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Non-linear stress relaxation behaviour of crosslinked polyester resins in simple extension

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A series of crosslinked polyester resins have been prepared by curing an orthophthalic unsaturated resin containing different amounts of either of two flexibilizers, one bifunctional and the other monofunctional. The samples thus obtained show a variety of morphologies and mechanical properties over a wide range. Stress relaxation measurements in simple extension at room temperature were made at various strains in the region of the non-linear behaviour. It has been found that the relaxation curves can be superimposed by a shift along the logarithmic time axis, with shift factors that are in a good linear relation to the initial stress, and with slope and intercept values characteristic of every material. This property makes it possible to determine, at any strain, relaxation master curves covering a notable time range, and clearly to single out the stress upper bound of the linear behaviour range as the intercept on the stress axis.

(Keywords: polyester resins; stress relaxation; non-linear viscoelasticity; relaxation master curves; flexibilizers)

INTRODUCTION

Non-linear behaviour of polymeric materials in stress relaxation experiments has been over the years the subject of many investigations[1]. Various types of non-linearity effects have been observed on different polymeric materials, mostly depending on their structure and morphology, and on their rubbery, glassy or semi-crystalline nature.

Such different behaviours can hardly be satisfactorily described by the non-linear viscoelastic theories proposed so far, which are still too complicated to be of practical interest, or not applicable in other than very restricted conditions.

Experimental results suggest, however, that many non-linear effects may be often considered and analysed according to a kind of 'rheologically simple' behaviour. In various cases, for example, it was found that relaxation curves at different strain levels, or creep curves at different stress levels, outside of the linear region, could be superimposed when plotted on double- or semilogarithmic scales by shifting them along the (vertical) modulus or compliance axis, or along the (horizontal) time axis, or both.

Examples of vertical superimposability have been reported for creep or stress relaxation of elastomers[2–5] and polyethylenes[5,6], and horizontal for cellulose monofilaments[7], terylene[8], nitrocellulose and glass-reinforced phenolic resins[2]. Superimposability that requires both vertical and horizontal shifts has been reported for nylon[8], acrylonitrile–butadiene–styrene (ABS)[9] and polycarbonate[10].

In the present work the stress relaxation has been studied, in simple extension at different strain levels, of a series of materials obtained by adding two different types of flexibilizing additives to an unsaturated polyester resin. These crosslinked materials, depending on type and amount of the added flexibilizer, show different morphologies and a variety of mechanical properties over a range from brittle glassy to tough rubber-like behaviour.

It will be shown that in all cases a superimposability of the relaxation curves at various strain levels is possible, leading to master curves with simple correlations of the relative shift factors, which allow one clearly to distinguish linear and non-linear regions, and to make more reliable extrapolation of the data towards considerably longer loading times.

EXPERIMENTAL

Materials

All the starting materials of the present study were kindly supplied by DSM Italia S.p.A., Como, Italy.

The basic resin was a typical orthophthalic unsaturated polyester (DSM Neoxil 276N5) in 67 wt% styrene solution. Two different types of commercial flexibilizers were added to the basic resin. Both are solutions of polyester resins in styrene: the first one (DSM 12616) is crosslinkable with itself (in the following it will be denoted as CF), while the second (DSM Neoxil 226) (in the following NF) is essentially non-crosslinkable, but can react with the basic resin yielding flexible dangling chains on the basic network. The two flexibilizers were added to the basic polyester in amounts of 15%, 30% and 45% by weight.

The mixtures were cured at room temperature by adding 0.5% by weight of methyl ethyl ketone peroxide, and 0.5% of a 6% cobalt naphthenate solution in styrene. The mixtures were poured between two clamped glass plates separated by rubber strips to give a nominal thickness of 2.5 mm. After 1 day at room temperature the resin sheets were removed from the glass plates and post-cured for 4 h at 140°C in an air circulated oven.

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Table 1 Denomination and characteristics of the materials

Denomination	Flexibilizer (wt%)	Glass transition (°C)	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Toughness[a] ($\mathrm{MJ\,m^{-3}}$)
Resin	0	125	4.40	62	1.6	0.52
Flexibilizer CF[b]	100	11	0.39	13	62.0	5.18
Flexibilizer NF[c]	100	−20	–	–	–	–
CF15	15	114	4.38	71	2.1	0.83
CF30	30	94	4.36	78	3.2	1.60
CF45	45	69	3.51	63	5.0	3.43
NF15	15	−10, 63, 118	3.17	80	3.6	1.79
NF30	30	−10, 55, 110	2.62	47	8.0	3.13
NF45	45	−15, 55, –	1.21	28	20.0	4.99

[a] Defined as the energy to break, and calculated as the area under the stress–strain curve
[b] Crosslinkable with itself
[c] Non-crosslinkable with itself

Six different material samples have thus been obtained, whose denominations and characteristics are reported in *Table 1*.

