus the temperature T of poly-condensation. These results have been derived from the stress-strain curves plotted for each distinct temperature of poly-condensation for temperatures $T = 20^\circ, 80^\circ, 130^\circ, 150^\circ, 200^\circ$ and 225°C . These stress-strain diagrams were plotted in Fig. 2 [2].

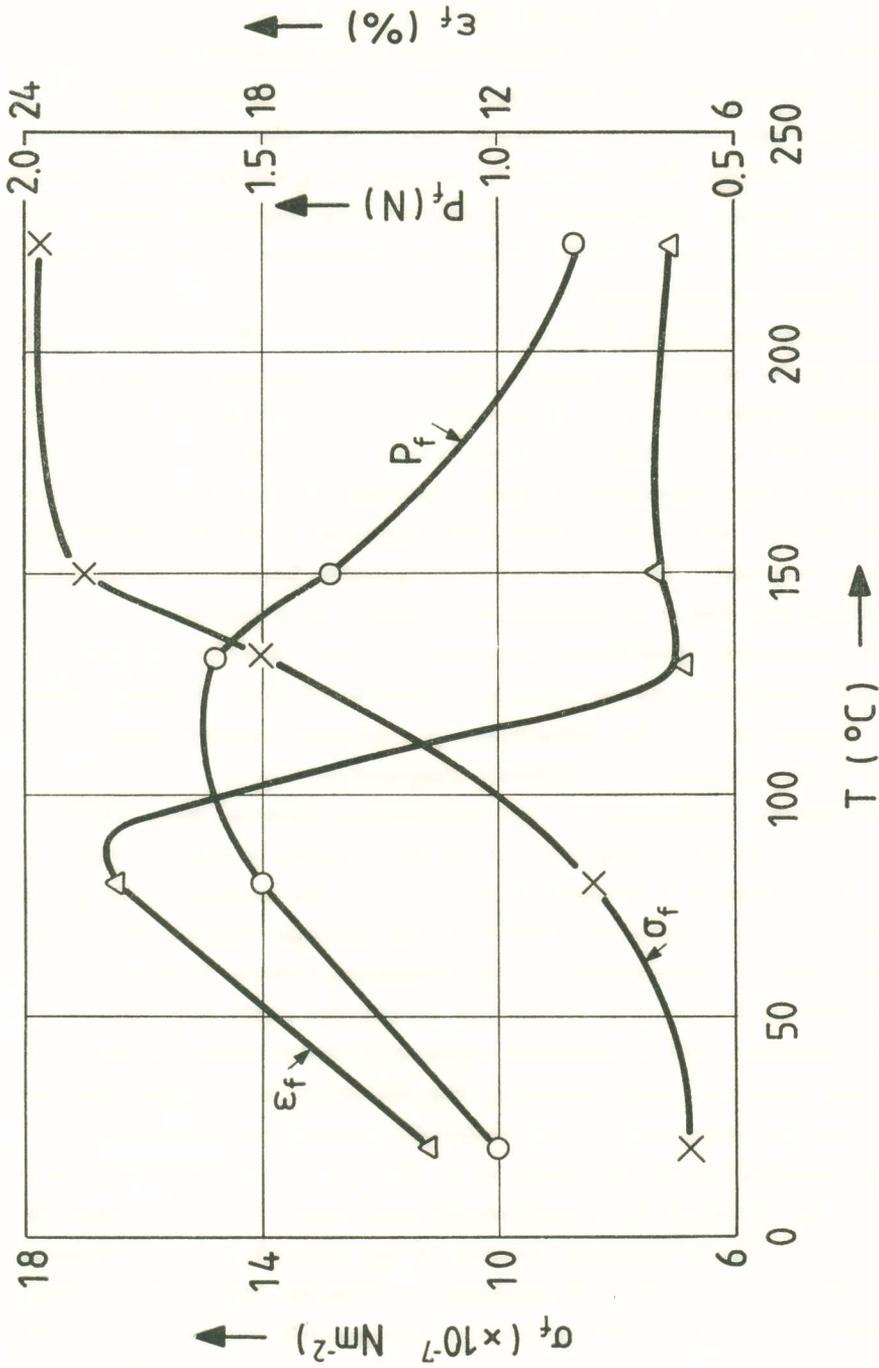


Fig. 1. Variation of the applied load P_f and the respective σ_f -stress and ϵ_f -strain at the initiation of failure, versus the temperature T of poly-condensation.

It is clear from these figures that the behaviour of the polyimide varies with temperature. Three distinct zones of temperature may be identified. The interval between 20°C and 80°C, which is characterized by a large ductility of the material (*ductile zone*). The intermediate-temperature interval, between 80°C and 150°C, defined as a *transition zone*, where the material changes progressively properties from ductile to brittle, and finally the interval above 150°C, where the behaviour of the polymer is typically brittle (*brittle zone*).

Of special interest is the first zone from 20°C to 80°C, inside which the values of the strains at fracture achieved their maxima, giving elongations varying between 14 and 22 percent. It has been shown [2] that the σ_f -stress at fracture of the membrane was continuously increasing with the increase of the temperature of poly-condensation and this increase was explained by the fact that a continuous rejection of the dimethylformamide, which was added by an amount of 25 percent, happened in this zone, thus reducing the degree of imidization to only 3 to 4 percent.

The polyimide membranes prepared in this interval of reaction-temperature developed, during loading, a constrained form of elastic deformation, engendering at the exhaustion of elasticity necking phenomena, indicated in the respective stress-strain diagrams of Fig. 2.

The intense imidization in the temperature interval from 100°C to 150°C has as a result to engender an abrupt increase of the σ_f -stress at fracture and a respective decrease of the ε_f -strain. The increase of the molecular interactions in volume and density in the polymer created this change of the character of deformation of the membrane, which tended progressively to become brittle. Fig. 2 indicates clearly the rapid reduction of the ε_f -strain, combined with a respective increase of the σ_f -stress of the specimens in this transition zone. However, this maximum in ε_f -strain does not coincide with the maximum of the externally applied load P.

The stabilization of the limits of ε_f and σ_f for temperatures above 150°C may be explained by a stereophasic imidization, which increases the imperfections of the membranes, because of the difficulty of the transport process of the excesses of the poly-condensation from the bulk of the polymer.

Besides the study of the influence of the reaction temperature on the mechanical properties of the polymer, it was necessary to study the fracture behaviour of the membranes, in order to have a clear picture of

