The influence of a new chemical cross-link system on the mechanical behaviour of aliphatic polyamides

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Special polyamide chains were polymerized such that they contained reactive sites situated either at the chain ends or at both the chain ends and within the chains. The degree of cross-linking is determined by the amount of a specific silane (cross-link silane), which causes cross-linking by formation of condensed silicon centres.

The influence of the degree of cross-linking on the deformation behaviour was studied for uniaxial deformation over a wide range of temperatures and strain rates. A linear dependence of yield stress on the degree of cross-linking was found. The yielding behaviour was treated as an activated rate process and described by a site-change model, in which the height of the energy barrier is determined by the amount of cross-link silane, i.e. by the degree of cross-linking.

1. Introduction

Aliphatic polyamides (nylons) are partially crystalline thermoplastics. The various types of nylon in use differ from each other in the ratio and position of amide groups (CONH) with respect to CH_2 groups in the linear macromolecular chains. Independent of this ratio they show characteristics which make them interesting for many technical applications.

A disadvantage of nylons is their creep behaviour under constant stress. The intermolecular hydrogen bonds are not strong enough to prevent chain-sliding caused by an applied stress. The material flows and changes its geometrical form. One way to improve the creep behaviour is to cross-link the polymer chains.

The purpose of this work is to investigate the influence of the degree of cross-linking on the mechanical behaviour, especially the stress–strain curve, over a wide range of temperatures and strain rates.

2. A new chemical cross-link system for aliphatic polyamides

Processes to cross-link thermoplastic materials, mainly olefines such as polyethylene, are well known and can be divided into radiation and chemical cross-linking. In both cases cross-linking occurs statistically in the polymer structure and is accompanied by the breaking of existing bonds and/or by secondary reactions. Consequences are e.g. discolorations and bad influence on the electrical properties.

The new cross-link system, developed by the research department of EMS-Chemie AG, avoids these negative aspects. It can be outlined in three reaction steps as follows.

(i) Firstly, special nylon chains were polymerized, which already contained reactive sites either at the chain ends (favourable structure) or at both the chain ends and within the chains.

(ii) Secondly, this special polyamide melt was thoroughly mixed with the cross-link silane. During this mixing, one cross-link silane molecule reacts with one reactive site of the polymer chain.

(iii) Thirdly, the real cross-linking occurs by contact with water. The cross-link silane, already grafted to a chain, is hydrolysed to the Si–OH group, followed by condensation to –Si–O–Si– bridges.

In the case of few silane molecules we will mainly find a lengthening of the PA chains (Fig. 1). Excess silane molecules lead to multifunctional, condensed silicon centres and form a network (Fig. 2). Therefore, the amount of cross-link silane in the material determines the degree of cross-linking.

3. Experimental materials

The experimental materials used were nylon-12 with varying degree of cross-linking. Tensile specimens
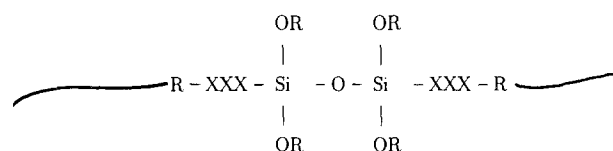

Figure 1 Chain lengthening by –Si–O–Si– bridges.

TABLE I Chain structure, content of cross-link silane, cross-link parameter x and names of investigated materials

Reactive sites	Reactive sites (μ mol g^{-1})	Cross-link silane (μ mol g^{-1})	Cross-link silane (%)	Cross-link parameter x	Name
only at the chainends	65	0	0.00	1.0000	PA 12/0
	65	25	0.59	1.0059	PA 12/1
	65	50	1.18	1.0118	PA 12/2
	65	65	1.53	1.0153	PA 12/3
also within the chains	100	100	2.36	1.0236	PA 12/SP4

(ASTM-D-638-77a Type V) were shaped by injection moulding at a temperature about 250 °C. After injection moulding, the specimens were stored in water at 60 °C for three days, to ensure that all cross-linkable chains are really cross-linked. Subsequently specimens were dried in a vacuum oven at 90 °C for 14 h and kept in a dessicator, to eliminate the influence of water on the deformation behaviour. The uptake and loss of water were about 1.7%, independent of the degree of cross-linking.

The thickness and width in the middle of the tensile specimen were 3.15 and 3.10 mm, respectively. Details of the sample geometry are shown in Fig. 3.

Specimens with five different degrees of cross-linking were investigated as shown in Table I. Table I shows the chain structure, the content of cross-link silane, the names of the investigated materials and the cross-link parameter x.