Characterizations

Glass transition temperatures of the materials have been determined by differential scanning calorimetry, performed with a Mettler TA 3000 apparatus, at a scanning speed of 20°C min^{-1}, in a temperature range from −150 to 200°C.

Dog-bone specimens for tensile mechanical testing according to ASTM D638 were cut from the moulded plates by a disc saw and shaped to their final dimensions using a milling machine. The specimen dimensions were nominally 15 mm in width of the narrow section, 50 mm in gauge length and 2.5 mm in thickness.

Tensile stress–strain curves were obtained at constant strain rate 10% min^{-1}, at 23°C, with an Instron 1121-10 KN tester equipped with an optical strain gauge. For every material the stress–strain curve is given as an average of six specimens.

Stress relaxation measurements

The stress relaxation tests were made in uniaxial tension, at 23°C, using the same type of specimens and test machine as for stress–strain measurements.

The predetermined deformation was applied at a constant strain rate of 10% min^{-1}. A rather slow ramp function was chosen in order to avoid possible fracture of the specimens during the application of the strain or at the beginning of the relaxation measurement. In fact in our experiments the higher strain levels were in some cases rather close to the breaking value of the material at the same strain rate.

The application of the strain in a finite time (not in an 'instantaneous' way) clearly affects the early period of the relaxation behaviour. It has been suggested[2,11] that the influence of the transient strain input should become negligible after an elapsed time at constant strain, which, depending on the strain level and on the material properties, can be estimated from 2 to 10 times that required to impose the strain itself. Accordingly, in all our relaxation experiments the stress data have been recorded starting 1 min after the predetermined constant strain was reached.

RESULTS AND DISCUSSION

The addition of the two types of flexibilizer, CF and NF, leads to different structures and morphologies of the crosslinked mixtures, as revealed by the glass transition temperatures reported in *Table 1*.

All the CF mixtures show a single transition, indicating a homogeneous structure in which segments of the network meshes of the basic resin are probably partially and randomly substituted by segments of the flexibilizer. The transition temperatures decrease with increasing amount of flexibilizer, and the experimental values (*Table 1*) are in fairly good agreement with those calculated with the simplest rule of mixtures:

$$T_g = T_{ga}w_a + T_{gb}w_b$$

where T_{gi} and w_i are the transition temperatures (K) and the weight fractions of the pure $i = \mathrm{a}$ and b components, giving the values 108, 91 and 79°C for the CF15, CF30 and CF45 samples respectively.

The NF mixtures show on the contrary three transitions (two in the case of the NF45 sample), which clearly indicate a polyphasic network structure. The lowest and the highest transition temperatures are close, respectively, to that of the flexibilizer (−20°C) and of the basic resin (125°C). The intermediate one should correspond to a phase of mixed composition.

The addition of the CF and NF flexibilizers leads to different mechanical behaviours of the corresponding materials, as may be seen from the tensile stress–strain curves reported in *Figure 1*. Namely, the CF flexibilizer increases the elongation at break without a substantial decrease of stiffness (especially in the CF15 and CF30 mixtures) and strength. On the contrary the NF flexibilizer causes a substantial decrease of stiffness and strength, and a remarkable increase of elongation at break. The increasing addition of flexibilizer gives rise in any case to a progressive toughening, which is more appreciable in the case of the NF flexibilizer, as may be seen in *Table 1*.

Stress relaxation measurements have been made with all the materials at different strain values ε_0. The results are reported in *Figures 2* and *3* where the relaxation modulus $E(t)$, calculated as $\sigma(t)/\varepsilon_0$, is plotted *versus* log t. For all the materials the smallest strain value was chosen such as to be probably included in the linear behaviour region.

