

# Heterogeneous blends of recycled poly(ethylene terephthalate) with impact modifiers: phase structure and tensile creep

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**Abstract:** Several types of photomicrographs have concurrently shown that impact modifiers (IMs) form particles (on a micrometre scale) which are evenly dispersed in a recycled poly(ethylene terephthalate) (PET) matrix; their adhesion to the latter is high enough that fracture surfaces (produced in liquid nitrogen) do not follow the interface. An essential part of the tensile creep of PET corresponds to the elastic time-independent component; the time-dependent component is rather limited, even if relatively high stresses are applied. Thus, the tensile compliance of PET is virtually independent of the applied stress, which indicates linear viscoelastic behaviour. The compliance of PET/IM blends (93/7, 90/10, 85/15 (by weight)) grows with the IM content and its time-dependence becomes more visible. The effects of the two types of IM used in this study seem to be practically identical from the viewpoint of dimensional stability of the blends. The logarithm of compliance grows with the logarithm of time faster than linearly, and this tendency becomes more apparent with increasing fraction of IM. Even if the strain-induced free volume is taken into account, a noticeable upswing of the compliance for longer creep periods ( $t > 1000$  min) is evident. This cannot be interpreted as a consequence of the flow, because the recovery following the creep has proved the complete reversibility of the previous deformation. A simple empirical equation is proposed, which provides a plausible prediction of the creep behaviour of PET with dispersed impact modifiers.

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**Keywords:** polymer blends; poly(ethylene terephthalate); impact modifiers; creep; free volume

## INTRODUCTION

As generally recognized, the potential applications of polymeric materials are usually determined by their mechanical properties. End-products made of thermoplastics are frequently exposed to a long-lasting dead load (constant external force), which means that their dimensional stability and resistance to creep become significant characteristics. Thus, a knowledge of creep behaviour over appropriate intervals of time, stress and temperature is of great practical interest.<sup>1,2</sup> Although the creep of many polymers has been described in the literature, relatively little is known about the creep of polymer blends, as documented by recent monographs.<sup>3–6</sup> So far, the creep behaviour of blends has been studied rather sporadically,<sup>7–13</sup> attention has been paid mainly to blends containing a dispersed (discontinuous) minority component.<sup>7–11</sup> However, two-component heterogeneous blends were traditionally treated in analogous ways to individual polymers (simple materials) and no models attempted to predict the creep of blends on the basis of experimental data on the creep of the constituents.

In view of the variability of polymer blends, it is highly desirable to have means for anticipating their physical properties as a function of their composition. In our previous publications on heterogeneous two- or three-component polymer blends, we proposed a versatile predictive scheme for tensile modulus  $E$ ,<sup>14–22</sup> storage  $E'$  and loss  $E''$  moduli,<sup>22</sup> creep compliance  $D(t)$ ,<sup>23</sup> yield strength  $S_y$ ,<sup>14–16,18,21,24</sup> tensile strength  $S_u$ ,<sup>15,17,18,21</sup> and permeability to gases  $P$ .<sup>17,18,25,26</sup> In addition, interfacial adhesion<sup>27</sup> and the effect of partial miscibility of the components on  $E$  and  $S_y$ <sup>20</sup> have been analysed. An essential feature of the proposed predictive format is that all considered properties of a blend are inter-related because they are calculated for a certain phase structure by applying an identical set of input parameters for all predicted properties.

Recently, we have modified our predictive format for the time-dependent compliance  $D(t)$  of heterogeneous binary blends in the regions of linear<sup>23,28</sup> and non-linear<sup>28,29</sup> stress–strain relationships. This format allows for (i) the creep of components and (ii) phase structures encompassing both particulate

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(Received 20 November 2002; accepted 4 June 2003)

Published online 10 May 2004

and co-continuous phase structures. Many polymers, in particular crystalline ones, show non-linear viscoelastic behaviour even at relatively low strain (1 %), which means that the produced strain is no longer linearly proportional to the acting stress (the compliance rises with acting stress). The stress-strain non-linearity observed in tensile creep experiments can be viewed<sup>29</sup> (at least partly) as a consequence of the strain-induced volume dilatation which occurs<sup>1,30,31</sup> in materials whose Poisson ratio is smaller than 0.5. If the correction is made for generated fractional free volume in polypropylene (PP) and its blends with poly(styrene-co-acrylonitrile) (SAN), the creep curves obtained for a series of applied stresses are approximately superposable.<sup>28,29</sup> The objective of this present communication is to study (i) phase structure, (ii) short-term creep and (iii) long-term creep of recycled poly(ethylene terephthalate) (PET) and its blends with two types of impact modifiers (IMs) incorporated in amounts of up to 15 wt%. In particular, we will attempt to evaluate the effects of IMs on the produced creep and to fit the non-linear creep by the proposed format, considering the effects of strain-induced volume dilatation.

## PREDICTIVE FORMAT FOR THE CREEP OF HETEROGENEOUS POLYMER BLENDS

### Empirical functions for the compliance of thermoplastics

The creep deformation,  $\varepsilon(t, \sigma, T)$ , depending on time  $t$ , stress  $\sigma$  and temperature  $T$ , is usually viewed as consisting of three components:<sup>1,2</sup> (i) elastic (reversible, instantaneous) deformation,  $\varepsilon_e(\sigma, T)$ ; (ii) viscoelastic (reversible, time-dependent) deformation,  $\varepsilon_v(t, \sigma, T)$ ; (iii) plastic (irreversible, time-dependent) deformation,  $\varepsilon_p(t, \sigma, T)$ :

$$\varepsilon(t, \sigma, T) = \varepsilon_e(\sigma, T) + \varepsilon_v(t, \sigma, T) + \varepsilon_p(t, \sigma, T) \quad (1)$$

The corresponding tensile compliance,  $D(t, \sigma, T) = \varepsilon(t, \sigma, T)/\sigma$ , reads as follows:

$$D(t, \sigma, T) = D_e(\sigma, T) + D_v(t, \sigma, T) + D_p(t, \sigma, T) \quad (2)$$