The number of reactive sites n_s was determined by an acid–base titration method. This corresponds to the average molecular weight M_c for the material containing reactive sites only at the chain ends

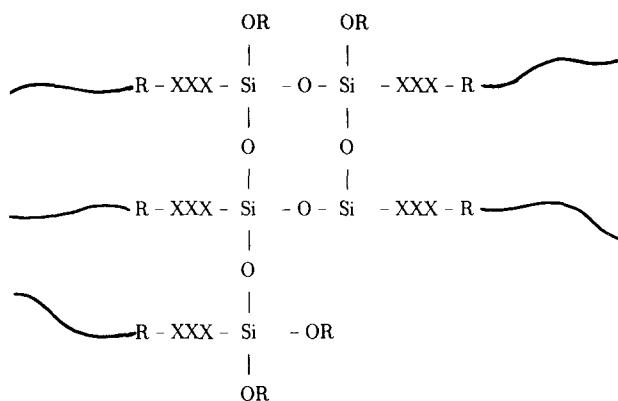$$M_c = \frac{1}{n_s/2} = \frac{2}{65\ \mu mol\ g^{-1}} \simeq 30\,800\ g\,mol^{-1}$$

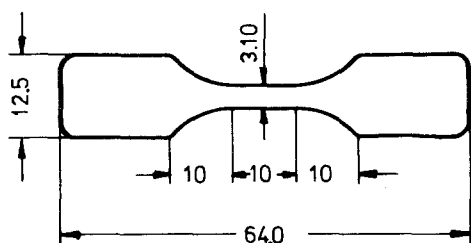Figure 2 Multifunctional, condensed silicon centre.

Figure 3 Sample geometry.

For the case that every chain is involved in the network, one chain before cross-linking is equal to a "network chain" after cross-linking.

This means that the "chain molecular weight" M_n for the ideal network without imperfections is equal to the molecular weight M_c of the chains before cross-linking.

The greatest number n of network chains per unit volume can be calculated as follows

$$n = \frac{N_A}{M_n}\rho \simeq 2 \times 10^{19}\ \frac{1}{cm^3}$$

where N_A is Avogadro's constant and ρ the density of nylon-12. The density ρ was found to be 1.012 g cm^{-3}, independent of the degree of cross-linking (see Section 6.1).

4. Yield as an activated rate process
Eyring and co-workers [1] developed a simple site change model, which describes the relationship between the rate of site changes, the temperature, the stress and the strain rate.

It is assumed that deformation of the polymer causes chain molecules or parts of a chain molecule to move over potential energy barriers. The basic molecular process could be either intermolecular (e.g. chain-sliding) or intramolecular (e.g. change in the conformation of the chain). The situation is illustrated schematically in Fig. 4.

With no stress acting at dynamic equilibrium, chain segments moving with a frequency over the energy
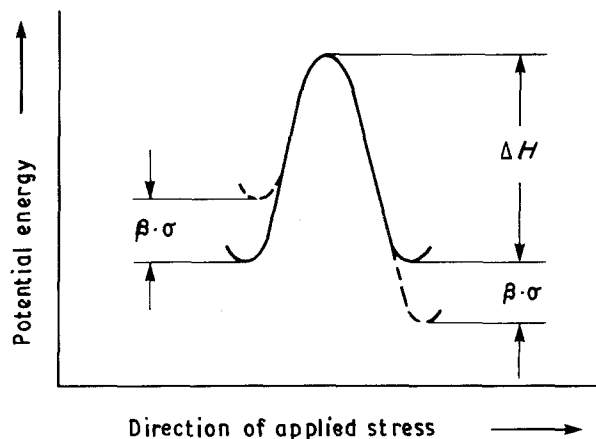
Figure 4 Energy double well of the one-dimensional site change model. An applied stress σ produces shifts $\beta\sigma$ of the energy barrier ΔH.

barrier ΔH in each direction, where the frequency ν of site changes is given by

$$\nu = \nu_0 \exp\left(-\frac{\Delta H}{RT}\right) \qquad (1)$$

in which ν_0 is the frequency with which chain segments try to overcome the energy barrier, R the gas constant and T the absolute temperature. The exponential factor describes how often an attempt to overcome the energy barrier ends with a site change. The energy barrier ΔH is characteristic for each polymer.

It is assumed that the applied stress σ produces linear shifts $\beta\sigma$ of the energy barrier in a symmetrical fashion. We then have site changes in the direction of the applied stress

$$\nu_1 = \nu_0 \exp\left(-\frac{\Delta H - \beta\sigma}{RT}\right) \qquad (2)$$

and against the applied stress

$$\nu_2 = \nu_0 \exp\left(-\frac{\Delta H + \beta\sigma}{RT}\right) \qquad (3)$$

β is the activation volume or the Eyring volume. It describes how the polymer reacts to the applied stress. High values of β result in many site changes at low stress. It is assumed that the plastic strain rate $\dot{\varepsilon}_p$ is given by the difference of the site changes in the forward direction and in the direction opposing the applied stress

$$\dot{\varepsilon}_p \propto \nu_1 - \nu_2 = \frac{\nu_0}{2}\exp\left(-\frac{\Delta H}{RT}\right)\sinh\left(\frac{\beta\sigma}{RT}\right) \qquad (4)$$

How can the Eyring expression of activated flow (Equation 4) be applied on the deformation process of cold drawing?

