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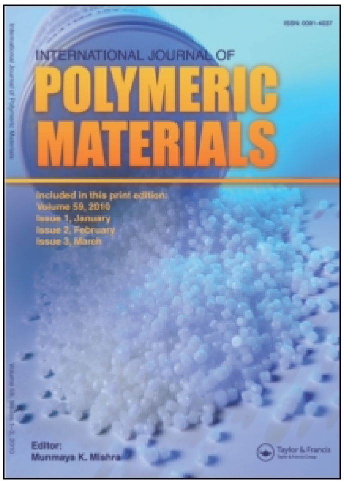

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Mechanical Properties of Multiblock Polyamide-Polyoxirane Copolymers

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The mechanical properties of alternating polyamide-polyoxirane copolymers $(P_1-P_2)_n$ were evaluated. The polyamide component of these copolymers consisted of poly(lactams), of poly(N-methyllactams) or of their statistical copolymers with a molecular weight ranging from 1,400 up to 15,000. Two different molecular weights (1,400 and 9,000) were chosen for the polyoxirane component. The dynamic mechanical spectra were determined with a Rheovibron viscoelastometer at a frequency 110 Hz and within a temperature range from −190°C to 60°C. The stress–strain curves were measured with a table model of an INSTRON tester at room temperature. The dynamic mechanical behaviour indicates a reduced crystallinity of N-methyl substituted polyamides with respect to unsubstituted polyamides and a microdomain structure of some of the polyamide-polyoxirane copolymers. The stress–strain curves reflect the temperature position of the main transition, the fraction and molecular weight of the polyoxirane component and the possibility of a strain hardening of the material. The copolymer samples exhibited both plastic and viscoelastic deformation mechanism which was reflected in a delayed elasticity after unloading. Some of the samples exhibited an unusually high strain-at-break, i.e. up to 1,500%. A repeated testing of fragments of once broken test pieces showed that after drawing there was a large increase in tensile strength of some samples, up to six times the original value.

INTRODUCTION

A number of block copolymers of polyamides have been already described especially in the patent literature.[1] There are, however, only very few papers in which the properties of these products are examined more deeply or systematically. Findings presented in the literature permit the inference that the mechanical properties of polyamide type products are worth attention,[2–5] but are not so attractive from the technical point of view as are the properties of polyurethanes, of styrene-butadiene copolymers or of poly-(tetramethyleneterephthalate-b-tetramethylene oxide). As far as we know, block copolymers of polyamides have not yet been utilized on a commercial scale, unlike the polymers mentioned above.

This work has as its objective to extend the knowledge of the mechanical properties of soluble block copolymers of polyamides with polyoxirane of the $(P_1 - P_2)_n$ type, recently prepared by two of the authors;[6] their molecular structure, endgroups, molecular weight and the content of components were well defined. The mechanical behaviour of the copolymers was characterized by using two different methods: namely, by a dynamic mechanical measurement with a Rheovibron viscoelastometer and by tensile measurement at a constant test rate with an INSTRON tester. The dynamic mechanical measurement provides components of the complex modulus of elasticity within a broad range of temperatures (dynamic mechanical patterns). The maxima of the loss modulus E'' indicate temperatures at which changes in the mobility of the main or side chains take place. The loss maxima are usually denoted α, β, γ, in the direction of decreasing temperature, the α maximum corresponding to the glass transition of the polymer. The temperature corresponding to the α maximum, T_α, lies somewhat higher than the actual glass transition temperature, T_g, depending on the measuring frequency (for 110 Hz, $T_g \simeq T_\alpha - 30°C$, for 1 Hz, $T_g \simeq T_\alpha - 17°C$).

The basic ultimate characteristics of the system under investigation may be determined from the stress–strain curves: tensile strength, strain-at-break, toughness (work up to break), and the yield point. Important information is also provided by the shape of the curve itself. With increasing temperature a polymer passes from the brittle into the tough and rubbery region;[7,8] in the case of different polymers the decisive role is played by the temperature difference between the temperature of measurement and the glass transition temperature, T_g.

EXPERIMENTAL

Materials

The polyamide component of the samples taken for investigation consisted of poly(lactams) or of copoly(lactams) with a molecular weight between 1,380 and 15,000, terminated with amino groups. Polyamide prepolymers which contain N-methyllactam monomeric units (Table I) are soluble in some chlorinated solvents.[9] The following monomers were used in the preparation of polyamide prepolymers:[9] 6-hexanelactam (HL), 8-octanelactam (OL), N-methyl-8-octanelactam (MOL), 12-dodecanelactam (DL), N-methyl-12-dodecanelactam (MDL).