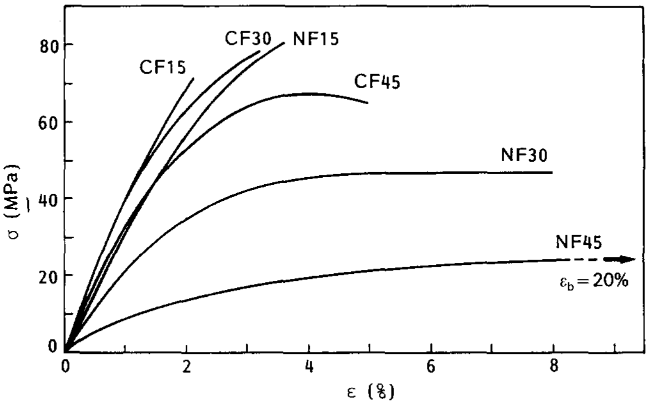

Figure 1 Tensile stress–strain curves, at 23°C, of the flexibilized CF and NF materials of *Table 1*

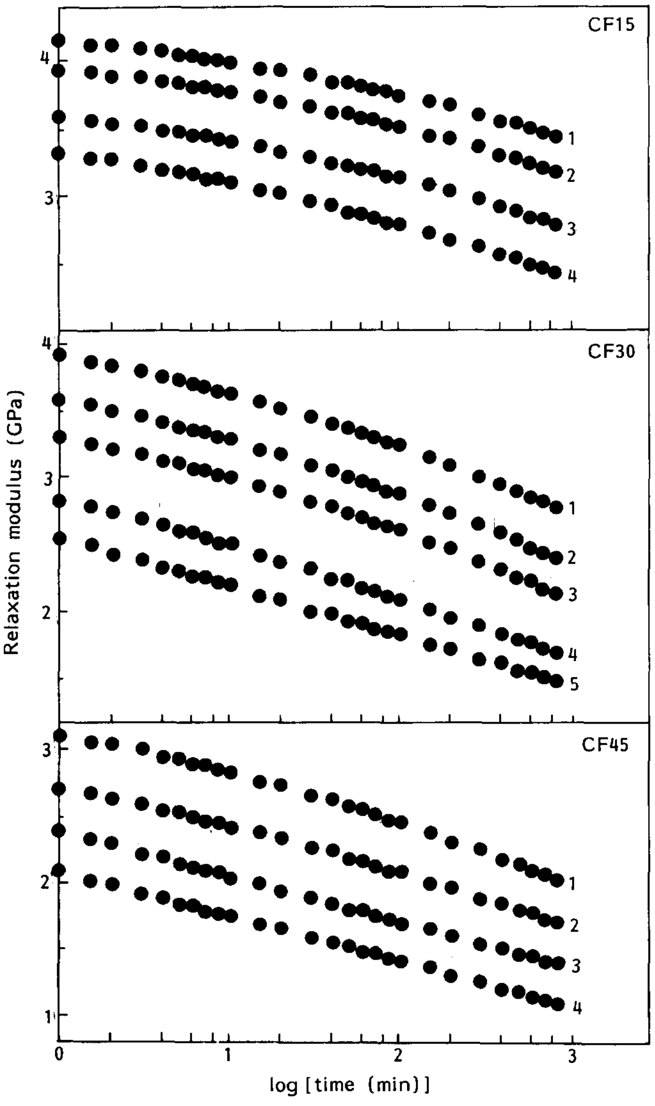

Figure 2 Tensile relaxation modulus vs. log time of the flexibilized CF materials at the following strain values: CF15 (1) 0.35%, (2) 0.80%, (3) 1.28%, (4) 1.77%; CF30 (1) 0.68%, (2) 1.11%, (3) 1.47%, (4) 2.01%, (5) 2.40%; CF45 (1) 0.44%, (2) 1.44%, (3) 1.91%, (4) 2.48%

The non-linear behaviour of every material is clearly revealed by the different shape of the modulus–time curves measured at any given strain value. In the figures this seems to be not immediately evident, especially for the relaxation curves of the stiffer materials (as for the CF mixtures with lower flexibilizer content); it is however to be noted that their shape is strongly influenced by the chosen representation scale (when, for example, a logarithmic modulus scale was used, shape differences would be more easily recognized).