Many workers [2–5] have considered that the yield stress σ_y denotes the point at which the internal viscosity falls to a value such that the applied strain rate $\dot{\varepsilon}$ is identical with the plastic strain rate $\dot{\varepsilon}_p$ predicted by Equation 4. For temperatures less than T_G we can neglect the site changes with the applied stress, because site changes without stress are nearly impossible. Thus the strain rate $\dot{\varepsilon}$ is given by

$$\dot{\varepsilon} \propto \nu_1 = \nu_0 \exp\left(-\frac{\Delta H - \beta\sigma_y}{RT}\right)$$

$$\dot{\varepsilon} = \dot{\varepsilon}_1 \exp\left(-\frac{\Delta H}{RT}\right)\exp\left(\frac{\beta\sigma_y}{RT}\right) \qquad (5)$$

and

$$\dot{\varepsilon} = \dot{\varepsilon}_0(T)\exp\left(\frac{\beta\sigma_y}{RT}\right) \qquad (6)$$

Rearranging Equation 6 gives

$$\sigma_y = \frac{RT}{\beta}\ln\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0(T)}$$

$$\sigma_y = \frac{RT}{\beta}\ln\dot{\varepsilon} + \sigma_{01}(T) \qquad (7)$$

where $\sigma_{01}(T) = -\frac{RT}{\beta}\ln\dot{\varepsilon}_0(T)$.

Equation 7 predicts a linear relationship between the yield stress σ_y and the logarithm of the strain rate $\dot{\varepsilon}$

in a constant strain rate test. The slope of a plot of the yield stress σ_y against the logarithm of strain rate $\dot{\varepsilon}$ is given by RT/β, which makes it possible to calculate the activation volume β.

Up till now no statements about the morphological or molecular structure of a given polymer have been made. The degree of crystallinity, cross-linking or orientation for example are involved in ν_0, ΔH and β. In fact, the plastic deformation, involving site changes, is hindered by the degree of cross-linking. The idea is to take these physical aspects into account by varying the energy barrier ΔH. This situation is illustrated schematically in Fig. 5. ΔH_0 is the energy barrier for the uncross-linked material and $\Delta H_x = x\Delta H_0$ the energy barrier for the cross-linked material. The parameter x is determined by the degree of cross-linking and, therefore, we call x the cross-link parameter. It seems evident that x is determined by the amount of cross-link silane in the material. The greater the amount of cross-link silane that the material contains, the higher will be the degree of cross-linking. This leads to an increase in the energy barrier and a reduction in the rate of site changes. Table I shows the cross-link parameter determined from the amount of cross-link silane.

Substitution of ΔH by $\Delta H_x = x\Delta H_0$ in Equation 5 and rearrangement gives

$$\sigma_y = \frac{\Delta H_0}{\beta}x - \frac{[\ln(\dot{\varepsilon}_0/\dot{\varepsilon})]RT}{\beta} \qquad (8)$$

$$\sigma_y = \frac{\Delta H_0}{\beta}x + \sigma_{02}(T) \qquad (9)$$

where $\sigma_{02}(T) = -\frac{[\ln(\dot{\varepsilon}_0/\dot{\varepsilon})]RT}{\beta}$.

Equation 9 predicts a linear relationship between the yield stress σ_y and the cross-link parameter x. The slope of a plot of σ_y against x is given by $\Delta H_0/\beta$. This makes it possible to evaluate the activation energy ΔH_0 for a given activation volume β.

5. Experimental procedure
5.1. Density measurement
The specimen density was obtained using a density gradient column containing n-heptane and carbon tetrachloride as the flotation liquid.
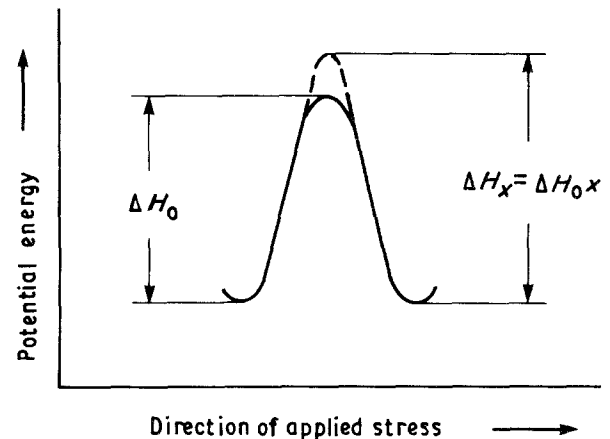

Direction of applied stress ⟶

Figure 5 Energy double well of the one-dimensional site change model with variable energy barrier ΔH_x.

5.2. DTA measurement

Thermal measurements were carried out using a Mettler TA2000 B thermal analyser (DTA). A heating rate of $10\,^{\circ}C\,min^{-1}$ was adopted. The DTA diagrams are standardized according to mass. The accuracy of the temperature is $\pm 1\,^{\circ}C$.

5.3. Wide-angle X-ray scattering (WAXS) measurements

WAXS patterns were obtained using a flat-plate camera mounted on an X-ray generator with a copper target. A nickel filter was deployed to obtain monochromatic CuK_α radiation ($\lambda = 0.154$ nm). Measurements were made with the X-ray beam aligned perpendicularly to the axis of the tensile specimen.

5.4. Stress–strain measurements

Tests at constant strain rate were made using a Zwick testing machine type 1454. The testing length of the specimen was 20 mm. The elongation rates were (1.25, 5, 12.5, 50, 125)% min^{-1} and the temperatures were $(-60, -20, 22, 80, 130)\,^{\circ}C$. Tests were made after keeping the specimens for half an hour at the required temperature. The relative error of the stress–strain measurement is approximately 5%. The yield stress was taken as the first maximum in the stress–strain curve.