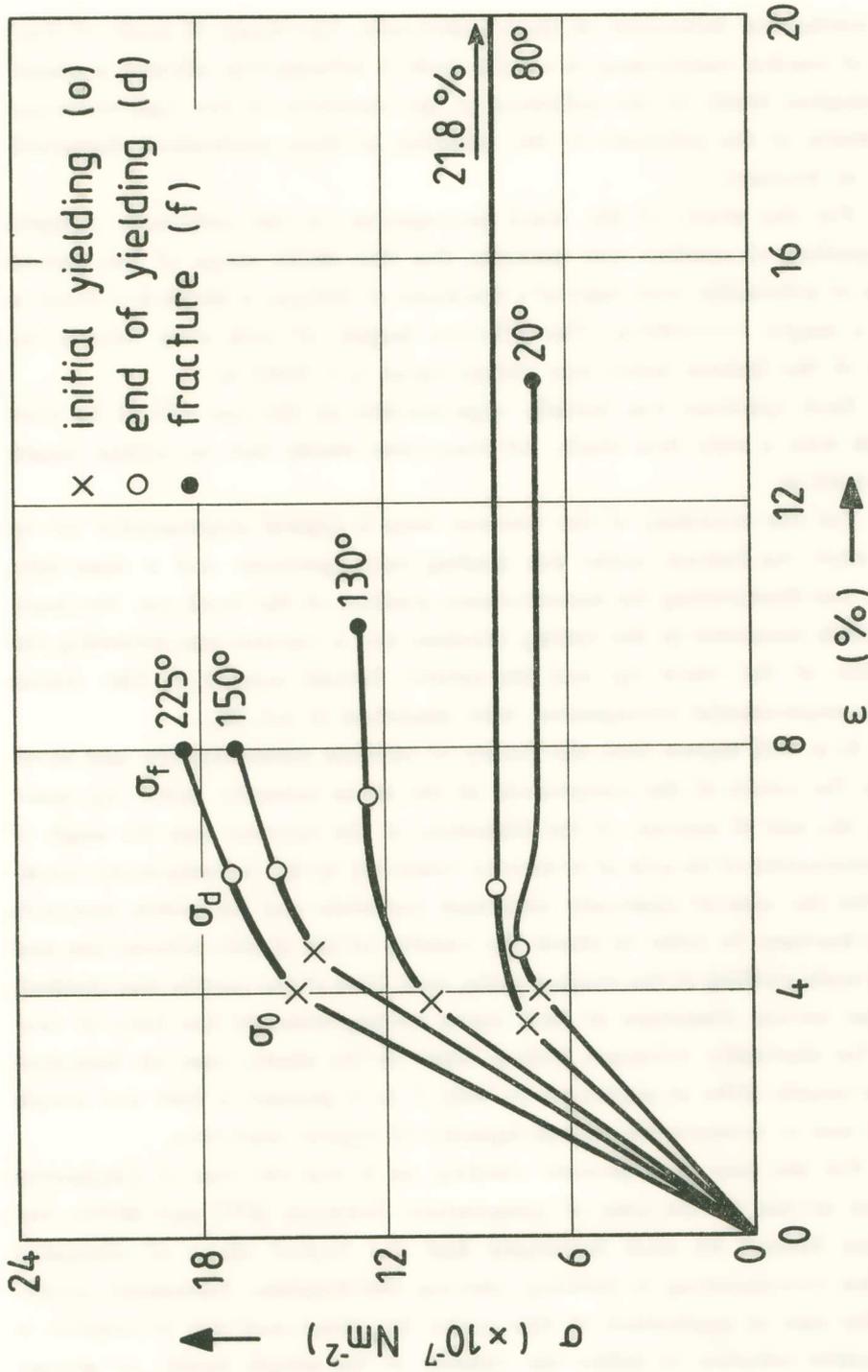


Fig. 2. Stress-strain diagrams of polyimides for each temperature T of poly-condensation.

the mechanical behaviour of these substances. The study of mode of fracture of cracked membranes in simple mode-I deformation allowed a phenomenological study of the influence of the variation of the high-molecular structures of the polymers to the variation of their mechanical characteristics at fracture.

For the study of the crack propagation in the polyimide samples the method of caustics was used [3]. For this study strips of the various types of polyimides were used of a thickness of 100 μm , a width $w = 0.035$ m and a length $l = 0.090$ m. The effective length of each strip outside the grips of the Instron tester was always equal $l_e = 0.045$ m.

Each specimen was initially edge-cracked on the one side at its mid-length with a very thin blade. All transverse cracks had an initial length $a_0 = 0.005$ m.

For the recording of the fracture tests a typical experimental set-up was used. An Instron tester was loading each specimen and a laser-light beam was illuminating the instantaneous position of the crack tip. The loading levels measured in the testing machine and a camera was recording the position of the crack tip and the caustic formed around it. The details of the experimental arrangement were described in ref. [4].

It is well known that the theory of caustics yields directly and accurately the values of the components of the stress intensity factor, by measuring the size of anyone of the diameters of the caustics and the angle of the orientation of its axis of symmetry relatively to the instantaneous crack-axis for the case of elastically deformed materials and for brittle materials up to fracture. In order to check the validity of the elastic deformation and small-scale yielding of the cracked plate, each form of the caustic was checked, so that several diameters of each curve corresponded to the form of caustics for elastically deformed bodies. Since in the elastic case all diameters of the caustic differ at maximum by only 5 to 6 percent, a first and simple check was to measure the almost equality of typical diameters.

For the case of large-scale yielding, as it was the case of polyimides treated at the ductile zone of temperature (between 20°C and 80°C), the caustics formed by such specimens had the typical shape of elongated caustics corresponding to yielding, obeying the Dugdale - Barenblatt model. For the case of application of this model the shape and size of caustics is a sensitive criterion to define the validity of the simple model, or anyone

of its modifications, depending on the amount of strain hardening of the material. However, in all our cases the elongated shape of caustics was typical for the simple model and its theory was directly applied [5].

Fig. 3 presents a series of photographs of caustics formed at the tips of the cracks at the initiation of the crack propagation for loading levels corresponding to regions above the yield stress of each type of material. It is obvious from this figure that, while the caustics for reaction temperatures of $T = 20^{\circ}\text{C}$ and 225°C were completely circular, corresponding to brittle materials, all other caustics (for temperatures $T = 80^{\circ}$, 130° and 150°C) were very narrow and elongated curves, indicating an elastic-perfectly plastic behaviour of the substance.

By using the simple relations derived from the application of the simple Dugdale - Barenblatt model, we could define the size R of the plastic zone and the respective value of the stress intensity factor. These quantities were derived from the simple relations valid for the Dugdale - Barenblatt model for elastic perfectly plastic materials [6] :

$$\frac{a}{a + R} = \cos\left(\frac{\pi}{2} \frac{\sigma_{\infty}}{\sigma_0}\right) \quad (1)$$

$$R = \frac{\pi K_I^2}{8\sigma_0^2} \quad (2)$$

where, a is the length of the edge-crack, σ_{∞} is the remotely applied stress and σ_0 is the yield stress of the material.

From the orientation of all caustics it was evident that only the K_I -component of the stress intensity factor was operative and no shear phenomena appeared at the tips of the cracks. In order to evaluate the instantaneous stress intensity factor from the caustics in the case of application of the Dugdale - Barenblatt model, use was made of the nomogram given in ref. [5], where the characteristic dimensions of the caustics were connected with the externally applied stress at infinity σ_{∞} , normalized to the yield stress σ_0 of the material in simple tension.

Fig. 4 presents the variation of the ratio of the transverse to the respective longitudinal diameter of the caustic in terms of the applied stress to the specimen (σ_{∞}), normalized to the yield stress (σ_0) of the material in simple tension. From this nomogram, together with relations (1) and (2),