Storage of experimental creep data in a graphical form is impractical although it is widely used. If the data can be fitted by an equation, then evaluation of creep rate, interpolation or extrapolation of creep deformation, quantitative description of the effects of external variables, etc. are facilitated. Many attempts have been made<sup>1,2,32-34</sup> to describe creep as the product of independent functions of time, stress or temperature, ie  $D(t, \sigma, T) = C_p g_1(t) g_2(\sigma) g_3(T)$ . The parameters of such empirical equations are customarily determined *a posteriori* by fitting the experimental data. While  $g_3(T)$  is usually identified with the Williams-Landel-Ferry (WLF) or Arrhenius equations, of the numerous empirical functions proposed for  $g_1(t)$  and  $g_2(\sigma)$  we have found<sup>28,29</sup>

the following equation<sup>35</sup> to be suitable for both the short- and long-term tensile creep behaviour of PP and its blends:

$$D(t, \sigma) = W(\sigma)(t/\tau_{rm})^n \quad (3)$$

where  $W(\sigma)$  is a function of the stress,  $\tau_{rm}$  is the mean retardation time and  $0 \leq n \leq 1$  is the creep curve shape parameter reflecting the distribution of retardation times. Under the assumption that  $D_p(t, \sigma) = 0$ , formally similar equations were proposed in a number of papers<sup>28,29</sup> for the viscoelastic component of compliance,  $D_v(t, \sigma) = D(t, \sigma) - D_e(\sigma)$ .

### Compliance of blends with one continuous component and one discontinuous component

To describe the compliance of this type of blends, we can modify the equations derived for the modulus of particulate systems. If the minority polymer '2' of the volume fraction  $v_2$  having a lower compliance  $D_2(t) < D_1(t)$  is dispersed in polymer '1', the compliance  $D(t)$  of the blend can be expressed by the Kerner-Nielsen equation:<sup>1</sup>

$$D(t) = D_1(t)(1 - B\psi_2 v_2)/(1 + ABv_2) \quad (4)$$

The quantities are defined<sup>1</sup> as follows:  $A = (7 - 5v_1)/(8 - 10v_1)$ , where  $v_1$  is the Poisson ratio of the matrix;  $B(t) = [D_1(t)/D_2(t) - 1]/[D_1(t)/D_2(t) + A]$ ;  $\psi_2 = 1 + [(1 - v_{2max})/v_{2max}^2]v_2$ , where  $v_{2max}$  is the maximum packing fraction of the particles of component '2.' If the matrix '1' has a lower compliance than the dispersed component '2', eg as in rubber-toughened plastics, then inverted relations hold, as follows:

$$D(t) = D_1(t)(1 + ABv_2)/(1 - B\psi_2 v_2) \quad (5)$$

where  $A = (8 - 10v_1)/(7 - 5v_1)$  and  $B(t) = [D_2(t)/D_1(t) - 1]/[D_2(t)/D_1(t) + A]$ .

### Tensile creep of viscoelastic materials as a non-iso-free volume process

The phenomenological theory of viscoelasticity has shown<sup>1,30,36-40</sup> that the effects of temperature and pressure on the viscoelastic behaviour of polymers can be plausibly interpreted in terms of the dimensionless fractional free volume, defined as follows:

$$f = (V - V_{oc})/V_{oc} \quad (6)$$

where  $V$  is the specific volume and  $V_{oc}$  is the specific volume occupied by molecules (extrapolated from the melt to 0K without change of phase<sup>40</sup>). The glassy state of polymers is usually viewed<sup>1,2,30,36-40</sup> as an iso-free-volume state with a constant fractional free volume  $f_g = 0.025$ . Expansion of the fractional free volume at  $T > T_g$  is routinely described by the following equation:

$$f = f_g + \alpha_{fv}(T - T_g) = f_g + \Delta f_T \quad (7)$$

where  $\alpha_{fv}$  is the expansion coefficient of the free volume which can be approximated as the difference between the coefficients above and below  $T_g$ , ie  $\alpha_{fv} = \alpha_1 - \alpha_g$ .

The mechanics of solids<sup>1,30,31</sup> shows that a body deformed in tension increases its volume if its Poisson ratio  $\nu < 0.5$ . As long as tensile creep experiments with thermoplastics are performed at mechanically reversible strains (smaller than the yield strain), the increment  $\Delta V_e/V = \Delta f_e = (1 - 2\nu)\varepsilon$  can be identified<sup>29,31</sup> with a contribution  $\Delta f_e$  to the fractional free volume  $f$ . Consequently, Equation (7) can be extended to the following form:

$$f = f_g + \alpha_{fv}(T - T_g) + (1 - 2\nu)\varepsilon = f_g + \Delta f_T + \Delta f_e \quad (8)$$

In terms of the free-volume approach,<sup>36,37</sup> the available  $f$  controls the retardation (or relaxation) times:

$$\ln \tau_r = \ln \Omega + (B/f) \quad (9)$$

where  $\Omega$  corresponds to the frequency of thermal motion inside a potential well and  $B$  ( $\cong 1$ ) is a numerical factor related to the ratio between the volume of a 'jumping' segment and the volume of critical vacancy necessary for a segment jump. The effects of temperature<sup>1,36-40</sup> and/or compression<sup>31</sup> on retardation time,  $\tau_r$ , can be taken into account through a shift (eg of a creep curve) along the time scale:

$$\log a = \log [\tau_r(f_2)/\tau_r(f_1)] \quad (10)$$

where  $f_2 > f_1$  are the fractional free volumes. If the free volume is solely affected by temperature in the interval  $T_g < T < (T_g + 100\text{K})$ , then the time-temperature shift factor  $\log a_T$  mostly obeys the WLF equation,<sup>15,38-40</sup> the constants of which are related to the available fractional free volume ( $f_g + \Delta f_T$ ). Combining Equation (9) for the mean retardation time  $\tau_{rm}$  with Equations (8) and (10), we obtain<sup>28,29</sup> the following equation for the time-strain shift factor  $\log a_\varepsilon(t)$ , defined as the ratio of the retardation times  $\tau_{rm}[\varepsilon(t), T_c]$  at a strain  $\varepsilon(t)$  for time  $t$  and  $\tau_{rm}[\varepsilon_1 = 0, T_c]$  for initial time  $t_1 = 0$  (at a temperature  $T_c$ ):

$$\log a_\varepsilon(t) = -(B/2.303)[(1 - 2\nu)M\varepsilon(t)/(f_g + \Delta f_{T_c})]/[(1 - 2\nu)M\varepsilon(t) + (f_g + \Delta f_{T_c})] \quad (11)$$

where  $M$  is to be calculated<sup>28,29</sup> as the mean ratio of actual (microscopic) strain of the creeping phase and measured (macroscopic) strain of a test specimen.