6. Results and discussion

6.1. Density measurement

The density is $1.0120\ g\,cm^{-3}$ for all degrees of cross-linking, compared with a value of $0.99\ g\,cm^{-3}$ given in the literature [6] for fully amorphous nylon-12. This suggests a degree of crystallinity not depending on the degree of cross-linking.

6.2. DTA measurements

Fig. 6 shows DTA diagrams for nylon-12 at various degrees of cross-linking. An endothermal effect (glass transition) was observed at about $50\,^{\circ}C$, caused by the glass transition. The melting temperature (maximum of the melting-peak) for all specimens was observed at about $180\,^{\circ}C$. The enthalpy is independent of the degree of cross-linking. This means that the degree of crystallinity does not depend on the degree of cross-linking. However, the width of the melting peak, which relates to the crystal size distribution, does depend on the degree of cross-linking. The width of the melting peak increases with increasing degree of cross-linking.

The independence of the degree of crystallinity on the degree of cross-linking shown by density and DTA measurements is important for the evaluation of stress–strain behaviour in dependence on the degree of cross-linking. Starkweather *et al.* [7] and other workers showed the influence of the degree of crystallinity on mechanical behaviour of polyamides, i.e. the yield stress.
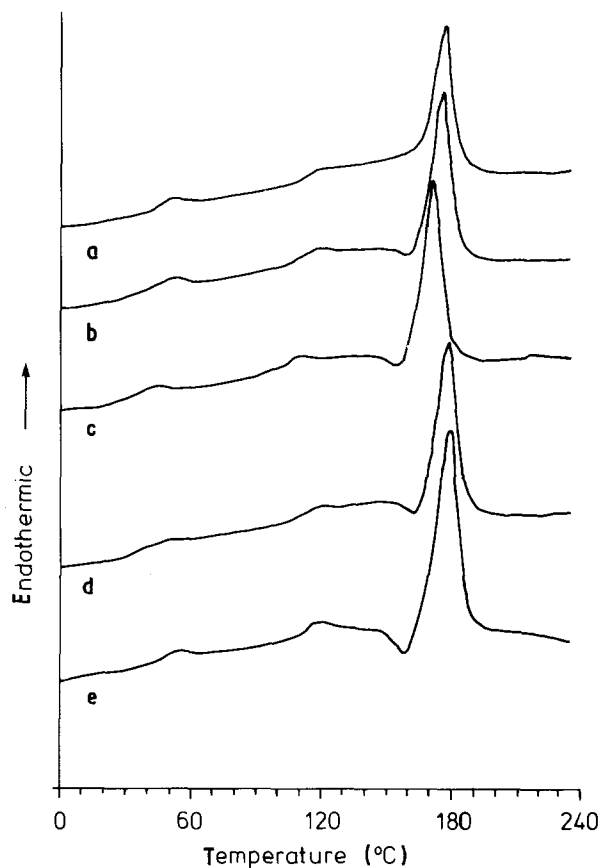

Figure 6 DTA diagrams for nylon-12. Parameter is the degree of cross-linking. Heating rate $10\,^{\circ}C\ min^{-1}$. (a PA12/SP4, b PA12/3, c PA12/2, d PA12/1, e PA 12/0).

6.3. Wide-angle X-ray scattering measurements

Figs 7 to 10 show WAXS patterns of nylon-12. The structure and unit cell dimensions of nylon-12 are already well described in the literature [8] and will not be discussed in this work. We want to evaluate the
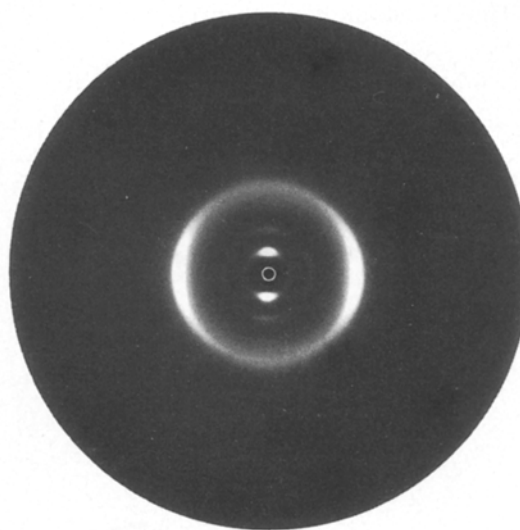

Figure 7 WAXS pattern for weak, cross-linked nylon-12, PA 12/1. Molecular orientation along the axis of the specimen tensile is seen.
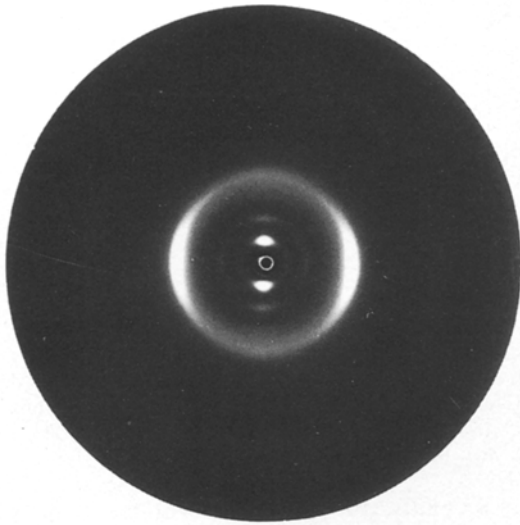
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Figure 8 WAXS pattern for high, cross-linked nylon-12, PA 12/SP4. Molecular orientation along the axis of the specimen tensile is seen.

degree of molecular orientation, because molecular orientation significantly influences the stress–strain behaviour of polymers.