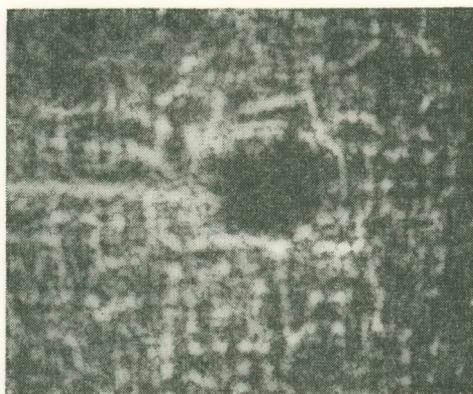
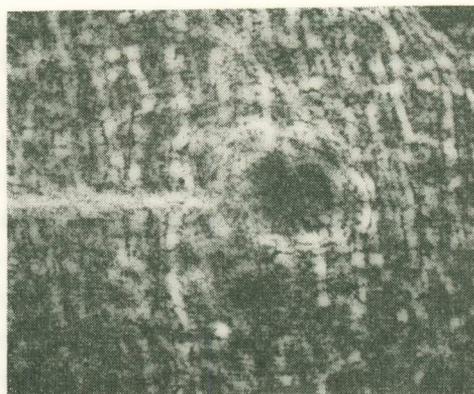
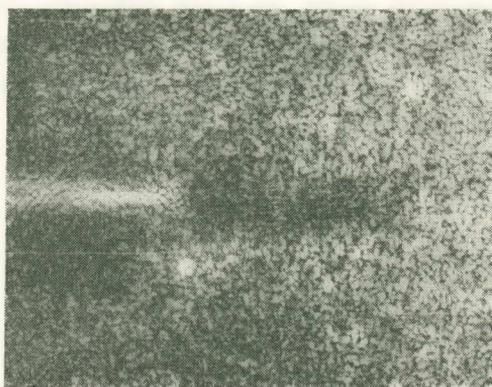
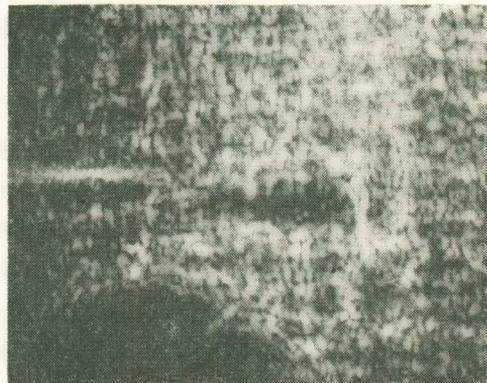
(a) $T=20^{\circ}\text{C}$ (b) $T=225^{\circ}\text{C}$ (c) $T=80^{\circ}\text{C}$ (d) $T=130^{\circ}\text{C}$ (e) $T=150^{\circ}\text{C}$

Fig. 3. Series of photographs showing caustics for loading levels above the yield stress of each type of material.

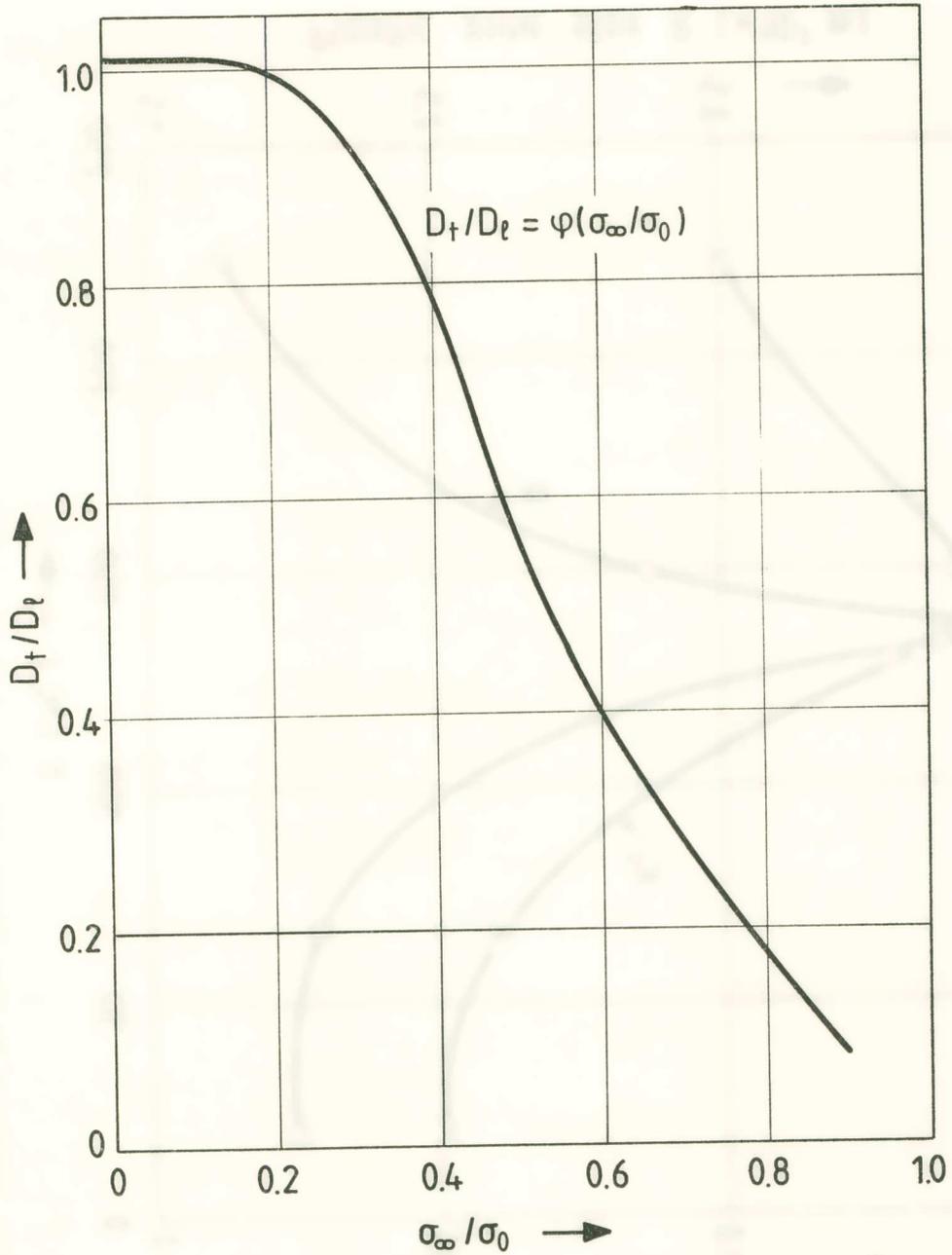


Fig. 4. Variation of the ratio of the transverse (D_t) to the longitudinal (D_l) diameters of caustics, versus the ratio of the remotely applied stress σ_∞ to the yield stress σ_0 of the material.