If the mean retardation time  $\tau_{rm}$  of Equation (3) obeys Equation (10), then:

$$\log D(t, \sigma) = [\log W(\sigma) - n \log \tau_{rmi} - n \log a_\varepsilon(t)] + n \log (t) = \log C(t, \sigma) + n \log (t) \quad (12)$$

which can be rearranged<sup>28,29</sup> into the following form:

$$\log D(t^*, \sigma) = [\log W(\sigma) - n \log \tau_{rmi}] + n[\log t - \log a_\varepsilon(t)] = \log C^*(\sigma) + n^* \log t^* \quad (13)$$

where:

$$\log t^* = \log t + (B/2.303)[(1 - 2\nu)M\varepsilon(t)/(f_g + \Delta f_{T_c})]/[(1 - 2\nu)M\varepsilon(t) + (f_g + \Delta f_{T_c})] \quad (14)$$

can be viewed as the 'internal' time of the creep experiment. The parameter  $n^*$  represents a limiting value of  $n$  corresponding to the creep in a pseudo iso-free-volume state. In other words, the plots of  $\log D(t)$  versus  $\log t$  and  $\log D(t^*)$  versus  $\log t^*$  would hypothetically coincide for  $\Delta f_e = 0$ , ie for extremely low stresses and strains. It should be noted that the value of the time-strain shift factor,  $\log a_\varepsilon(t)$ , is not a constant for a creep curve (as in the time-temperature superposition), but rises with the creep time due to the continuously increasing free volume in the creeping specimen.

## EXPERIMENTAL

### Materials

Poly(ethylene terephthalate) was produced by Eco Selekt Italia Srl (Salerno, Italy) as a recycled product obtained from bottles used for beverages (density ISO 1183(A): 1.328 g ml<sup>-1</sup>; MVR ISO 1133 = 115 ml(10 min<sup>-1</sup>); intrinsic viscosity ISO 1628 - 5 = 0.70 dl g<sup>-1</sup>). To improve its impact properties required in intended applications, blends of PET with polymeric impact modifiers were prepared.<sup>41</sup> Two types of IM were used: (1) Paraloid EXL, which is a commercial core/shell acrylic impact modifier, and (2) Lucalen A3110 MQ 244, which is a commercial ethylene/acrylic acid/acrylate terpolymer. Thus, two series of blends were prepared: (1) blends with 3, 5, 7, 10 and 15 wt% of Paraloid, and (2) blends with 7, 10, 15 wt% of Lucalen.

The polymers were mixed in a single-screw extruder (Model EEGT/35/L-D36/ESI) working at 160 rpm and at about 280°C. The pellets produced were used for feeding a Sandretto injection molding machine, Model 310/95 (average barrel temperature, 270°C; injection pressure, 13.5 MPa; mold temperature, 12°C), to produce ASTM D638 dumb-bell-shaped specimens (length, 210 mm; thickness, 3.3 mm; gauge length, 80 mm; gauge width, 12.8 mm) for measurements of the mechanical properties. The specimens used for creep studies were stored for more than six months at room temperature to avoid any interfering effects of physical ageing during measurements.

### Electron microscopy studies

*Scanning electron microscopy of fractured, scratched and etched surfaces*

- (i) Injection molded dumb-bell-shaped specimens were fractured in the middle of their length

in liquid nitrogen; the fracture surfaces, which were approximately perpendicular to the direction of injection, were sputtered with platinum and observed with a scanning electron microscope (TS 5130 Vega, Tescan).

- (ii) Scratched surfaces were prepared in liquid nitrogen by scratching the surface of specimens (in the middle of their length) with a sharp edge of fractured glass. To visualize the phase structure of scratched surfaces, two techniques were employed, as follows:
- Scratched surfaces were etched with various solvents or their vapours, eg methyl ethyl ketone, acetic acid, chloroform; after etching, the surfaces were sputtered with platinum. The best visualization of the phase structure of PET/Lucalen was achieved after 10 min of etching with acetic acid.
  - After scratching, specimens were stored at room temperature to permit volume relaxation of the components (IM particles with  $T_g$  lower than that of PET become more visible on the surface created at the liquid nitrogen temperature). For PET/Paraloid, 0.5 min of consequent etching with acetic acid was sufficient for the surfaces obtained via volume relaxation; the surfaces were sputtered with platinum and then observed by scanning electron microscopy (SEM).

#### *Scanning transmission electron microscopy analysis of RuO<sub>4</sub>-stained ultra-thin sections*

Stained sections were observed by scanning transmission electron microscopy (STEM) (TS 5130 Vega, Tescan, with a transmission adapter). Dumb-bell-shaped specimens were cut in the middle of their length in the direction perpendicular to the injection flow. Ultra-thin sections were cut with a microtome (Leica Ultracut UCT) cooled with liquid nitrogen. The temperatures of the specimen and the knife were  $-130$  and  $-55^\circ\text{C}$ , respectively. Ultra-thin sections were placed on a copper grid and stained for 1.5 h under vapours of RuO<sub>4</sub>, which were produced through the reaction of RuCl<sub>3</sub>· $x$ H<sub>2</sub>O with NaClO. This staining time was found optimal for both types of PET blends. For the resulting photomicrographs, the PET matrix appears 'dark', while the Lucalen or Paraloid IMs are displayed as 'light' particles.

#### **Tensile creep measurements**

Tensile creep measurements were carried out by using a simple 'dead-weight' apparatus, equipped with a mechanical load amplifier (lever) (11:1). The lengths of the specimens were measured with a mechanical displacement gauge with an accuracy of about 2  $\mu\text{m}$ , ie of about 0.0025 % (initial distance between grips, 80 mm; cross-section, 12.8 mm  $\times$  3.3 mm). Mechanical conditioning before each creep measurement consisted in applying a stress (for 1 min), which produced a strain larger than the expected

final strain attained in the following measurements; the recovery period after the mechanical conditioning was  $>1$  h. All creep tests were implemented at room temperature, ie  $21-23^\circ\text{C}$ .