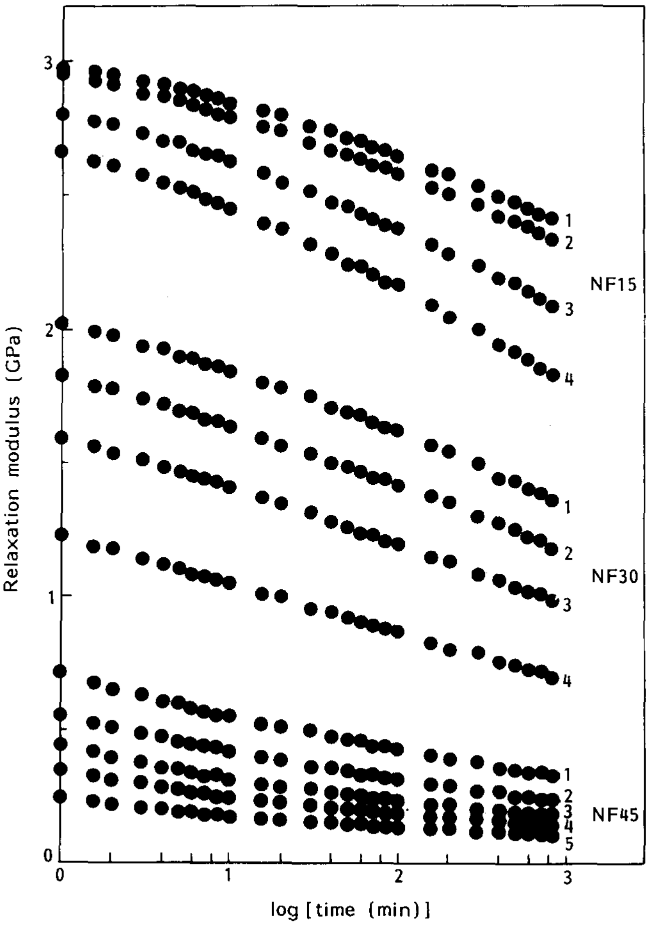

Figure 3 Tensile relaxation modulus vs. log time of the flexibilized NF materials at the following strain values: NF15 (1) 0.47%, (2) 0.92%, (3) 1.49%, (4) 2.03%; NF30 (1) 0.64%, (2) 1.18%, (3) 1.71%, (4) 2.73%; NF45 (1) 0.60%, (2) 1.44%, (3) 2.54%, (4) 3.80%, (5) 6.48%

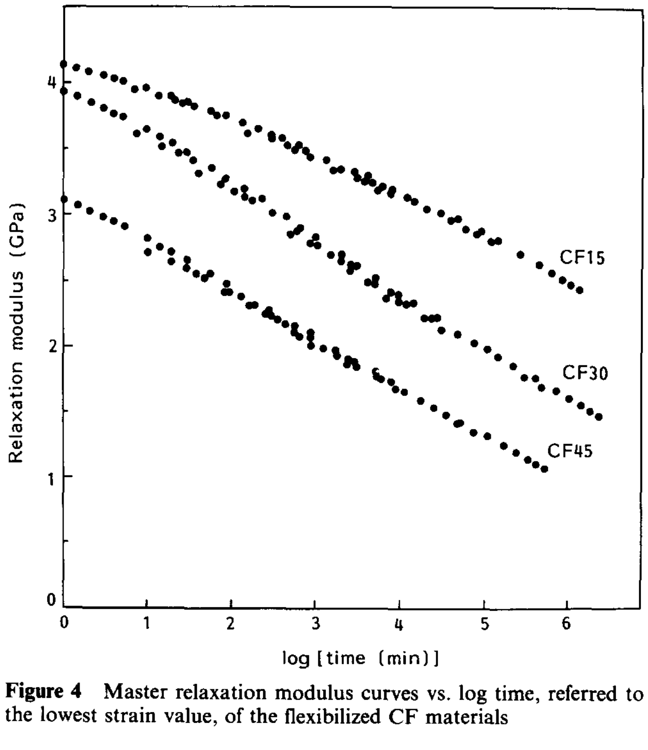

Figure 4 Master relaxation modulus curves vs. log time, referred to the lowest strain value, of the flexibilized CF materials