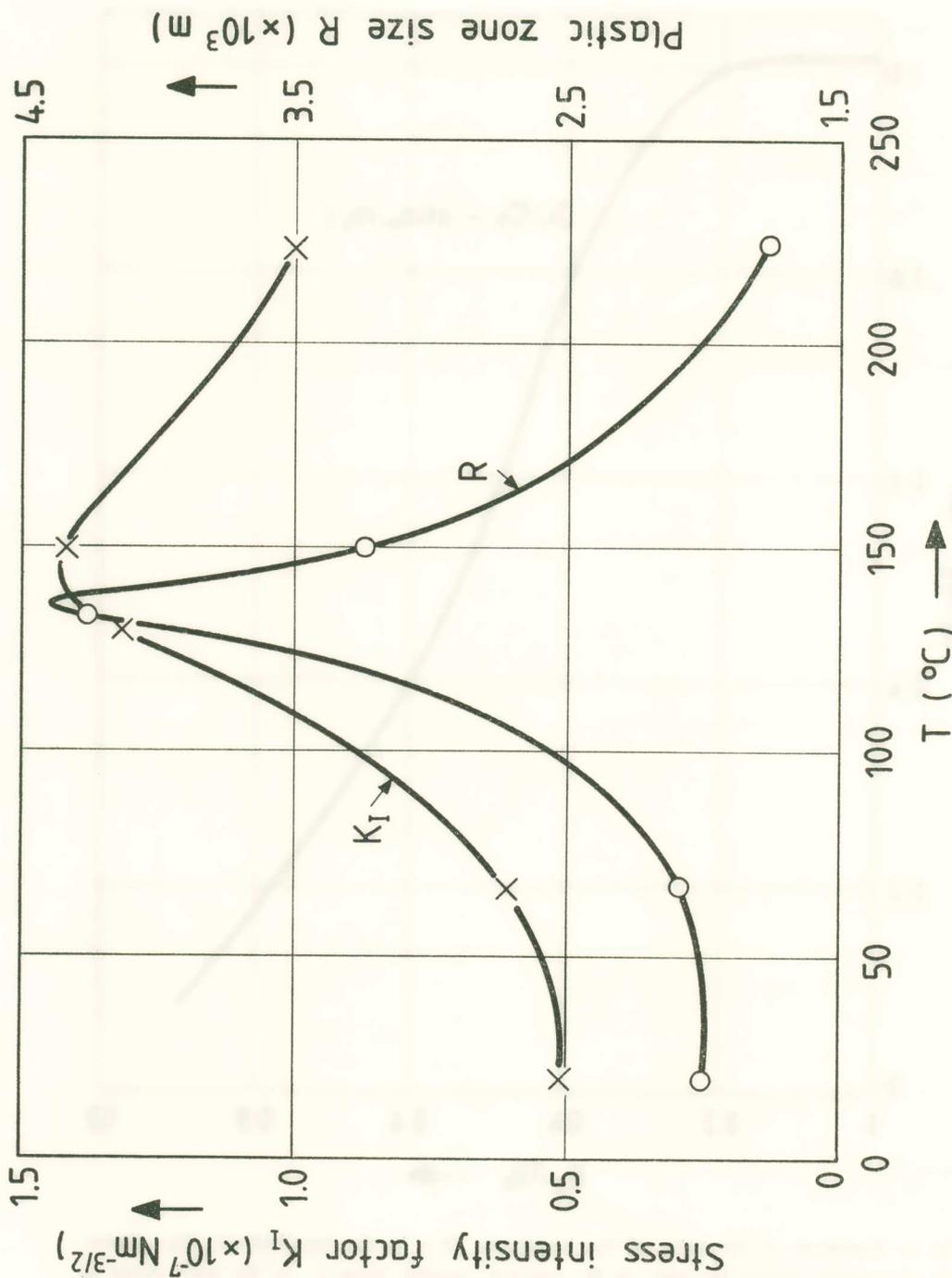


Fig. 5. Variation of the stress intensity factor K_I and the size of the plastic zone R, versus the temperature of imidization T for the initiation of yielding.

it made be possible to evaluate the size of the plastic zone R , and the value of the stress intensity factor K_I .

From this nomogram and by measuring the ratio of the transverse diameter to the longitudinal diameter of the caustic the stress σ_∞ can be evaluated knowing the yield stress σ_0 of the material in simple tension given in Fig. 2 with oblique crosses in the stress-strain diagrams. Then, by using relation (1) the length R of the plastic zone may be evaluated and from relation (2) the respective value of the stress intensity factor.

Fig. 5 presents the values for K_I and R , versus the temperature of imidization T for the initiation of yielding (points with oblique crosses in the diagrams of Fig. 2). It is clear again from the figure, which is in conformity with the mechanical behaviour of the various types of the polymer, that at the transition zone between 80°C and 150°C there is a drastic change in the mechanical behaviour of the substance.

RESULTS

It may be observed from the photographs of Fig. 3 that a substantial change in the structure of the polymer appears with the variation of temperature of poly-condensation. As this temperature increases from 20°C to 80°C the normally appearing interweaving macroscopic structure of the surface (at 20°C for example) becomes progressively more and more smoother and finely pitted (Fig. 3c). The overall texture of the surface of the membranes returns back to its normal interweaving texture, as the imidization temperature is increased (see for instance Fig. 3b). This kind of texture, which is shown in Fig. 3, remained unchanged from the unloaded state of the membranes, up to their end of complete failure of the strips.

If we take into consideration the considerable influence of the molecular interaction on the amount and the form of deformation of linear high-polymers of the type of polyimides, we can assume that the homogenization of the structure of the macromolecules in the polymer had as a result to make more uniformly distributed the influence of the molecular junctions, fact which counted on the mutual influence of the externally applied load P to the mode of deformation of the polymer.

For this reason and since the membranes in the region of $T = 80^\circ\text{C}$ presented a special character in the development of deformations, the high-

polymer presented at this temperature level a very ductile idiosyncrasy, developing very large elongations before fracture, much larger than those at ambient temperature.

There is no simple explanation of the loss of homogenization of the polymer as the temperature of polycondensation was raised above 80°C. However, there are some indications in the literature [7, 8] for a low-temperature tendency of destruction of the solution of the poly-amide acid by degradation, entailing hydrolysis, and perhaps also reaction with the solvent, which may be correlated with the reduction of the molecular weight of the polymer. It was found that the loading of the cracked plates related to the caustics presented in Fig. 3 corresponds to stresses lying at the neighbourhood of the initial yielding of the cracked-plates indicated with oblique crosses in Fig. 2.

For an increase of the loading in the zone of delayed elasticity, lying between oblique crosses and open-circles in the stress-strain curves of Fig. 2, the length R of the plastic zone continues to extend for increasing applied stress, so that at the end of this zone the lengths of the plastic zones have achieved some limiting value R_d , plotted in Fig. 6 together with the respective values of σ_d -stresses.

Fig. 7 gives the variation of the applied load and the respective strain developed at the end of delayed elasticity zone (open circles in Fig. 2), whereas in Fig. 8 typical photos were given of the propagation of the cracks for the ductile models at poly-condensation temperatures of 20°C and 80°C respectively at this stress-level. Both photos correspond to types of polymer with rather high ductility, so that, at this step of loading, all the transverse ligaments of the strips were plastically deformed (see the dark narrow strips in front of the cracks). The isolated or coalescing oblong zones in front of the main crack may be either caustics of the precursor plastic zone or crack-kinks under development. Their opening displacements were larger for the specimen of $T = 80^\circ\text{C}$ and the secondary disturbances were parallelly displaced by a small amount.

All other caustics for the remaining temperatures maintained the almost circular form of typical caustics with some amounts of elongation due to plasticity and there was no need to apply any plasticity model.

It was further observed that, while, at the initiation of yielding, plastic zones were developed and the typical caustics were formed, there was a