Short-term tensile creep measurements in the interval 0.1–100 min were performed with one test specimen at four gradually increasing stress levels (between 6.50 and 28.2 MPa) in order to estimate the linearity limit between stress and strain. Each short-term creep measurement was followed by a 22 h recovery period before another creep test (at an increased stress) was initiated. No permanent (plastic) deformation of the tested specimens was observed after recovery.

Long-term tensile creep experiments under a selected stress extended from 0.1 to 10 000 min. In this case, test specimens were used only for one measurement. As the plastic deformation (flow) is proportional to the creep time, the latter should be 100 times larger in the long-term creeps than in the corresponding short-term creeps. A very small permanent deformation of the selected specimens was observed after 20 d of recovery in the creep apparatus. Thus, it can be concluded that no irreversible deformation was produced in these creep experiments.

## **RESULTS AND DISCUSSION**

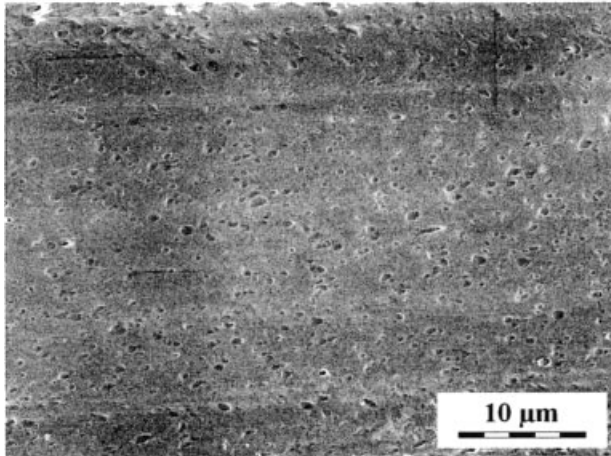
### **Phase structure of PET/impact modifier blends**

The scratched and etched surfaces of the PET/Lucalen blends show (Fig 1a) that the number and size of the Lucalen particles increase in proportion to the Lucalen fraction in the blends. Imprints of etched-off particles can be observed on the surfaces of all prepared blends, consisting of a continuous PET matrix and dispersed Lucalen particles. The appearance of the prepared surfaces of the PET/Paraloid blends is rather different (Fig 1b) because etching produces circular holes on the treated surfaces. Paraloid appears to be dissolved in acetic acid much faster than Lucalen, which makes the reliability of the observed images somewhat uncertain. The SEM images of the fractured surfaces (not shown here) did not permit the resolution of the constituting phases in the studied blends. This result provides evidence that the interface adhesion between the components in both types of blends is so high that fracture surfaces do not follow the interface.

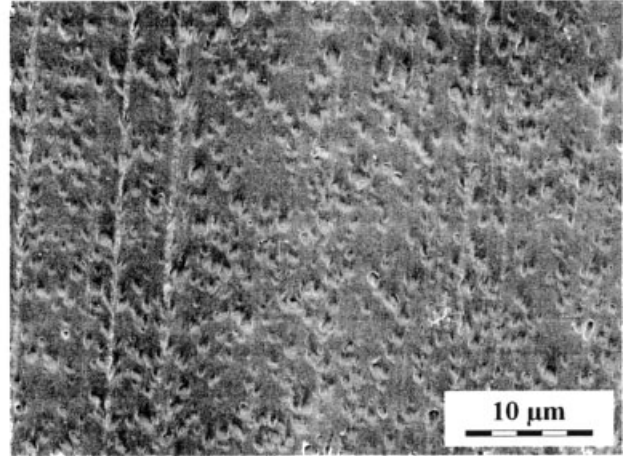
For these reasons, ultra-thin stained sections were prepared and analysed. Figure 2a clearly shows that Lucalen forms particles on the micrometre scale. The particles are oblong due to their orientation in the direction of injection; their size distribution covers approximately one order of magnitude. The structure of the PET/Paraloid blends is more complex (Fig. 2b): relatively large and irregular particles of Paraloid can be seen (small dark particles probably evidence the presence of a very small quantity of impurities). It is difficult to explain why the Paraloid particles maintain irregular shapes, which obviously leads to a relatively high interface area and related Gibbs energy.

(a)