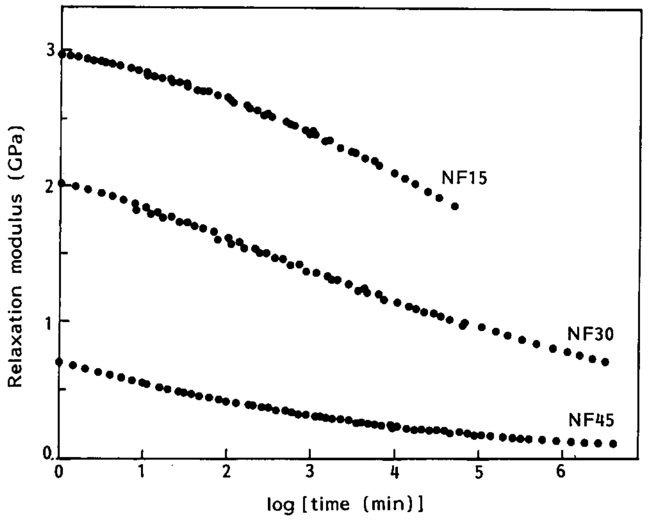

Figure 5 Master relaxation modulus curves vs. log time, referred to the lowest strain value, of the flexibilized NF materials

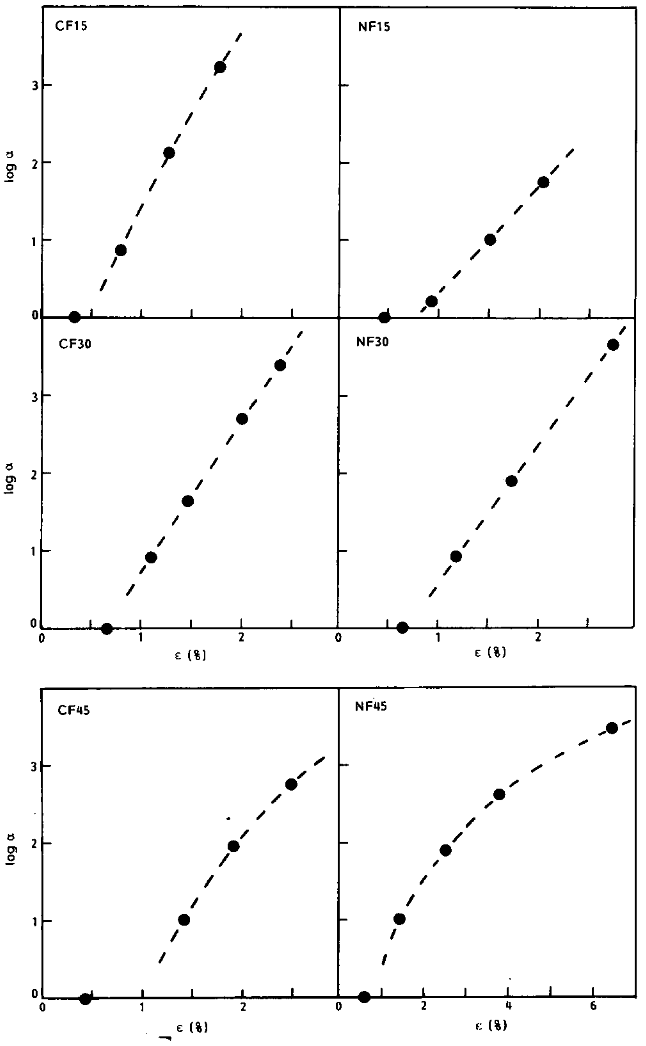

Figure 6 Semilogarithmic plots of the strain dependence of the horizontal shift factors determined by forming master curves of *Figures 4* and *5*

For each material, the curves obtained at different strains can be superimposed onto a single master curve by shifting along the horizontal logarithmic time axis.

The results of a superimposition are shown in *Figures 4* and *5*, where the master curves for every material are referred to the lowest strain value, which is still in the region of linear behaviour. Superimposability appears to be satisfactory, with deviations that never exceed 5%. The resultant master curves cover a time interval that in most cases exceeds 10^6 min, i.e. a range that actually allows the evaluation of mechanical properties of the materials to a fairly long term.

The shift factor values with which the master curves were constructed are reported in *Figure 6* as a function of the strain in a semilogarithmic plot. For stiffer materials, where possible strain values are relatively small, the relation appears to be near to a linear one, whereas it develops in a more convex way for tougher materials, to which greater strains, up to about 6%, can be applied.

The same shift factors are reported in a similar plot in *Figure 7*, this time as a function of the initial stress. It is interesting to note that, in such a representation, the relation appears to be quite linear for all the materials, in whatever range of applicable stresses.

Experimental studies on different polymeric materials considering the relation between shift factors and strain have previously been reported[2,7–10], but only in a few of them is the quantitative nature of that relation discussed.