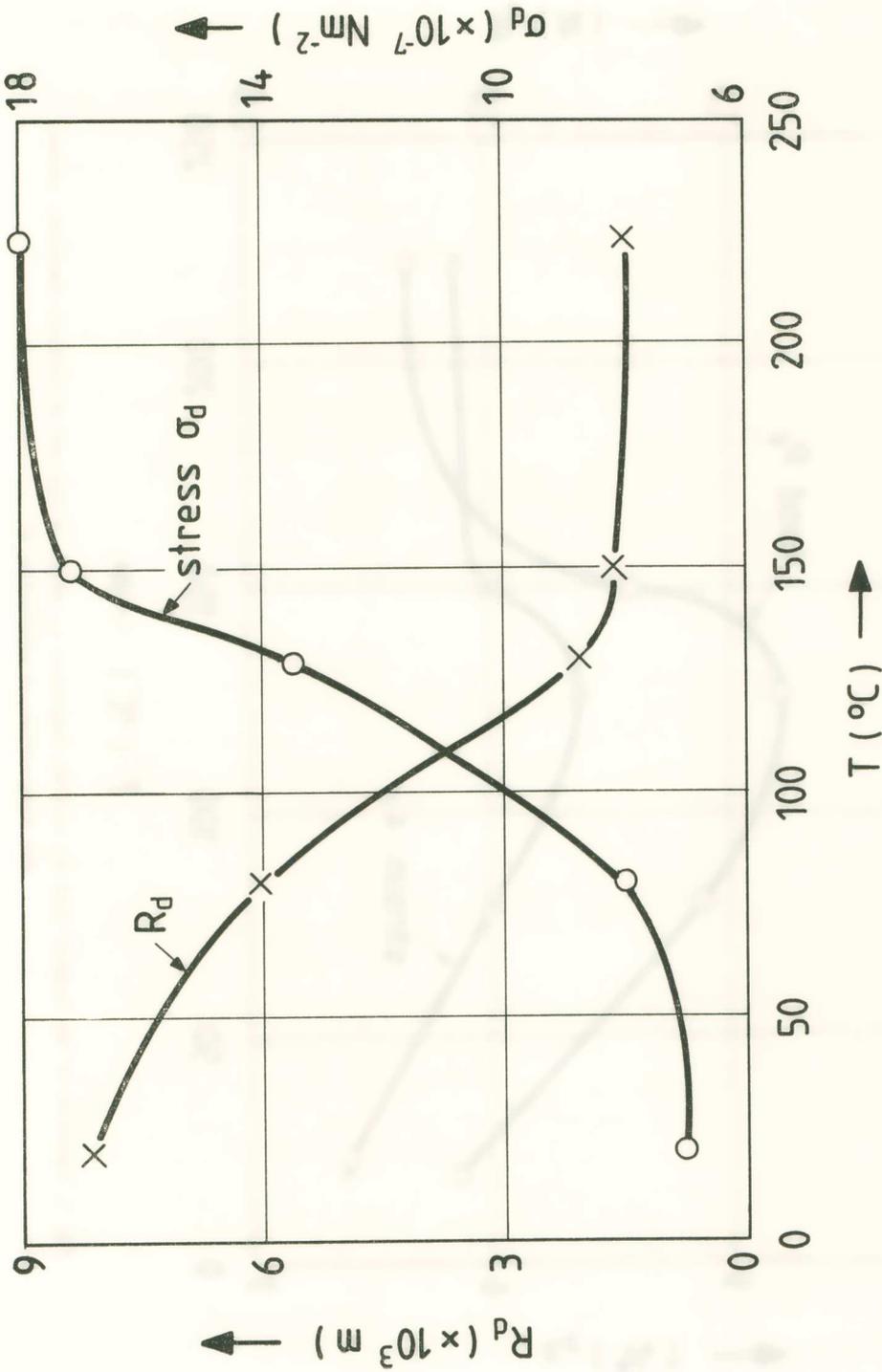


Fig. 6. Variation of the length of the plastic zone R_d and the respective σ_d -stress at the end of delayed elasticity, versus the temperature of imidization T .

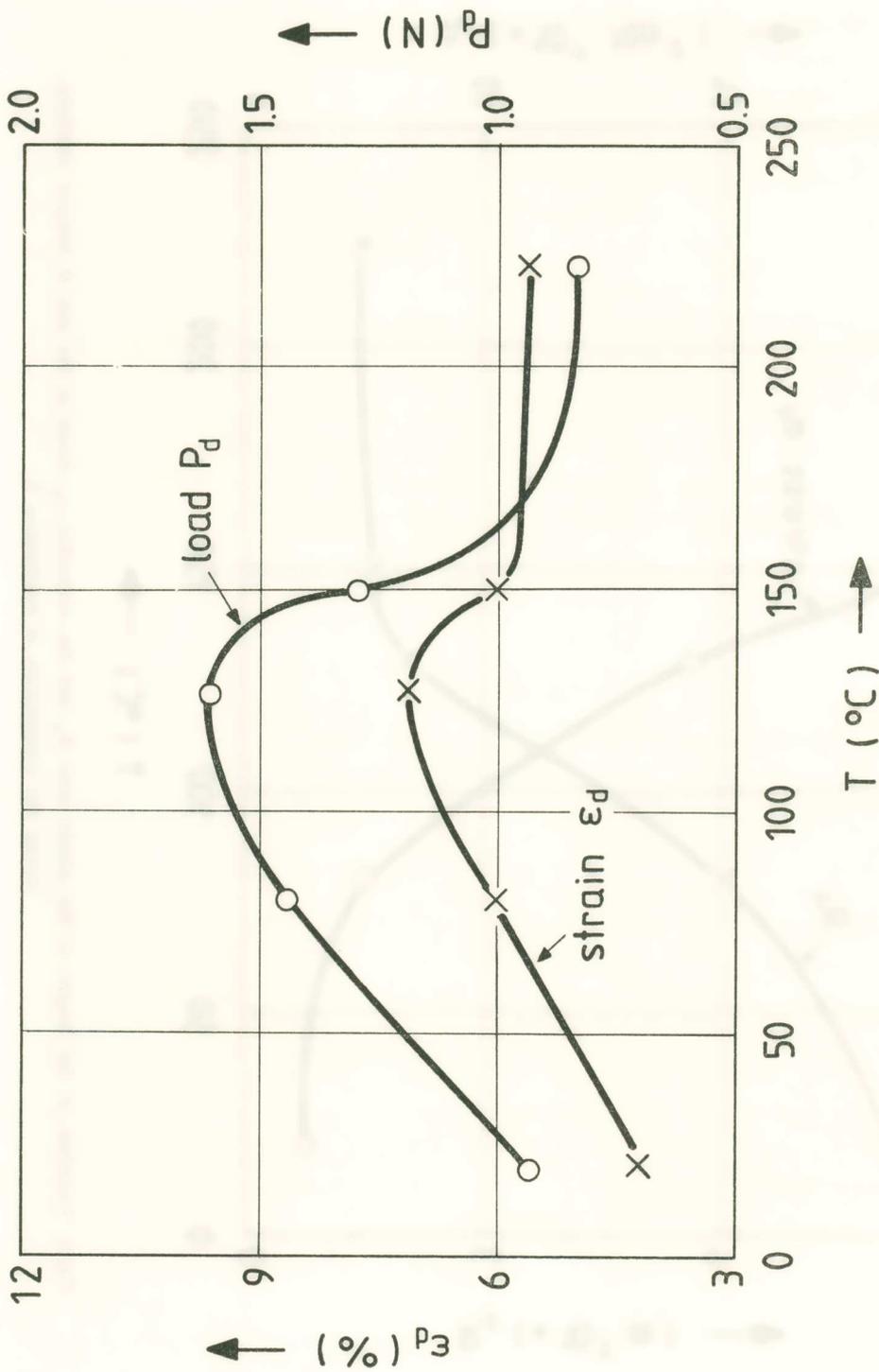
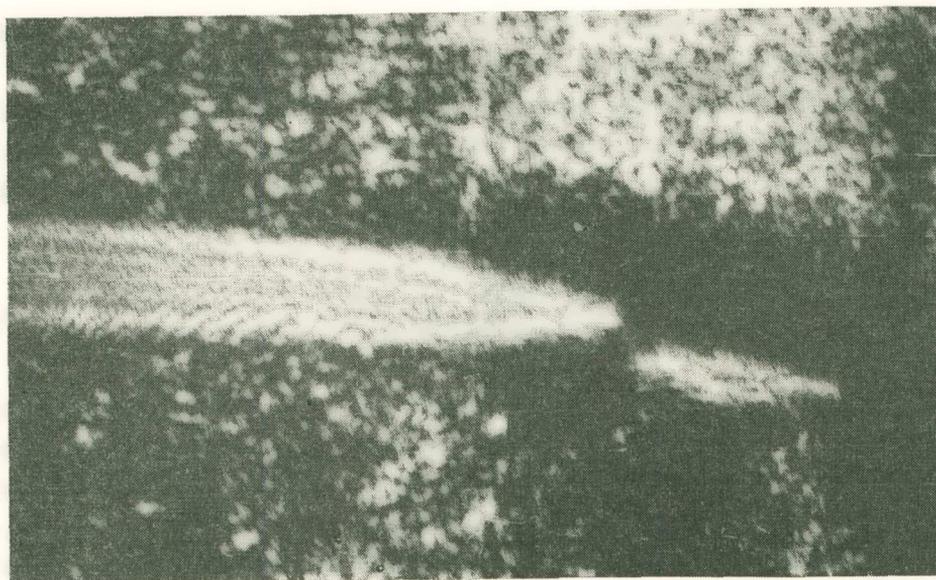
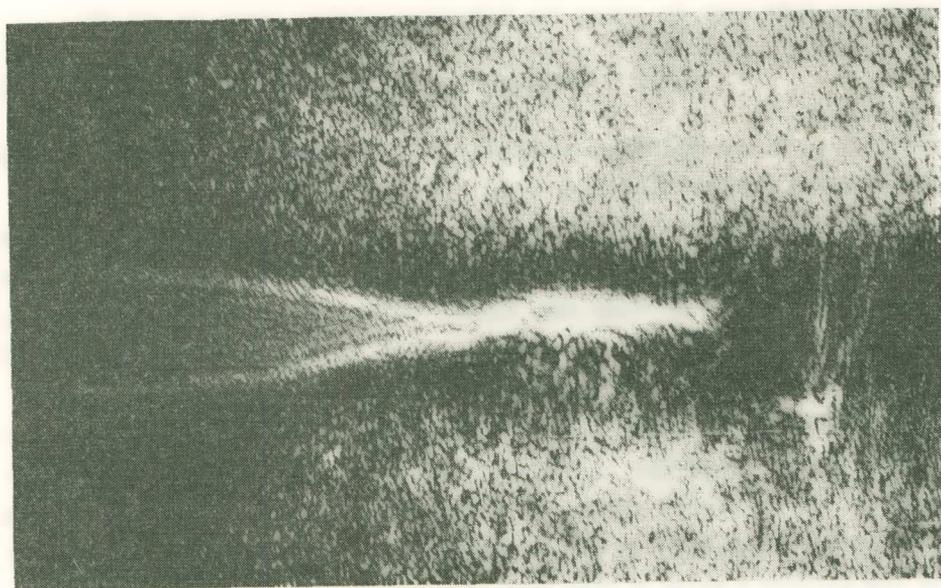