Polyoxirane prepolymers were synthesized by a new route[6] from polyethylene glycol (Koch & Light, product "for laboratory use"), molecular weight 1,000 and 6,000.

TABLE I

Formulation and mechanical characteristics of polyamide (A) and polyoxirane (E) prepolymers

Sample	Components		m mol. %	$\bar{M}_n$	T_a °C	σ_b MPa	ϵ_b %
A1	DL	MDL	66	8,420	−10	18.4	490
A2	DL	MOL	42	4,610	−2	13.0	28
A3	OL	MDL	55	7,120	−15	10.9	710
A4	—	MDL	87	8,260	—	7.9	2
A5	HL	—	—	1,380	—	40.3	51
A6	HL	—	—	15,000	64^a	118	62
E1	Oxirane	—	—	1,420	-15^a	—	—
E2	Oxirane	—	—	9,090	-7^a	—	—

Abbreviations of starting monomers are given in the Experimental. Symbols: m—fraction of N-methyl substituted amide bonds, $\bar{M}_n$—number average molecular weight, T_a—main transition temperature at a frequency of 110 Hz (^{a}estimated from a value for 1–5 Hz, Refs. 13, 15, 18), σ_b—tensile strength, ϵ_b—strain-at-break.

The prepolymers of polyamides were joined with polyoxiranes carrying isocyanate endgroups or with hexamethylene diisocyanate in solution under defined conditions which did not give rise to side reactions leading to branching or crosslinking.[6] The concentration of reactants was equimolar, with the exception of samples B5 and B6, where [$-$NCO]/[$-NH_2$] was 0.5 and 2, respectively. The homopolymer content in the products did not exceed 5%. The fraction of monomers (lactams) and molecular weight of the prepolymers used are given in Table I; the participation of prepolymers in block copolymers and molecular weight of the copolymers are given in Table II. The data were obtained[6] viscometrically, by determination of the endgroup content, by elemental analysis and by ^{1}H NMR spectrometry.

Samples of prepolymers extracted with benzene and water[9] and samples of copolymers extracted with water and cyclohexane[6] were dissolved in chloroform to a 10% solution and evaporated on "Teflon" dishes at 25°C for 7–10 days. The remaining solvent was removed by evacuation at 0.27 kPa and 25°C within 48 hours, and after that again at 0.13 kPa/50°C during another 48 hours. Films of poly(6-hexanelactam) A5, A6 and of block copolymers B11 and B12 were cast from a solution of 2,2,2-trifluoroethanol and dried in the same way.

The molecular structure of copolymers under investigation can be expressed as follows:

Polyoxirane block:

$[-CH_2CH_2O-]_x$, x=24 (sample E1); 200 (E2)

Polyamide block:

where ○ denotes constitutional units —$NH(CH_2)_pCO$— or —$N(CH_3)$—$(CH_2)_qCO$— and ● denotes the corresponding units carrying end amino groups; the average number of units ○, ● in the block is 41 (sample A1; p = 11, q = 11); 26 (A2; p = 11, q = 7); 38 (A3; p = 7, q = 11); 41 (A4; q = 11); 16 (A5; p = 5).

The block copolymers are either an alternating sequence of the polyamide-polyoxirane blocks:[6]

or are composed only of linked polyamide blocks (chain-extended samples B1, B2, Table II).

where ◆ denotes the unit of chain extender, —$CONH(CH_2)_6NHCO$—. The number of polyamide blocks in the chain, *n*, is given in Table II.

Measurement of dynamic mechanical properties

The dynamic mechanical properties were determined with a Rheovibron DDV II viscoelastometer. Test pieces, approximately 2 mm wide and 40 mm long, cut from films 60–400 μm thick, were used in the measurement. The measuring frequency was 110 Hz, at which the instrument achieves the highest accuracy. The apparatus performs a cyclic tensile deformation of the test pieces, providing values of components of the tensile (Young) complex modulus $E^* = E' + iE''$. The sample was fixed in the clamps of the apparatus, the measuring cell was cooled with liquid nitrogen to −190°C and then heated at a constant rate of 1°C/min up to 100°C. E' and E'' values were determined in intervals of 5°C.