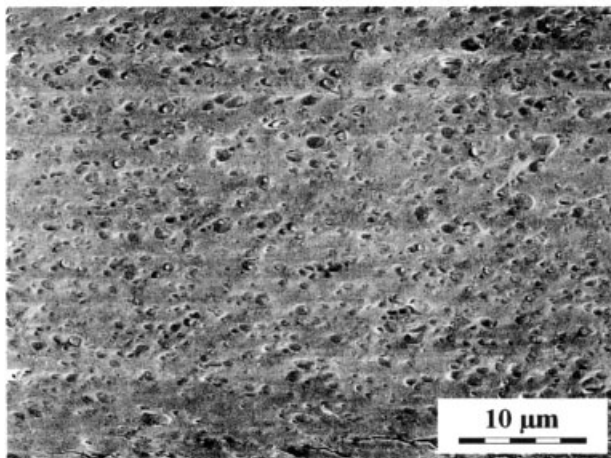
PET + 3 % Lucalen



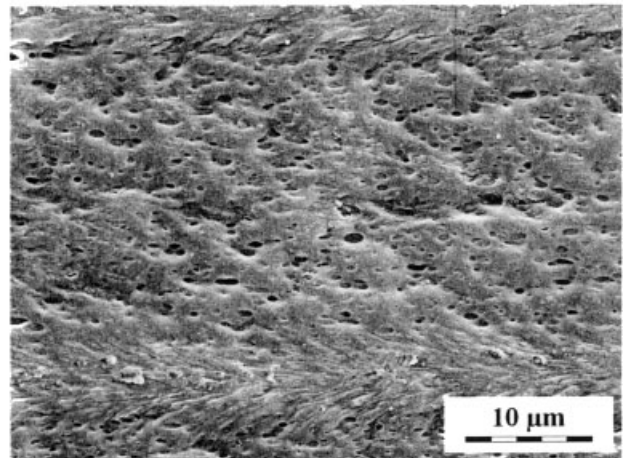
PET + 5 % Lucalen



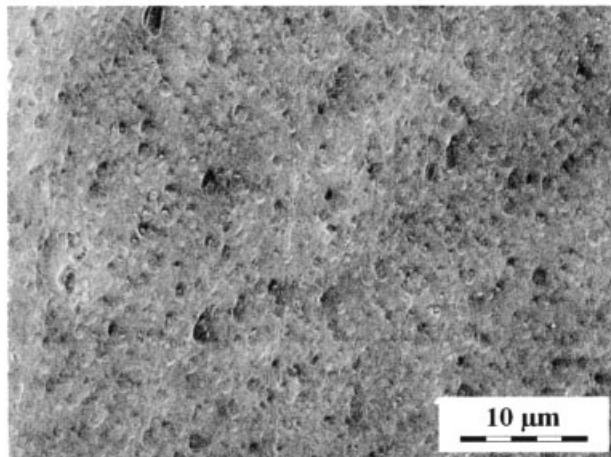
PET + 7 % Lucalen



PET + 10 % Lucalen



PET +15 % Lucalen



**Figure 1.** Scanning electron photomicrographs of scratched surfaces: (a) PET/Lucalen blends, etched in  $\text{CH}_3\text{COOH}$  for 10 min; (b) PET/Paraloid blends, etched as specified.

As a consequence, a higher propensity to physical ageing could be expected for PET/Paraloid blends in comparison with PET/Lucalen blends.

#### Short-term tensile creep of PET/impact modifier blends

The tensile compliance,  $D(t)$ , of PET (Fig. 3a) is virtually independent of applied stress (up

to 28.27 MPa), which indicates linear viscoelastic behaviour in the studied stress region. An essential part of the strain produced by an applied load corresponds to the elastic time-independent component, which occurs immediately after loading. As the viscoelastic compliance,  $D_v(t)$ , is low, representing only a few percent of the (total) compliance  $D(t)$ , its measurement—particularly at low stresses—is rather

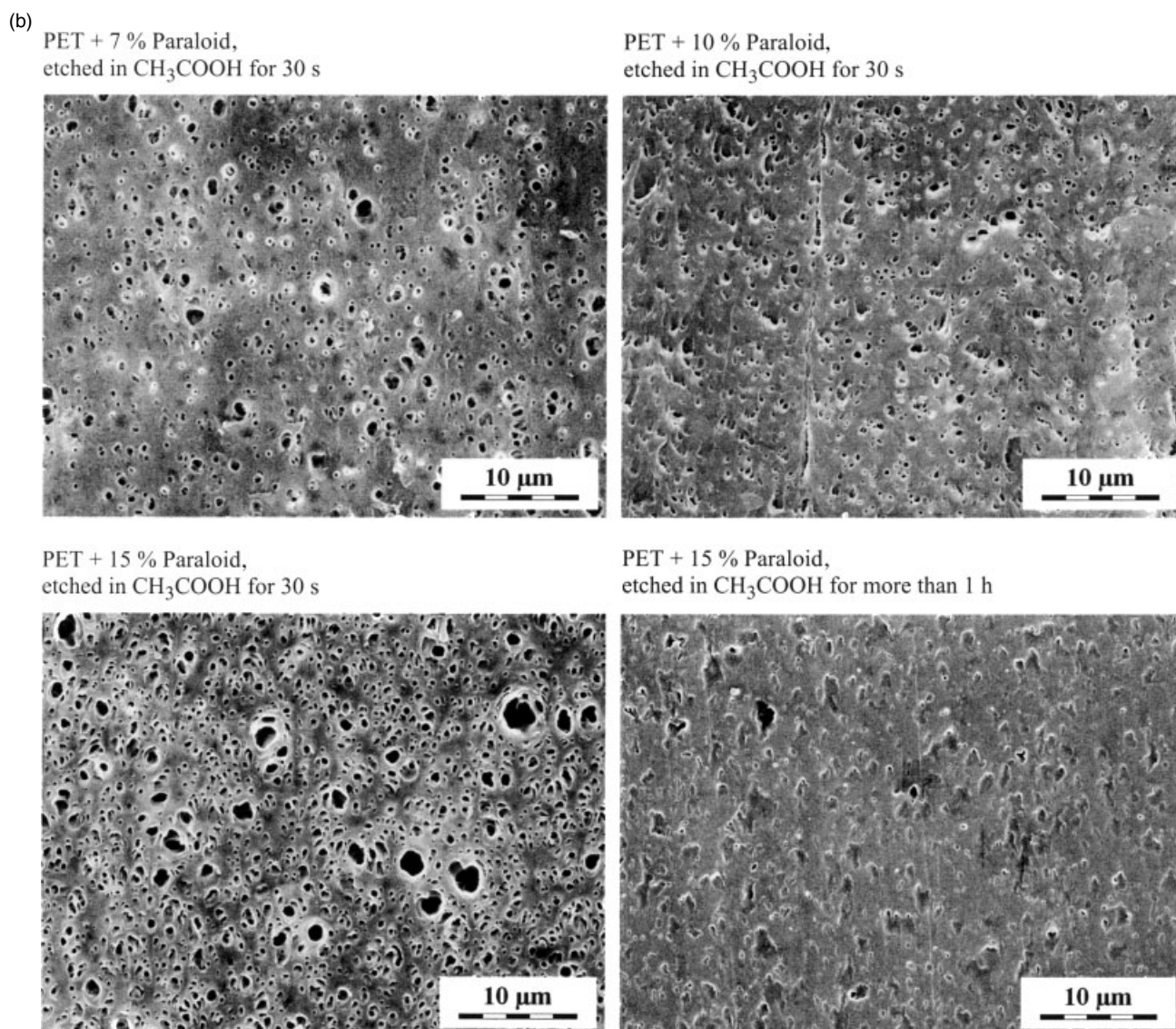


Figure 1. Continued.

inaccurate, which is demonstrated by the irregular effects of stress on the dependence of  $\log D_v(t)$  on  $\log t$  (consequently, it would be difficult to fit  $\log D_v(t)$  versus  $\log t$  by a suitable function). The values of  $n$  or  $n^*$ , read off as the slopes of the  $\log D(t)$  versus  $\log t$  or the  $\log D(t^*)$  versus  $\log t^*$  (not shown) plots, are very low, and independent of the applied stress (Table 1).