Fig. 7. Variation of the applied load P_d and the respective ϵ_d -strain at the end of delayed elasticity, versus the temperature of imidization T .



(a) $T=20^{\circ}\text{C}$



(b) $T=80^{\circ}\text{C}$

Fig. 8. Photographs showing the extension of the plastic zone ahead of the crack-tip at the end of delayed elasticity.

loading interval for which a compulsory increase of the externally applied stress was necessary to make the development of further plasticity.

In order to define the applied load, corresponding to each step related to each caustic, since its evaluation was inaccurate from the testing machine, a recourse was made to classical formula of caustics interrelating K_I with the characteristics of the caustics [3]. This relation is :

$$K_I = \frac{2\sqrt{2\pi}}{3z_0 d \lambda_m^{3/2} c_t} \left(\frac{D_t}{\delta_t} \right)^{5/2} \quad (3)$$

where z_0 is the distance between the specimen and the reference screen where the caustic is formed ($z_0 = 0.72$ m), d the thicknesses of the plates, λ_m the magnification ratio of the optical set-up, δ_t a correction factor, which for typical caustics is $\delta_t = 3.17$, and D_t the transverse diameter of the caustic.

The optical constant c_t was determined from standard tests where centrally perforated strips were subjected to simple tension. By knowing the diameter $2R$ of the central perforations of the strips and the σ_∞ -stress applied at infinity, it was possible to evaluate the optical constant c_t for traversing light-rays by using the following relation given in ref. [9] :

$$\sigma_\infty = - (3/4\lambda_m)^3 (D_{\max}/4\sqrt{R})^4 (1/z_0 d c_t) \quad (4)$$

where, D_{\max} is the maximum diameter of the caustic created by the stress concentration around the small hole.

The values of the stress-optical constant derived by Eq. (4) can be inserted in Eq. (3) and thus the K_I -factor may be evaluated for the elastic case. A comparison between the values of the stress intensity factor K_I derived using Eqs. (1), (2) and the nomogram of Fig. 4 and using Eqs. (3) and (4), shows a good agreement for the elastic case (brittle zone).

In order to complete the evaluation of the spectrum of the mechanical and optical properties of the polyimides for different reaction temperatures at the transition zone we have evaluated their refractive indices n_0 at the unloaded state, as well as their elastic moduli and Poisson's ratios. For this purpose a series of tests were first undertaken to evaluate the variation of the refractive index n_0 for the various types of polymers. A series of samples of diluted polyimides to form thin films were measured at a

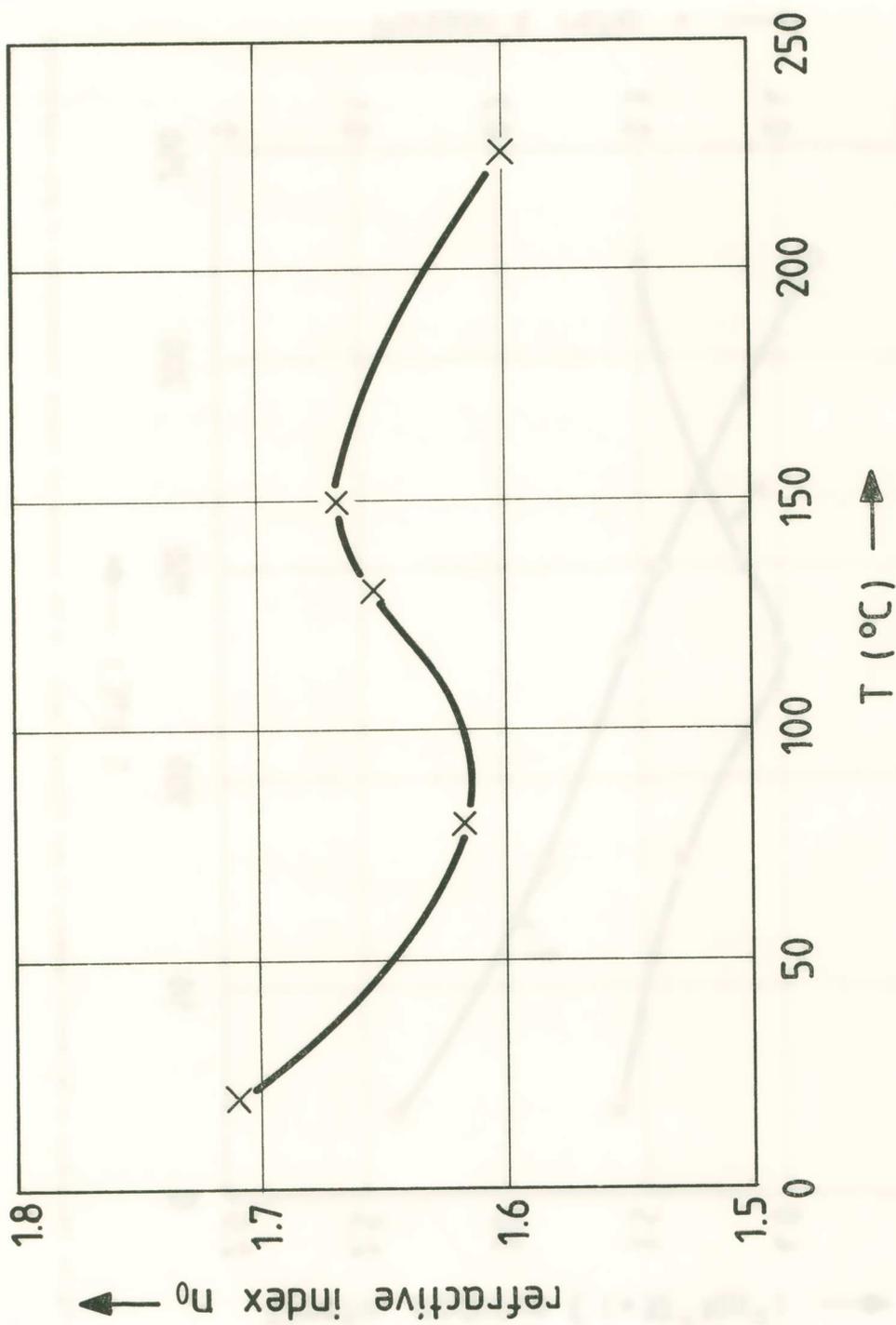


Fig. 9. The values of the refractive index n_0 of the unloaded polymer at various temperatures of poly-condensation.