The WAXS patterns (Figs 7 and 8) of all cross-linked specimens do not differ significantly from each other and show molecular orientation along the axis of the tensile specimen. The WAXS patterns (Fig. 9) of the uncross-linked specimen show a smaller degree of molecular orientation parallel to the axis of the tensile specimen. Fig. 10 shows WAXS patterns for the annealed (190 °C, 2 h) specimen with highest degree of
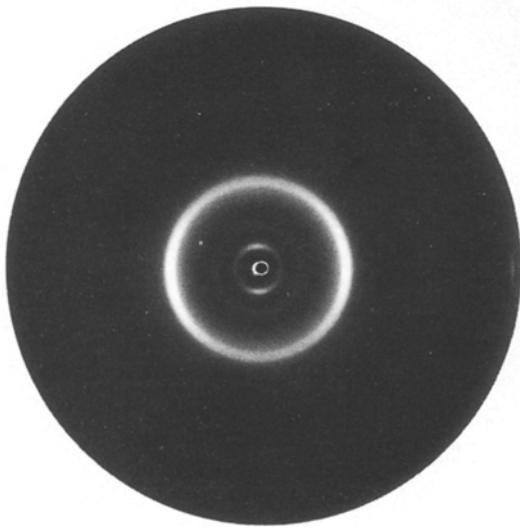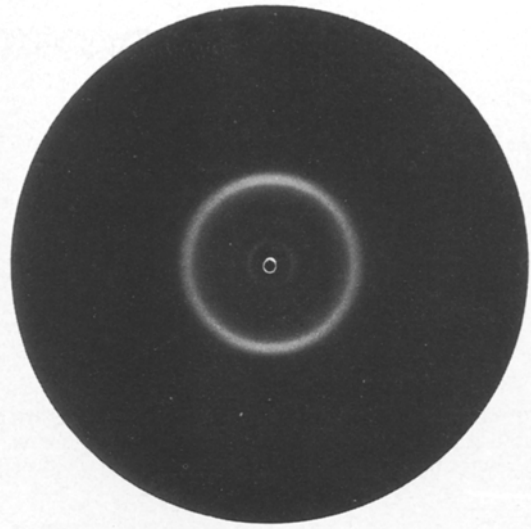

Figure 10 WAXS pattern for annealed (190 °C, 2 h), high cross-linked nylon-12, PA 12/SP4. Molecular orientation has disappeared.

cross-linking. The molecular orientation has disappeared. This is related to a shrinkage of the tensile specimen of about 25%.

In the literature [9] it is shown that the yield stress increases with increasing degree of orientation. We have to take account of this fact when evaluating the yield stress dependence on the degree of cross-linking.

6.4. Stress–strain behaviour

Fig. 11 shows the stress–strain curves of dried nylon-12 at a constant strain rate of 12.5% min^{-1} and at a constant temperature of 22 °C for various degrees of cross-linking. The stress–strain behaviour is typical for the deformation process of cold-drawing. The elongation at the yield point is about 30% and is independent of the degree of cross-linking. With increasing degree of cross-linking, the yield stress and tensile strength increase, whereas breaking elongation decreases and the yield peak becomes less pronounced.
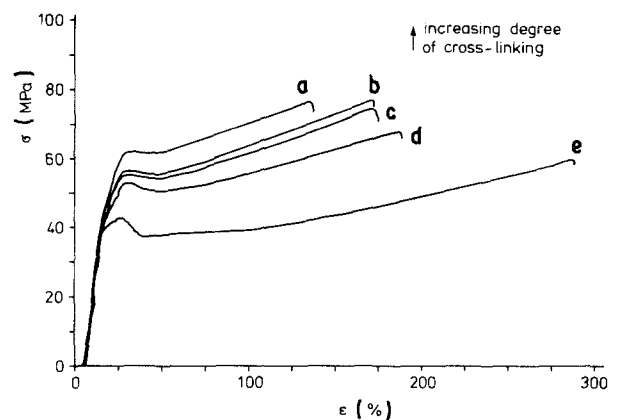

Figure 9 WAXS pattern for uncross-linked nylon-12, PA 12/0. A weak molecular orientation along the axis of the specimen tensile is seen.