The creep behaviour of the impact modifiers was not studied because test specimens could not be prepared. In general, we can presume that ordinary impact modifiers are rubber-like or leather-like materials, having a much higher compliance than the PET matrix. Thus, the contribution of a dispersed IM to the creep resistance of a PET blend will be almost negligible. It is obvious that the viscoelastic properties of the PET/IM blends are mainly associated with the properties of PET. In a simplified manner, an IM can be viewed as a 'diluent', which decreases the creep resistance of the PET matrix.

In order to apply the theory of linear viscoelasticity to the creep of polymeric materials, it is necessary to perform the creep experiments at very low

stresses, so as to produce the (not necessarily linear) dependencies of  $\log D(t)$  on  $\log t$ , which are independent of the applied stress. However, such an approach is impractical, because (i) the linearity limit between stress and strain is usually very low (below 1 % strain) and uncertain, (ii) the relative accuracy of creep measurements is low, and (iii) the effect of stress remains unspecified, which is a serious shortcoming from a practical point of view. Therefore, this communication deals mainly with experiments performed at relatively high stresses, at which the effect of strain-induced dilatation on the creep behaviour may be of increasing importance.

The effect of four selected stress levels on the time-dependence of  $D(t)$  for two series of the PET/IM blends (93/7, 90/10, 85/15 (by weight)) is summarized in Table 1. To avoid an excessive number of figures, the effect of stress on  $D(t)$  and  $D_v(t)$  is visualized, in Figs 3b and 3c, only for blends with 15 % IM. These figures reveal that the studied blends have a somewhat higher compliance than PET because



**Table 1.** Effect of tensile stress on the parameters characterizing the compliance of PET and its blends with impact modifiers

Stress (MPa)	log C	n	R <sup>2</sup>	log C*	n*	R <sup>2</sup>
PET						
7.07	-0.3952	0.0059	0.7318	-0.3973	0.0057	0.7185
14.14	-0.3837	0.0044	0.9452	-0.3871	0.0043	0.9460
21.21	-0.4036	0.0039	0.8607	-0.4079	0.0039	0.8633
28.27	-0.3949	0.0051	0.9592	-0.4022	0.0050	0.9605
PET/Lucalen = 93/7						
7.18	-0.3223	0.0034	0.6780	-0.3239	0.0034	0.6803
14.36	-0.3288	0.0031	0.9189	-0.3415	0.0031	0.9199
21.55	-0.3278	0.0037	0.8351	-0.3327	0.0037	0.8366
28.73	-0.3272	0.0078	0.9526	-0.3399	0.0075	0.9551
PET/Lucalen = 90/10						
6.49	-0.2581	0.0047	0.9291	-0.2603	0.0047	0.9298
12.98	-0.2904	0.0055	0.9416	-0.2961	0.0054	0.9429
19.468	-0.2855	0.0052	0.8915	-0.2922	0.0052	0.8947
25.95	-0.2854	0.0087	0.9152	-0.2997	0.0085	0.9204
PET/Lucalen = 85/15						
7.35	-0.2642	0.0051	0.9519	-0.2669	0.0050	0.9252
14.69	-0.2698	0.0047	0.9516	-0.2746	0.0047	0.9527
22.04	-0.2708	0.0085	0.8781	-0.2832	0.0083	0.8846
29.39	0.2789	0.0168	0.8907	-0.3093	0.0158	0.9047
PET/Paraloid = 93/7						
6.95	-0.3202	0.0047	0.9384	-0.3224	0.0047	0.9390
13.90	-0.3411	0.0038	0.8391	-0.3442	0.0038	0.8414
20.84	-0.3539	0.0043	0.9598	-0.3589	0.0042	0.9607
27.79	-0.3387	0.0070	0.9328	-0.3498	0.0069	0.9360
PET/Paraloid = 90/10						
7.05	-0.3110	0.0044	0.7833	-0.3130	0.0044	0.7853
14.09	-0.3227	0.0064	0.9369	-0.3283	0.0063	0.9385
21.14	-0.3466	0.0072	0.9426	-0.3554	0.0071	0.9445
28.18	-0.3294	0.0126	0.9234	-0.3494	0.0121	0.9300
PET/Paraloid = 85/15						
6.90	-0.2704	0.0104	0.8627	-0.2756	0.0103	0.8659
13.80	-0.2805	0.0067	0.9631	-0.2868	0.0066	0.9642
20.71	-0.2709	0.0105	0.9263	-0.2854	0.0102	0.9310
27.61	-0.2590	0.0180	0.9292	-0.2909	0.0169	0.9388

C, n: parameters of Eq 12 for real time t

C\*, n\*: parameters of Eq 13 (M = 1) for "internal" time t\*

R: correlation coefficient

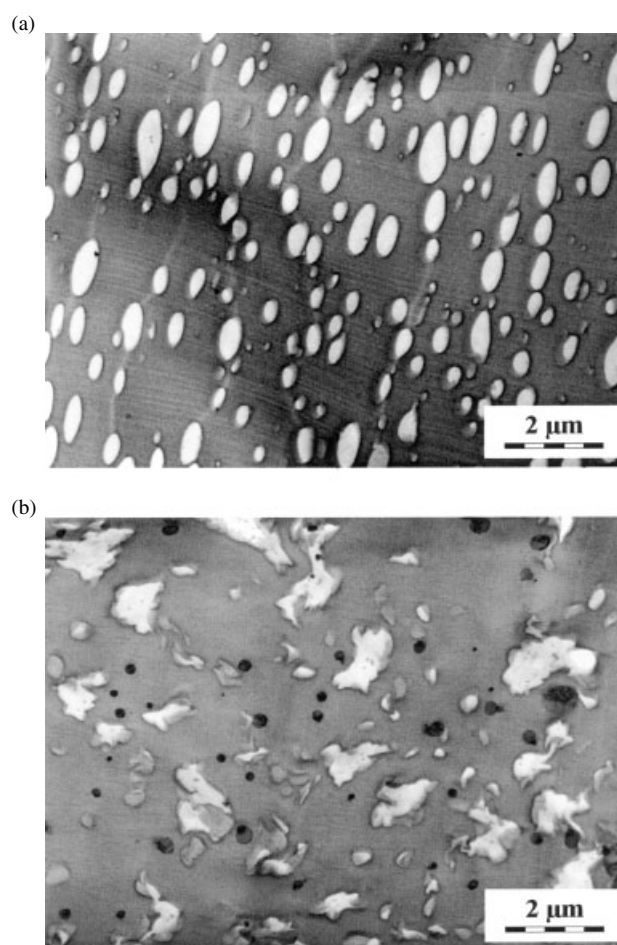
of the 'diluting' effect of the IM; however, increase in the compliance  $D(t)$  with applied stress is very small. Thus, the rise of  $D_v(t)$  with applied stress might be mainly viewed as a subtle indication of the non-linear viscoelastic behaviour of the PET blends over the interval of the applied stresses. Table 1 provides evidence for the very low values of the parameters  $n$  and  $n^*$ , which are comparable with those of PET. The small differences between  $n$  and  $n^*$  indicate the insignificant role of the strain-induced free volume. Nevertheless, we can see a slight increase in both parameters with (i) the applied stress, or (ii) the IM content in the blends.