Stress–strain curves

The stress–strain curves were determined with a table model of the INSTRON tester at the crosshead speed 2 cm/min. The test pieces were in the form of strips, about 0.5 cm wide, effective length being 2.25 cm and thickness 60–400 μm. The resulting values of tensile strength, σ_b, and those of strain-at break, ϵ_b, were calculated as the mean values from several (mostly three) tests. In some cases the tensile test was repeated once again on fragments of the broken (drawn) test piece, and the ultimate characteristics were related to the new cross-section of the test piece.

RESULTS AND DISCUSSION

Dynamic mechanical behaviour

Prepolymers and chain-extended polymers Three selected samples of the starting prepolymers of polyamides A1, A2 and A3 were used to determine the temperature dependences of components of the tensile complex modulus E' and E'' (Table I). The results are plotted in Figure 1, together with the mechanical relaxation pattern of the "chain-extended" sample B2, in which the polyamide blocks are connected by a low-molecular weight chain extender to form a longer chain. Each of the four samples exhibits three mechanical dispersions; the temperatures of the main loss maximum, T_α, are given in Table I.

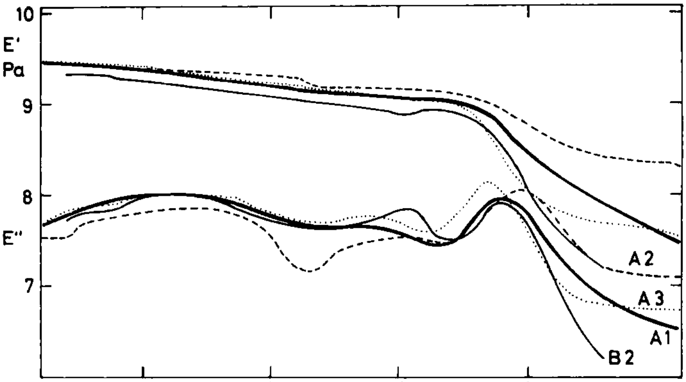

FIGURE 1 Temperature dependence of components of the complex Young modulus of starting prepolymers of polyamides and of the copolymer B2; curves denoted as samples in Tables I and II.

The glass transition temperature of poly(12-dodecanelactam)[10] and of poly(N-methyl-12-dodecanelactam)[11] is approximately 42°C and −32°C (assessed by DSC), respectively. Our partially methylated specimens A1, A2, A3 display the main (glassy) transition at temperatures −10°C, −2°C, and −15°C (Table I). The methyl substitution on the amide groups obviously accounts for a reduction of the number of hydrogen bonds and for an internal plasticization. The content of 70% of methylated component, which corresponds to our sample A1, has also been found[12] to decrease considerably the crystallinity of poly(12-dodecanelactam). Accordingly, the least methylated sample A2 exhibits not only the highest $T_\alpha = -2°C$ but also the highest storage modulus above the glass transition temperature. In the temperature range below T_α, samples A1, A2, and A3 exhibit (Figure 1) two maxima of the loss modulus: The low-temperature (γ) maximum at about $-130°C$ and secondary (β) maximum around $-50°C$. The former is commonly assigned to a short-range motion of backbone segments in amorphous regions[13] while the latter is believed to originate from the γ relaxation process due to interaction polymer–diluent[18] (traces of moisture or an equilibrium amount of the monomer suffice to produce a perceptible β peak). The sample B2 (Figure 1), prepared by linking linear blocks A1, exhibits the same $T_a = -10°C$ as the starting sample, while its storage modulus in both the glassy and rubbery region is lower and the decrease of modulus with temperature above T_a is much faster. Thus, the low-molecular weight chain extender leads to a decrease in the rigidity of the system presumably due to further reduction of crystallinity. The temperature locations of the γ or β loss maxima of samples A1 and B2 virtually coincide.