Figure 11 Stress–strain curves of dried nylon-12 at constant strain rate of 12.5% min^{-1} and constant temperature of 22 °C for all degrees of cross-linking. (a PA 12/SP4, b PA 12/3, c PA 12/2, d PA 12/1, e PA 12/0).
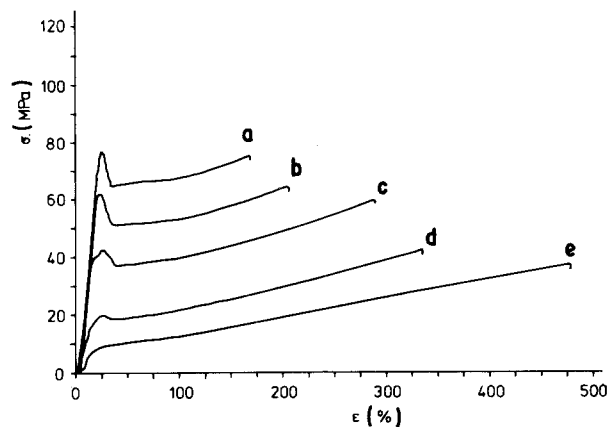
Figure 12 Stress–strain curves of dried uncross-linked nylon-12, PA 12/0 at a constant strain rate of 12.5% min⁻¹ for various temperatures. (a — 60 °C, b — 20 °C, c 22 °C, d 80 °C, e 130 °C).

Figs 12 and 13 show the stress–strain curves of dried, uncross-linked and highly cross-linked nylon-12 at a constant strain rate of 12.5% min⁻¹ for various temperatures.

The yield point vanishes with increasing temperature, especially for temperatures above the glass transition (50 °C). At all temperatures, the yield stress of the uncross-linked specimen (PA 12/0) is distinctly lower, up to 40%. This shows the effect of the cross-linkages over a wide range of temperatures.

Fig. 14 shows the dependence of the strain rate on the yield stress at a constant temperature of 22 °C for uncross-linked nylon-12 (PA 12/0). This is typical for all degrees of cross-linking. For all degrees of cross-linking, the yield stress increases with increasing strain rate.

Fig. 15 shows the measured yield stress σ_y as a function of the logarithm of strain rate $\dot{\varepsilon}$ at a constant temperature of 22 °C for all degrees of cross-linking. From our data we find that the plot of σ_y against $\ln \dot{\varepsilon}$ at different degrees of cross-linking gives a set of concurrent straight lines which fit Equation 7 fairly well. This set of parallel straight lines (slope RT/β) is the experimental proof that:

(i) Firstly, the yielding of nylon-12 can be described as an activated rate process, based on Eyring's theory of viscous flow.
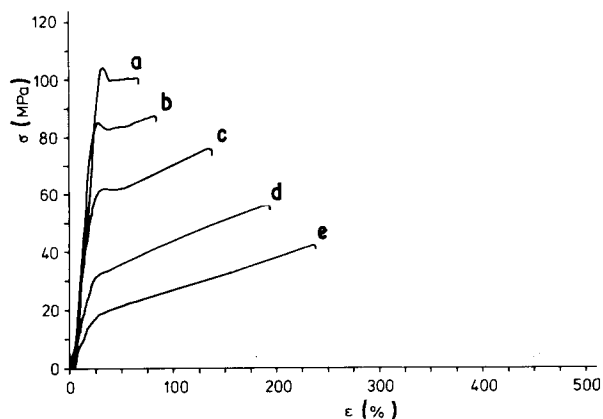

Figure 13 Stress–strain curves of dried, high cross-linked nylon-12, PA 12/SP4 at a constant strain rate of 12.5% min⁻¹ for various temperatures. (a — 60 °C, b — 20 °C, c 22 °C, d 80°C, e 130 °C).

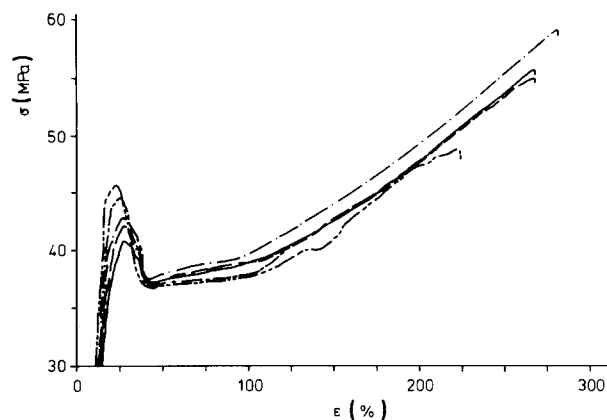*Figure 14* Stress–strain curves of dried, uncross-linked nylon-12, PA 12/0 at a constant temperature of 22 °C for various strain rates. (—— 1.25% min⁻¹, —— 5.00% min⁻¹, —·— 12.50% min⁻¹, —·— 50% min⁻¹, —-—- 125% min⁻¹).

(ii) Secondly, the activation volume β does not depend upon the degree of cross-linking and orientation.

(iii) Thirdly, the influence of cross-linking on the yield behaviour is given by the term σ_{01} (T) containing the activation energy ΔH_x.