The effects of the IM fraction on  $D(t)$  and  $D_v(t)$  in the short-term creep experiments are summarized in

Fig 4. Both  $D(t)$  and  $D_v(t)$  rise with the percentage content of IM, and  $D_v(t)$  represents a higher fraction of  $D(t)$  than in the case of PET. The effects of the two types of IMs seem to be practically identical from the viewpoint of creep behaviour (dimensional stability) of the blends. The slope of the  $\log D(t)$  versus  $\log t$  plots rises with increasing stress, which gives evidence for the necessity of long-term creep experiments. In all cases, the creep strain was completely recovered within 22 h.

#### Long-term tensile creep of PET/impact modifier blends

Figures 5 and 6 reveal that  $D_v(t)$  grows with the creep time, especially for  $t > 100$  min, and at  $t = 10\,000$  min may correspond to up to 50 % of  $D(t)$ . The  $\log D(t)$  versus  $\log t$  plots are approximated by straight lines, for which the values of the parameter  $n$  were read off. Table 2 shows that the parameter  $n$  of Equation (12) rises with the percentage of IM in the blends. As can be seen, Paraloid accounts for slightly higher values of  $n$  than Lucalen. Despite the low propensity of the PET blends to creep, we can see that  $\log D(t)$  grows with  $\log t$  faster than linearly and that this tendency, ie  $n = n(t)$ , becomes more apparent with rising fractions of IM. Obviously, Equation (12) does not fit



**Figure 2.** Scanning (transmission) electron photomicrographs of ultra-thin sections, stained in vapours of  $\text{RuO}_4$ : (a) PET/Lucalen = 85/15; (b) PET/Paraloid = 85/15.

all that well with the 'as-received' creep compliance of PET and its blends with impact modifiers.

In previous studies<sup>28,29</sup>, we have shown that Equation (3), re-written in the form of Equation (13), fits well the  $\log D(t^*)$  against  $\log t^*$  plot, ie under conditions that the strain-induced free volume is taken into account. The dependence of  $\log D(t^*)$  on  $\log t^*$  (in Figs 5b or 6b) nevertheless cannot be plausibly approximated by Equation (13) with  $M = 1$  (ie for an even distribution of strain-induced free volume throughout the specimen<sup>28,29</sup>) because they still perceptibly deviate from linearity. A noticeable upswing of  $\log D(t^*)$  with  $\log t^*$  for longer creep periods ( $t > 1000$  min) might be interpreted as a consequence of flow (the third components in Equations (1) and (2)), but recovery following short-term and long-term creeps has proved complete reversibility of the previous deformation. Thus, the non-linear dependence of  $\log D(t)$  on  $\log t$  is to be regarded as an inherent property of PET, which is manifested even after the introduction of corrections encompassing the effect of strain-induced free volume, ie the parameter  $n^*(t)$  grows (Figs 5b and 6b; Table 2) with the elapsed

time in creep experiments in an analogous way to the parameter  $n(t)$ .

To fit the experimental data over intervals of long creep times, Equations (12) and (13) could be tentatively modified in the following way:

$$\log D(t, \sigma) = \log C(\sigma) + (a' + a'' \log t) \log t \quad (15a)$$

$$\log D(t^*, \sigma) = \log C^*(\sigma) + (a^{*'} + a^{*''} \log t^*) \log t^* \quad (15b)$$

where  $a = a' + a'' \log t$  or  $a^* = a^{*'} + a^{*''} \log t^*$ . From Table 2, it is clear that the introduction of  $M = 1$  into Equation (13) does not bring a pronouncedly better fitting of the experimental data—in comparison with Equation (12), which is documented by low values of  $R^2$ . On the other hand, Equation (15a) fits the experimental data much better than Equation (12). Analogously, Equation (15b) provides a much better description of the experimental curves than Equation (13). Thus, it is quite obvious that substitution of  $n$  or  $n^*$  by  $a = a' + a'' \log t$  or  $a^* = a^{*'} + a^{*''} \log t^*$ , respectively, is much more important for a better fitting of the experimental data than introduction of corrections for the strain-induced free volume. However, while  $n$  or  $n^*$  show a clear monotonic growth with the fraction of IM in the blends, the parameters  $a'$  and  $a''$  (or  $a^{*'}$  and  $a^{*''}$ ) are rather scattered so that descriptions of their variations with blend composition are somewhat uncertain. Nevertheless, Table 2 indicates that fitting of the experimental data using Equations (15a) and (15b) is equally good; for this reason, we will now use a simpler procedure, employing Equation (15a), for a tentative prediction of the creep of PET/IM blends.

### Prediction of the tensile compliance as a function of time and stress

The term,  $\log C$ , can be evaluated by means of Equation (5), rewritten for  $t = 1$  in the following form:

$$\log C = \log C_1 + \log[(1 + ABv_2)/(1 - B\psi_2v_2)] \quad (16)$$

If  $v_1$  of the PET matrix is set at 0.4, then  $A = 0.8$ . As the ratio  $D_2(t_i)/D_1(t_i)$  in rubber-toughened plastics is likely to assume values between 10 and 100, then  $B$  is very close to 1. The maximum packing fraction,  $v_{2\max}$ , of the particles of IM in a continuous PET system is difficult to estimate. For simplicity, we can consider  $v_{2\max} = 0.64$ , as found for single-sized spheres. (In real blends, this value cannot be achieved because partial co-continuity of the components usually starts in the interval  $0.15 < v_2 < 0.30$ .) If  $v_{2\max} = 0.64$  is considered for the blends (with  $v_2 < 0.2$ ), the correction function reads  $\psi_2 = 1 + 0.8789v_2$ . For  $\log C_1 = -0.40$ , we obtain  $\log C = -0.317$  and  $-0.27$  for  $v_2 = 0.10$  and  $0.15$ , respectively. (In approximate calculations, we neglect small differences between the volume and weight fractions of IM.)