The dynamic mechanical properties of polyoxirane prepolymers E1 and E2 were not measured, because the samples were waxy and very brittle owing to the low molecular weight. The glass transition temperature of polyoxirane is a non-monotonous function of molecular weight[15] with a maximum of $-18°C$ at the molecular weight 6,000. The respective T_a (3 Hz) read off for our samples E1 and E2 are about $-28°C$ and $-20°C$, which may correspond to $-15°C$ and $-7°C$ for the frequency 110 Hz. Secondary dispersions of polyoxiranes are feeble and have not yet been studied in great detail.[13,16,17]

Block copolymers Since the T_a's of the starting poly(N-methyl-12-dodecanelactam) and polyoxirane are close to each other the block copolymers display only one main transition at about $-10°C$ (Table I; Figures 2 and 3). Due to this coincidence the dynamic mechanical measurements do not allow us to corroborate unambiguously the existence of a presumed domain structure. One can see (Figure 2 and Table II) that the combination of the prepolymer A1 with polyoxirane affects T_a in a rather complicated manner. For instance, in the sample B5 there was a slight rise in T_a, while T_a of the samples B3, and particularly B6 (with the highest polyoxirane content) decreased with respect to the prepolymer A1. Thus, a complex dependence of T_a and of the dissipation patterns on the block copolymer composition obviously reflects the interaction of the two components.

Copolymers B8, B9, and B12 differ in their chemical structure, in the length of polyamide blocks, and also in the content and molecular weight of the polyoxirane component (Table II and Figure 3). It is interesting that the loss and storage moduli of the sample B9 (with the component ratio approx. 50:50) indicate the existence of two main transitions, though the temperature location of transitions does not correspond to that of the components. A distinct separation of the main loss maxima is observable for the copolymer

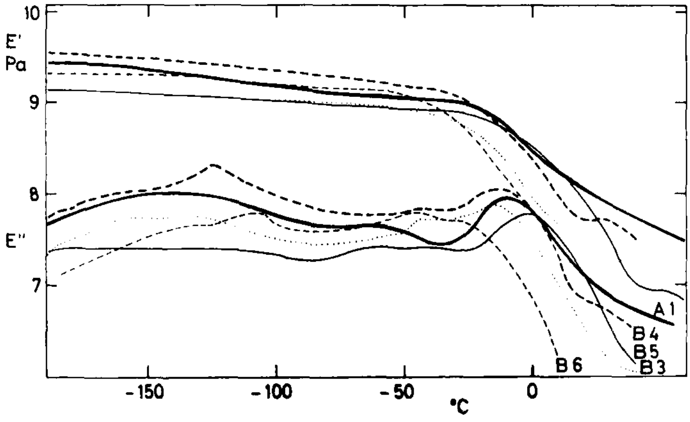

FIGURE 2 Temperature dependence of components of the complex Young modulus of copolymers of polyamide A1 with polyoxiranes E1, E2; curves denoted as samples in Table II.

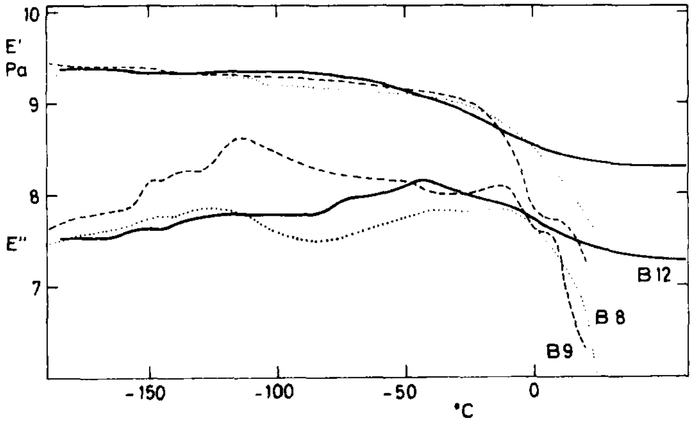

FIGURE 3 Temperature dependences of components of the complex Young modulus of polyamide-polyoxirane copolymers with various polyamide prepolymer; curves denoted as samples in Table II.

B12, which consists of blocks of poly(6-hexanelactam) and of polyoxirane with molecular weight, 1,420. T_a of polycaprolactam[10,18] at 1 Hz is approximately 50°C so that the loss maximum at 110 Hz lies beyond the temperature interval of measurements in this work. Thus, the loss maximum and the storage modulus drop at −45°C necessarily correspond to the main transition of the polyoxirane component. A further decrease in the storage modulus owing to the main transition of the polyamide component would occur above 70°C. The existence of a polyoxirane transition at −45°C suggests

TABLE II

Formulation and mechanical characteristics of copolymers of polyamides with polyoxiranes