The activation volume β is evaluated as follows. We first draw the set of straight lines which best agree with the data. The mean slope is taken as $\beta = 4.2$ nm³. For cross-linked nylon-6 we found an analogous
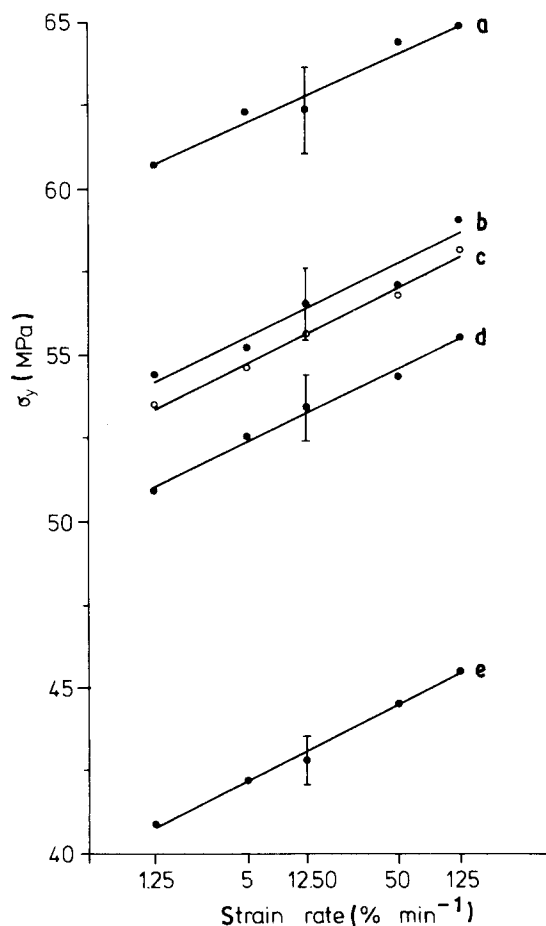

Figure 15 Measured yield stress σ_y as a function of logarithm of strain rate $\dot{\varepsilon}$ at a constant temperature of 22 °C for all degrees of cross-linking. The set of parallel straight lines is calculated from Equation 7. (a PA 12/SP4, b PA 12/3, c PA 12/2, d PA 12/1, e PA 12/0).
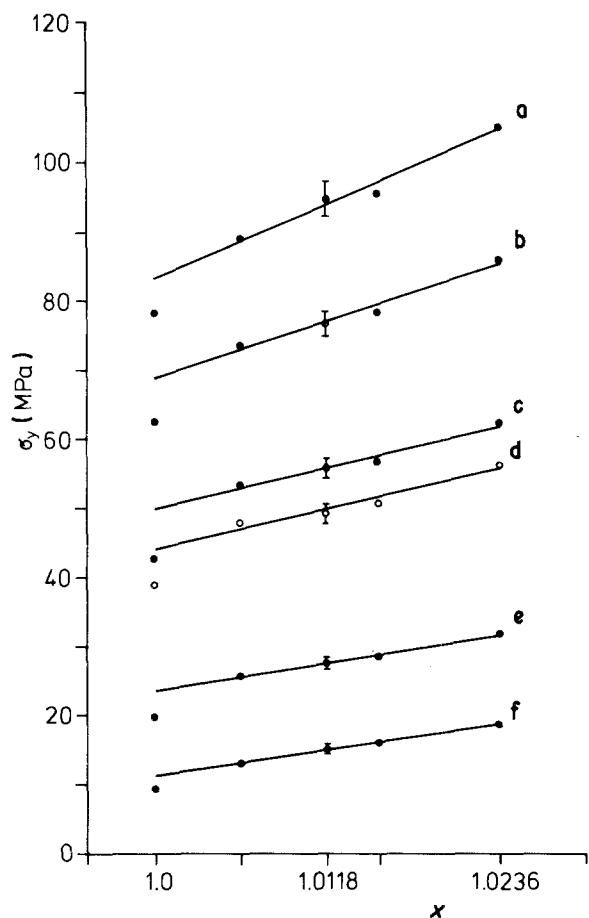
Figure 16 Measured yield stress σ_y as a function of the cross-link parameter x at a constant strain rate of 12.5% min^{-1} for various temperatures. The set of straight lines is calculated from Equation 9. (a $-$ 60°, b $-$ 20°C, c 22°C, d 22°C (wet), e 80°C, f 130°C).

Figure 17 Measured yield stress σ_y as a function of the cross-link parameter x at a constant temperature of 22°C for various strain rates. (○ 50% min^{-1}, ● 1.25% min^{-1}).

Figure 18 Measured yield stress σ_y as a function of the cross-link parameter x at a constant temperature of 22°C for various strain rates. (○ 125% min^{-1}, ● 5% min^{-1}).

stress–strain behaviour. The activation volume does not depend upon the degree of cross-linking and orientation. The value is 7.1 nm^3 for nylon-6 containing 5% water and 10.2 nm^3 for nylon-6 containing 9% water.