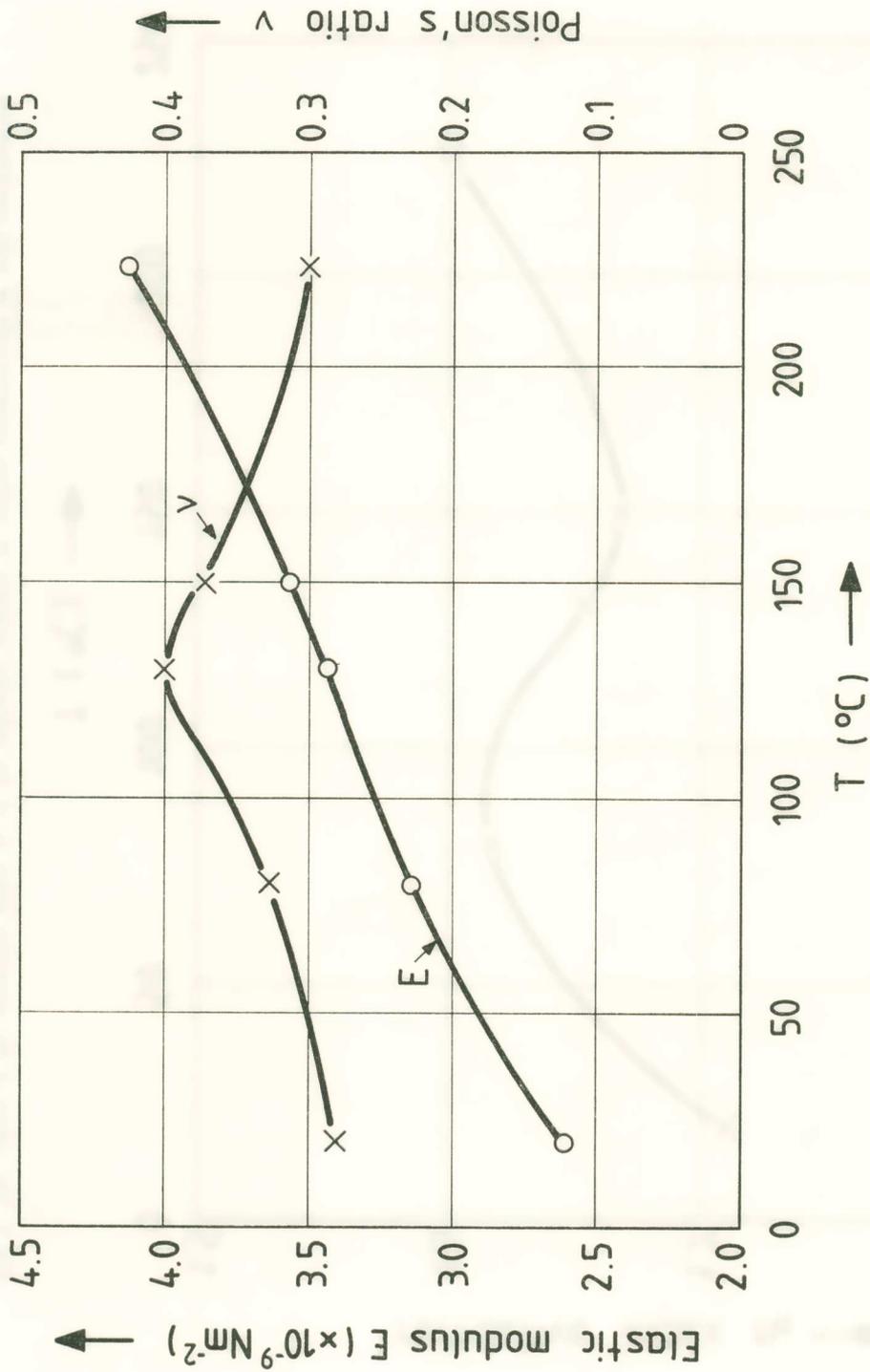


Fig. 10. The values of the elastic modulus E and Poisson's ratio ν of the polymer at various temperatures of poly-condensation.

refractometer. The values of the refractive index of the polymer prepared at various temperatures of poly-condensation were plotted in Fig. 9. It is again worthwhile remarking that the variation of the refractive index n_0 of the material follows a similar trend as its mechanical properties.

Finally, the elastic moduli [2] and Poisson's ratios of the materials were evaluated by using simple tension tests at an Instron tester and measuring the components of the longitudinal and transverse strains by appropriate strain gauges. Fig. 10 presents the variation of these quantities, versus the poly-condensation temperature T . It is worthwhile noting that, while the elastic modulus presents a linear variation with temperature, Poisson's ratio presents a typical wavy curve depending on T .

CONCLUSIONS

It has been established in this paper that a transition zone exists in the reaction process of polyimides, depending on the reaction temperatures during the preparation of the polymer. This zone extends between ambient and 80°C, where the polyimide membranes prepared present an extensive ductility giving ultimate strains of the order of 20 percent and more.

Above this zone the material passes a transition zone becoming progressively brittle, so that at a reaction-temperature of the order of $T = 200^\circ\text{C}$ it changes again to a brittle substance.

Besides the study of the variation of the mechanical properties of the polymers with a change in the reaction temperature the optical properties, that is their refractive index and the stress-optical constant, were evaluated and found to present a variation with reaction temperature having a bell-like shape, like their mechanical properties.

The study was extended to define the mode of fracture of cracked membranes by using the optical method of caustics. It was shown again that large plastic regions of a narrow oblong shape in front of the cracks were developed in the ductile region, whereas outside it, the material presented typical quasi-brittle almost circular caustics. The evaluation of the variation of the plastic zone was based on the simple Dugdale - Barenblatt model for elastic-perfectly plastic materials and the curves of variation of K_I , as well as the length of the plastic zones followed similar patterns.

From this experimental study it has been derived that the deformation properties of the polyimide membranes depend strongly on the macromolecular structure of the polymer and the distribution of their mutual influences.

It was shown that the strength of the membranes depends only insignificantly on the macromolecular properties of the polymers, but it is the result of the physical state of the material at the tip of the crack, of the extend of the plastic zone in front of the crack, as well as on the stress distribution there, and the stress intensity at the tip of the crack.

The application of the optical method of caustics together with the analysis of the mechanical and optical properties of the polymers yielded the possibility to define the mechanism of fracture in polyimide membranes. It was found that the crack starts to propagate only when the loading of the membrane forces it to enter on the zone of delayed elasticity, beyond the initial yield point. In all cases the crack was propagating steadily and rapidly as soon as the stress at the tip overpassed the limit of exhaustion of delayed elasticity.

A c k n o w l e d g m e n t s : The authors would like to express their gratitude to Messrs H. Georgiadis and Alex. Coutsembesis for helping them during the execution of the experiments contained in this research project.