Sample	Components		a %	$\bar{M}_n$	n	T_α °C	σ_b MPa	ϵ_b %
B1[a]	A1	—	99.1	64,000	7.4	—	45.5	810
B2[a]	A1	—	97.8	108,000	12.4	−10	26.7	680
B3	A1	E1	86.4	54,000	5.5	−15	53.6	650
B4	A1	E2	52.8	96,000	5.5	−12	49.8	920
B5	A1	E2	66.2	44,000	3.5	−3	—	—
B6	A1	E2	38.7	45,000	1.6	−20	—	—
B7	A2	E1	77.6	45,000	7.4	—	46.5	1,360
B8	A2	E2	35.0	74,000	5.4	−13	25.4	1,150
B9	A3	E2	46.5	74,000	4.6	−13 (+2)[b]	26.5	1,250
B10	A4	E2	49.3	106,000	6.1	—	23.3	1,490
B11	A5	E1	49.4	16,000	5.7	—	11.2	89
B12	A5	E1	61.6	4,500	1.6	−42	11.4	100

Symbols: a—weight fraction of polyamide blocks, $\bar{M}_n$—number average molecular weight, n—average number of polyamide (and with samples B3, 4, 7–12 also of polyoxirane) blocks, T_α—main transition temperature at a frequency of 110 Hz, σ_b—tensile strength, ϵ—strain-at-break.

[a] Polymer chains consist of polyamide blocks linked by low-molecular chain extender, hexamethylene diisocyanate.

[b] Sample has two maxima in the α-transition region.

that both components may form separate phases. (A one-phase system would display only one main transition most probably in a range about 0°C.) One can only speculate that also the other polyamide–polyoxirane copolymers have a two-phase structure in which blocks of the particular component form separate domains. The shifts of the temperature position of the main loss maxima of samples B8 and B9 may be regarded as evidence of an interaction of phases. Since the copolymers possess a multiblock structure with comparatively short blocks, one may expect (cf. Ref. 14) that the crystallinity of both phases is much lower than that in homopolymers, and that a partial mixing of components occurs on the phase boundary. As the domain size is comparable with the block length, the system can be regarded as pseudohomogeneous. It should be pointed out, however, that the morphology of block copolymers is also affected by the technique of preparation, in particular by the type of solvent.

Stress–strain curves

The different shape of the stress–strain curves of polyamide prepolymers (Figure 4) may be assigned mainly to differences in the main transition temperatures: With increasing T_α the strain-at-break measured at 25°C decreases and the initial modulus increases. The tensile strength σ_b defined as the maximum stress attained depends on T_α in a rather complicated way, because for samples

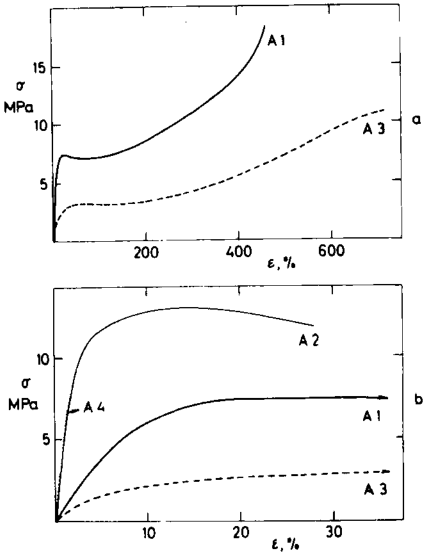

FIGURE 4 Stress-strain curves of copolyamides (prepolymers); curves denoted as samples in Table I.

with low strain-at-break it is given by the yield stress (sample A2), or by conditions of brittle fracture (A4), while for samples exhibiting cold drawing it is determined by the strain strengthening of the material (A1, A3). Besides the effect of temperature, there is also the effect of molecular weight, especially in the range of low temperatures, and eventually the effect of morphology, i.e. the amount and magnitude of crystalline domains. Hence, the effect of chemical composition on the tensile behaviour is usually reflected only indirectly, through the glass transition temperature, the ability to crystallize or to form certain supermolecular structures. In terms of molecular weight and crystallinity could be explained the behaviour of the poly(6-hexanelactam) samples A5,

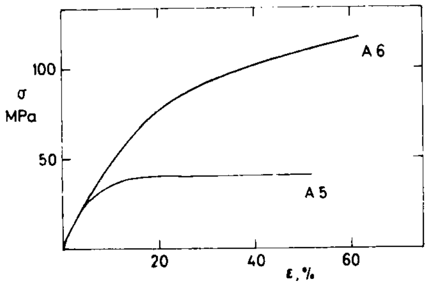

FIGURE 5 Stress-strain curves of polyamide samples A5, A6.