It may be stated in principle that, when a horizontal superimposability of relaxation curves appears to be feasible in a satisfactory way, the following property can

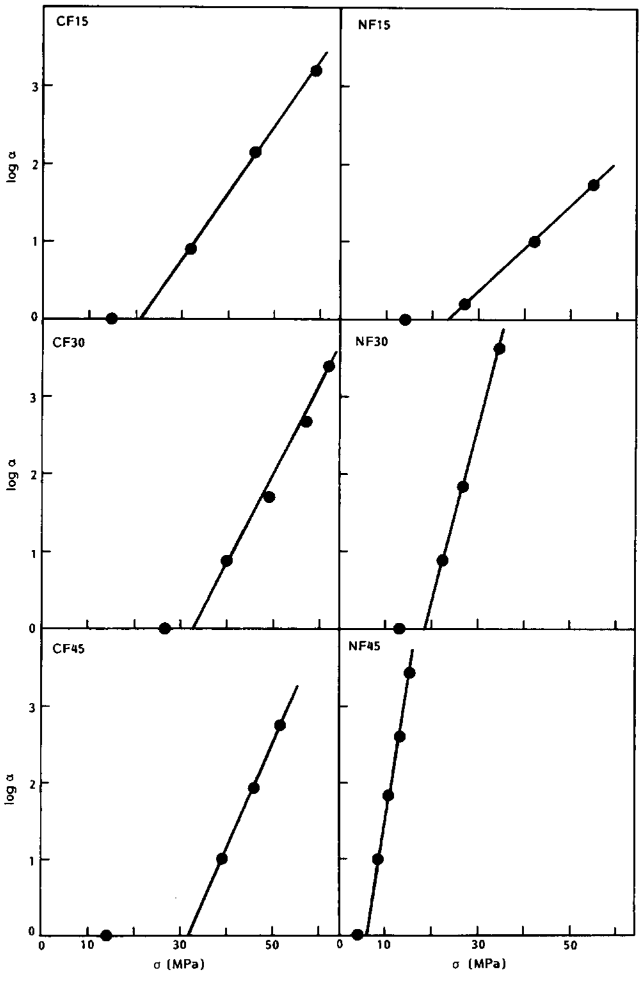

Figure 7 Semilogarithmic plots of the stress dependence of the horizontal shift factors determined by forming master curves of *Figures 4* and *5*

be symbolically expressed (at constant temperature):

$$E(\varepsilon_0, t) = E(\varepsilon_0', \alpha t)$$

E being the relaxation modulus, ε_0 and ε_0' two different strains, and α the shift factor. In classical viscoelastic terms it may also be said that the effect of strain is to shift the whole relaxation time spectrum by a constant amount α, which depends only on the value of the applied strain.

It is often suggested in the literature that the stress-induced decrease of the viscoelastic relaxation times, which is normally observed, should be related to the increase of free volume produced by the dilatation accompanying a uniaxial tensile deformation. Such an effect might then be accounted for by the WLF equation[10]. However, it could be observed that Struik[12] has experimentally observed that a non-linear strain-dependent behaviour similar to that of tensile tests can also be found in shear tests where dilatational effects are absent.

Figure 7, compared with *Figure 6*, seems to indicate a more general and simple relation:

$$\log \alpha = \beta(\sigma - \sigma_{\text{lin}}) \qquad (\sigma > \sigma_{\text{lin}})$$

where β is the slope of the representative straight line, and σ_{lin} is the value of σ as upper bound of the linear behaviour region.

Even if at present we cannot propose theoretical support for this experimental finding, it gives rise to some interesting practical results.

A first consequence is that the intercept on the stress axis of the shift factor straight line, specific to every material, allows the determination of the upper limit of the linear region behaviour of the considered material. Expressed in terms of corresponding strain values, the observed limits fall in the range 0.6–1.0%, which appear to be reasonable in our case.

The slope values β of the straight lines, also specific to every material, should reflect the 'sensitivity' of the material itself with respect to the stress that induces non-linearity. A progressive slope rise is obtained with the increasing addition of the two types of flexibilizers, and it may be seen that each flexibilizer produces a different incremental effect, according to its different effect on the structure of the mixtures.

This type of result, to our knowledge, has not been previously reported. It seems interesting to verify if a generalization is possible by studying other polymeric materials with different structural characteristics. Moreover, further work is also needed to investigate the effect of temperature on the different features of the observed behaviours.

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