ΠΕΡΙΛΗΨΙΣ

Αί μηχανικαί και ὀπτικάι ιδιότητες τῶν πολυϊμιδίων, πολυμερῶν χρησιμοποιουμένων εὐρέως ὡς ἐπικαλύψεων εἰς τὰς ἴνας τῶν συνθέτων ὑλικῶν μεγάλης ἀντοχῆς, ἐμελετήθησαν εἰς τὴν παροῦσαν ἐργασίαν. Ἡ ἐπίδρασις τῆς θερμοκρασίας ἀντιδράσεως ἐπὶ τῶν φυσικοχημικῶν ιδιοτήτων τῶν πολυμερῶν ἐμελετήθη καὶ προσδιωρίσθη κατὰ τὸ πέρασ τῆς διαδικασίας ἀντιδράσεως.

Τὰ πολυϊμίδια εἶναι σύγχρονα πολυμερῆ με ἐνδιαφέρουσας ιδιότητος ἀνακαλυφθέντα κατὰ τὰ τελευταῖα εἴκοσι ἔτη εἰς τὴν Σοβιετικὴν Ἐνωσιν καὶ τὰς Ἠνωμένας Πολιτείας. Ἀποτελοῦνται ἀπὸ στερεὸν ἀρωματικὸν σύστημα, ἀναπτυσσόμενον διὰ πολυσυμπυκνώσεως ἀρωματικοῦ διανυδρίτου (συνήθως πυρομελλιτικοῦ ἀνυδρίτου) καὶ ἀρωματικῆς διαμίνης. Εἰς τὰ πειράματά μας ἐχρησιμοποιή-

σαμε 4 : 4' διαμινο-δυσφαινύλ-αιθέρα και διανυδρίτη του βενζο-φαινοτετρακαρβικού οξέος (πυρομελλιτικού οξέος) εις διάλυσιν 10 τοῖς ἑκατόν. Τὸ πολυϊμίδιον παρεσκευάσθη διὰ πολυσυμπυκνώσεως τοῦ ἀρωματικοῦ διανυδρίτου καὶ τῆς ἀρωματικῆς ἀμίνης. Ἡ πρώτη βαθμὶς ἤτο διαλυτὸν πολυαμιδικὸν ὀξύ, τὸ ὁποῖον ἐν συνεχείᾳ, μετετρέπη εἰς πολυϊμίδιον διὰ περαιτέρω συμπυκνώσεως.

Τὰ πολυϊμίδια διατηροῦν τὰς ιδιότητάς των ἀμεταβλήτους εἰς ὑψηλὰς θερμοκρασίας ὑπερβαίνουσας τοὺς 400°C καὶ δύνανται νὰ ἀνθίστανται ἐκθέσεις βραχείας διαρκείας εἰς θερμοκρασίας 800°C. Ἡ ιδιότης των αὐτῆ, μετὰ τὴν ἐξαιρετὸν ἰκανότητα θερμικῆς μονώσεως, καθιστᾷ τὰ πολυμερῆ αὐτὰ κατάλληλα δι' ἐπιστρώσεις τῶν ἰνωδῶν ἐγκλεισμάτων συνθέτων ὑλικῶν ὑψηλῆς ἀντοχῆς σὲ ἐξωτερικὰς φορτίσεις καὶ ἀποτόμους ἀλλαγὰς θερμικῶν πεδίων. Χρησιμοποιοῦνται δὲ εὐρέως εἰς τὴν παρασκευὴν πολυ-συνθέτων ὑλικῶν καταλλήλων διὰ διαστημόπλοια καὶ ἄλλας σχετικὰς ἐφαρμογὰς, ὅπου αἱ διαχωριστικαὶ ὀριακαὶ στρώσεις μεταξὺ φάσεων τῶν ὑλικῶν πρέπει νὰ παίζουν τὸν ρόλον προσαρμοστοῦ εἰς τὴν μεταβαλλομένην μηχανικὴν καὶ θερμικὴν συμπεριφορὰν τῶν φάσεων τοῦ συνθέτου ὑλικοῦ εἰς εὐρὸν φάσμα θερμοκρασιῶν λειτουργίας.

Εἰς τὴν ἐργασίαν αὐτὴν μελετᾶται ἡ ἐξάρτησις τῶν διαγραμμάτων τάσεων - παραμορφώσεων τῶν πολυϊμιδίων, παρασκευαζομένων εἰς διαφόρους θερμοκρασίας ἀντιδράσεως, καθὼς ἐπίσης καὶ τῶν τάσεων καὶ παραμορφώσεων θραύσεως τῶν ὑλικῶν αὐτῶν. Περαιτέρω μετρεῖται ἡ μεταβολὴ τοῦ δείκτου διαθλάσεως καὶ τῆς τασεοπτικῆς σταθερᾶς τοῦ ὑλικοῦ συναρτήσῃ τῆς θερμοκρασίας ἀντιδράσεως. Τέλος, ἐμετρήθησαν ἡ μεταβολὴ τοῦ μέτρου ἐλαστικότητος καὶ τοῦ λόγου τοῦ Poisson τῶν διαφόρων τύπων μεμβρανῶν.

Διὰ τὴν μελέτην τῆς συμπεριφορᾶς τῶν πολυϊμιδίων ὑπὸ μορφὴν μεμβρανῶν εἰς θραῦσιν ἐγένοντο δοκιμαὶ εἰς ἐφελκυσμὸν ἀρχικῶς ρηγματωμένων μεμβρανῶν καὶ καθωρίσθη διὰ τῆς μεθόδου τῶν καυστικῶν ἢ ἔκτασις τῆς πλαστικῆς ζώνης R εἰς τὸ μέτωπον τῆς ρωγμῆς καὶ ὁ συντελεστὴς ἐντάσεως τῶν τάσεων.

Ἀπεδείχθη ὅτι τὰ πολυμερῆ αὐτὰ παρουσιάζουν μεταβατικὴν ζώνην ἀπὸ τῆς θερμοκρασίας περιβάλλοντος μέχρι τῆς θερμοκρασίας τῶν 80°C ὅπου ἡ ψαθυρὰ συμπεριφορὰ των μετατρέπεται ραγδαίως εἰς ὄγκιμον μετὰ παραμορφώσεις θραύσεως μέχρι 20 τοῖς ἑκατόν. Ἀπὸ τῆς ὀριακῆς αὐτῆς θερμοκρασίας καὶ μέχρι τῆς θερμοκρασίας τῶν 150°C παρουσιάζεται μεταβατικὴ ζώνη μεταβολῆς τῶν ιδιοτήτων τῶν πολυμερῶν, ἡ ὁποία μετατρέπει ἐκ νέου προοδευτικῶς τὰ ὑλικά αὐτὰ εἰς ψαθυρά. Ἀπὸ τῆς θερμοκρασίας τῶν 150° καὶ ἄνω τὰ ὑλικά μεταπίπτουν καὶ πάλιν εἰς τὴν ψαθυρὰν των κατάστασιν.

Ἡ μεταβολή αὐτῆ τῶν ἰδιοτήτων τῶν ὑλικῶν εἰς τὴν ζώνην θερμοκρασιῶν ἀπὸ 20°C μέχρι 150°C, ἡ ὁποία παρατηρήθη εἰς ἕλας τὰς ἰδιότητάς των, μηχανικὰς, φυσικὰς καὶ ὀπτικὰς, δύνανται νὰ ἐξηγηθῇ ἀπὸ τὴν ἐπίδρασιν τῆς θερμοκρασίας ἀντιδράσεως ἐπὶ τοῦ τρόπου διαμορφώσεως τῆς δομῆς τῶν πολυμερῶν.

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