A6 (Figure 5). While the initial parts of the curves coincide, the more than ten times higher molecular weight of the sample A6 was reflected in a higher yield stress, a higher elongation at break and in a much more pronounced strain strengthening.

The effect of prolongation of the polyamide chain by chain extender on the shape of the stress–strain curves can be seen in Figure 6. With prolongation of the chain the stress and strain at break for the samples B1, B2 have increased; it is somewhat surprising, however, that a more pronounced increase in the ultimate properties occurred just in the case of B1 with lower molecular weight (64,000). The sample B2 with molecular weight 108,000 exhibits lower initial modulus than the sample A1 which is in accordance with the dynamic mechanical data (Figure 3). An explanation of these results could be sought in the effect of the chain extender on the decrease in crystallinity, in agreement with the interpretation of the dynamic mechanical patterns in Figure 1.

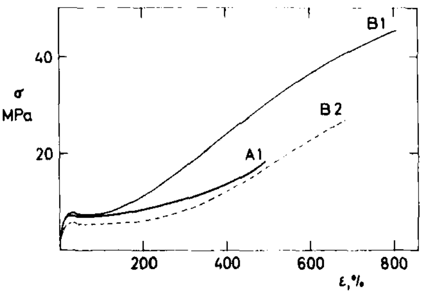

FIGURE 6 Effect of chain length (chain extension) on the shape of stress–strain curves of the polyamide copolymer; curves denoted as samples in Tables I and II.

The stress–strain curves for copolymers with a different composition and content of the polyoxirane components are shown in Figure 7. The initial part of the curves up to the yield point is obviously influenced predominantly by the polyamide component. The yield points of copolymers (5 MPa for B3 and B4; 11 MPa for B7 and B8) are only a little lower than those of the respective polyamide prepolymers (7.4 MPa for A1, 13 MPa for A2). The course of curves beyond the yield point reflects the properties of the polyoxirane components in the same way as for copolymers of polyoxirane and poly(hexamethyleneterephthalate), as described by Goodman, Peters and Schenck.[19] In our case, however, the highest tensile strength values are not found with the starting prepolymers, but with block copolymers with the polyoxirane content 13–22% (copolymers B3, B7). Although the strain-at-break exhibits a characteristic scatter, it can be said, nevertheless, that

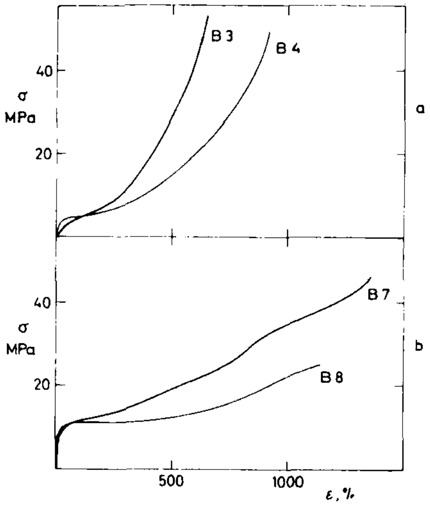

FIGURE 7 Effect of content of the polyoxirane components on stress–strain curves of polyamide–polyoxirane block copolymers: (a) polyamide component A1, (b) polyamide component A2.

it generally increases with the increase of polyoxirane content. In both cases the lower curves in Figure 7a,b (B4, B8) correspond to copolymers with a higher polyoxirane fraction and longer polyoxirane blocks. The stress–strain curves plotted in Figure 8 correspond to copolymers with various polyamide and polyoxirane components. Here too one can see the primary effect of the polyamide component on the yield points of the copolymers.

The samples under investigation exhibited a variously large contribution of Hooke's elasticity, which is reflected in the initial linear part of the curve. At larger deformations, plastic deformation occurred characterized by the yield point and cold drawing, as well as variously pronounced viscoelastic deformation, responsible to a decisive extent for the time and temperature dependence of the mechanical behaviour of polymers. Since the tensile measurement proceeded at constant temperature and test rate, the viscoelastic behaviour of the test pieces was reflected in a time-dependent reversibility of deformation after unloading or break. The strain strengthening attained in the first deformation cycle was not lasting in some of the samples, but after unloading the test piece gradually returned into the original state, exhibiting the so-called delayed elasticity. For some samples the degree of strain strengthening and its reversibility were evaluated by means of tensile tests of fragments of the test pieces after a certain rest period. The tensile strength was calculated from the cross-section of the test pieces before the beginning of a new tensile test. The sufficiently long fragments of sample B1