Fig. 16 shows the measured yield stress σ_y as a function of the cross-link parameter x at a constant strain rate of 12.5% min^{-1} for various temperatures. Figs 17 and 18 show the measured yield stress σ_y as a function of the cross-link parameter x at a constant temperature of 22°C for various strain rates. From our data we find that p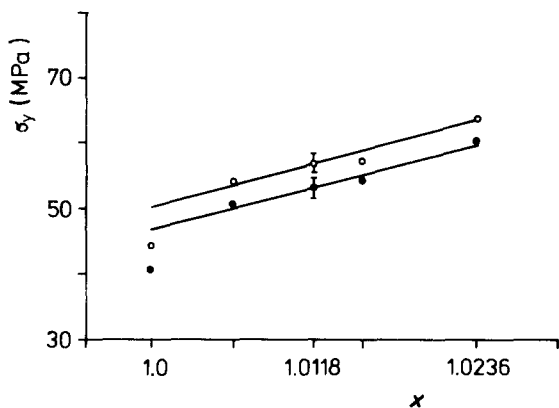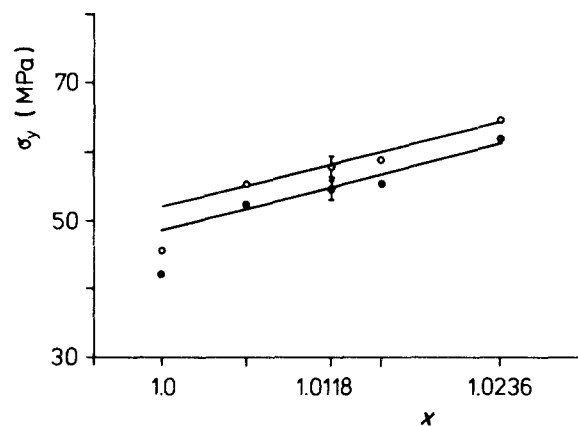lots of σ_y against x give sets of straight lines which fit Equation 9 fairly well. This set of straight lines (slope $\Delta H_0/\beta$), which best agree with the data, is the experimental proof that:

(i) Firstly, the influence of the degree of cross-linking on yielding can be described by varying the value of the energy barrier. Yield stress linearly increases with increasing degree of cross-linking.

(ii) Secondly, the slope $\Delta H_0/\beta$ of the graph does not depend upon the strain rate.

(iii) Thirdly, the activation volume β increases with increasing temperature, because the slope $\Delta H_0/\beta$ increases with decreasing temperature.

The activation energy ΔH_0 is evaluated by drawing straight lines, which best agree with data of the cross-linked material and by taking the activation volume β as 4.2 nm^3. The activation energy is calculated to be 1280 kJ mol^{-1} for dried nylon-12 and 1370 kJ mol^{-1} for nylon-6 (water content 5%).

For evaluating the slope $\Delta H_0/\beta$ we do not have to take into account the data of the uncross-linked material, because the degree of orientation differs from that of the cross-linked material (see Figs 7 to 9). At all temperatures the yield stress of the uncross-linked material lies distinctly beyond the straight lines (given by the cross-linked material). With increasing temperature (above the glass transition) the distance of the yield stress of the uncross-linked material to the straight lines becomes smaller, because during heating the orientation partially relaxes.

As a result of this behaviour, the influence of the degree of orientation on the yield stress could also be described by varying the energy barrier. With increasing degree of orientation, the site changes are more and more hindered. This could be mathematically expressed by increasing the energy barrier. In this context, we should remember Equation 9, in which the value of the yield stress is determined by the parameters ΔH_0 and β. The experimental facts that β does not depend upon the degree of cross-linking and ΔH does, and that β does depend upon the water content and ΔH does not, show that both the activation energy and activation volume are determined by the chemical and morphological structure of the polymer. We consider that the activation volume is determined

mainly by the chemical structure of the polymer chains, and less by the morphological structure, e.g. degree of cross-linking, orientation, crystallinity, which are involved in the activation energy. Further quantitative analysis is necessary in order to clarify the relationship between the activation energy and the activation volume and the chemical and morphological structure more satisfactorily.

The values of the activation energy and activation volume are of the order of magnitude of values found by other authors. Haward and Thackray [10] found for the activation volume values of 3.9 nm^3 (polymethylmethacrylate) and 5.7 nm^3 (polycarbonate). As we did, Holt [4] found that the activation volume of polymethylmethacrylate is dependent upon temperature. The slope $(\partial \sigma_y / \partial \ln \dot{\varepsilon})_T = RT/\beta$ decreases with increasing temperature, which requires that the activation volume of PMMA increases with temperature.

Bauwens–Crowet, Bauwens and Homes [2] however, found for polycarbonate that the activation volume does not depend upon temperature. Owen and Bonart [11] obtained for the activation energy of nylon-12 860 kJ mol^{-1} by using dynamic tensile compliance measurements. The large values of the activation energy are understandable when one notes that a site change involves the cooperation of many coupled segments.

7. Conclusions
The conclusions are as follows.

(1) Yielding of nylon-12 can be described as an activated rate process, based on Eyring's theory of viscous flow.

(2) The influence of cross-linking on the yield behaviour can be described by varying the value of the energy barrier. Yield stress linearly increases with increasing degree of cross-linking.

(3) The influence of the degree of orientation on the yield behaviour can be taken into account by the value of the energy barrier. The activation energy ΔH increases with increasing degree of orientation.

(4) The activation volume β does not depend upon the degree of cross-linking and orientation and increases with increasing temperature.

(5) The new chemical cross-link system distinctly improves the stress–strain behaviour of aliphatic polyamides. Yield stress and tensile strength increase over a wide range of temperatures.

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