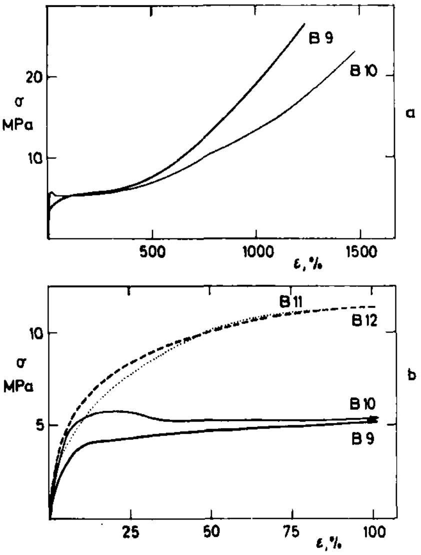

FIGURE 8 Stress–strain curves of copolymers with a different polyamide and polyoxirane component.

permitted to repeat the tensile test three times, each time after 5 minutes. Here, the tensile strength went on increasing (45.5→193→216 MPa), while strain-at-break was decreasing (808→320→260%). The same behaviour was observed with all the other copolymers under investigation with the exception of B11, where on the contrary there was a small rise in the strain-at-break. All tested samples showed dependence on the rest period between the first and the subsequent strain cycle. For sample B9 this is illustrated by Figure 9: With increasing rest period the tensile stress decreases, while strain-at-break increases. All results of the repeated tensile tests along with the original values of ultimate properties and strain-at-break are summarized

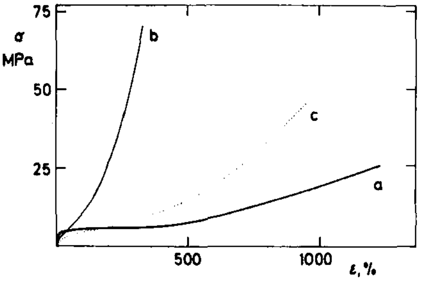

FIGURE 9 Effect of rest period on the shape of the stress–strain curve at repeated tensile tests of fragments of the test piece. Sample B9: (a) the virgin curve, (b) second test after five minutes, (c) second test after one hour.

in Table III. These values depend both on the degree of orientation and strengthening in the first loading cycle and also on the retraction of the test pieces. It should be pointed out that the very slow effect of delayed elasticity does not offer any prospects for its practical application in our copolymers, e.g. in elastic fibres. The unusually high degree of drawing of some copolymers (eight times for B1, 15 times for B10 etc.), which greatly exceeds extensibility of the conventional polyamides, is obviously due to the reduced crystallinity owing to the methyl substitution and copolymerization. The high orientation of chains yields a comparatively high tensile strength to the drawn samples. Although the highest values reached (193 MPa for B1) do not attain those usual for crystalline polyamides[20] (300–600 MPa), it may still be hoped that a suitable combination of chemical structure and conditions of drawing would permit to raise the strength still more.

TABLE III

Tensile strength, σ_b, and strain-at-break, ϵ_b, values at repeated tensile tests. Rest period: $^+$5 min. *one month

Sample	σ_b, MPa	ϵ_b, %
A1	$18.4 \rightarrow 78.2^*$	$490 \rightarrow 120^*$
A3	$10.9 \rightarrow 18.1^+$	$710 \rightarrow 330^+$
B1	$45.5 \rightarrow 193^+$	$810 \rightarrow 320^+$
B2	$26.7 \rightarrow 105^+$	$680 \rightarrow 170^+$
B3	$53.6 \rightarrow 158^*$	$650 \rightarrow 270^*$
B4	$49.8 \rightarrow 145^*$	$920 \rightarrow 360^*$
B7	$46.5 \rightarrow 141^+$	$1{,}360 \rightarrow 660^+$
B8	$25.4 \rightarrow 159^+$	$1{,}150 \rightarrow 290^+$
B9	$26.5 \rightarrow 71.4^+$	$1{,}250 \rightarrow 330^+$
B10	$23.3 \rightarrow 91.5^+$	$1{,}490 \rightarrow 590^+$
B11	$11.2 \rightarrow 13.5^+$	$89 \rightarrow 93^+$
B12	$11.4 \rightarrow 16.1^+$	$101 \rightarrow 98^+$

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