On the other hand, we have no theoretically justified means for predicting the parameters  $a'$  and

**Table 2.** Effect of tensile stress on the parameters characterizing the long-term compliance of PET and its blends with impact modifiers

Stress MPa	n			n*		
	log C	a', a''	R <sup>2</sup>	log C*	a*', a*''	R <sup>2</sup>
PET						
21.28	-0.4002	0.0082	0.8194	-0.4092	0.0081	0.8266
	-0.3997	0.0050		-0.3962	0.0058	
		0.0026	0.9589		0.0025	0.9640
PET/Lucalen = 93/7						
22.71	-0.3907	0.0204	0.8669	-0.4142	0.0194	0.8816
	-0.3899	0.0023		-0.3859	0.0087	
		0.0056	0.9789		0.0048	0.9836
PET/Lucalen = 90/10						
21.12	-0.3316	0.0150	0.8117	-0.3502	0.0145	0.8277
	-0.3306	0.0021		-0.3206	0.0135	
		0.0052	0.9646		0.0046	0.9736
PET/Lucalen = 85/15						
21.88	-0.2589	0.0270	0.7940	-0.2983	0.0251	0.8313
	-0.2573	0.0064		-0.2307	0.0283	
		0.0101	0.9670		0.0078	0.9841
PET/Paraloid = 93/7						
20.16	-0.3420	0.0191	0.9035	-0.3638	0.0182	0.9135
	-0.3413	0.0041		-0.3405	0.0051	
		0.0046	0.9899		0.0040	0.9920
PET/Paraloid = 90/10						
20.49	-0.3209	0.0286	0.8855	-0.3549	0.0266	0.9045
	-0.3199	0.0032		-0.3146	0.0112	
		0.0076	0.9859		0.0060	0.9913
PET/Paraloid = 85/15						
20.99	-0.2819	0.0398	0.8432	-0.3333	0.0356	0.8827
	-0.2759	0.0065		-0.2525	0.0270	
		0.0126	0.9842		0.0087	0.9942

C, n: parameters of Eq 12 for real time t

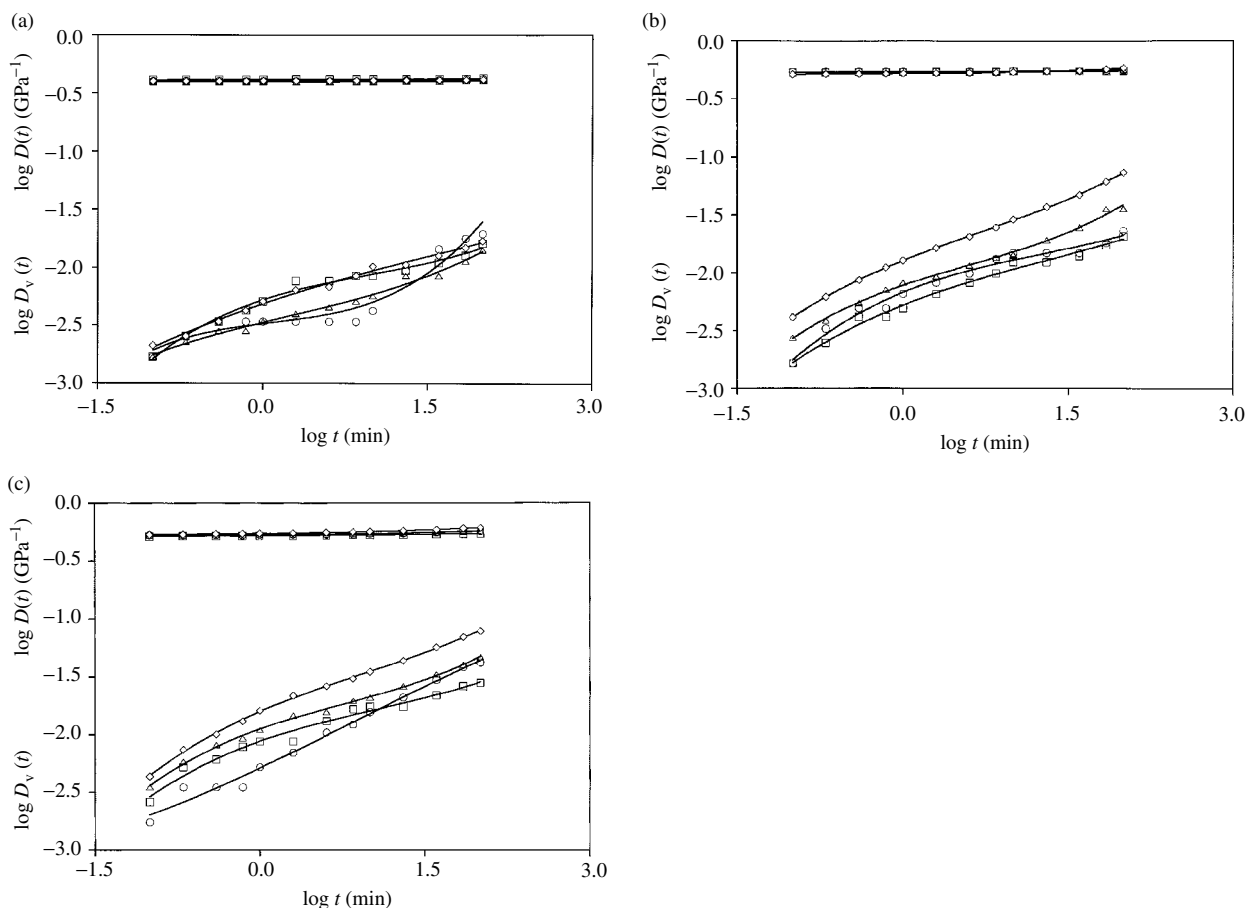
C\*, n\*: parameters of Eq 13 (M = 1) for "internal" time t\*

C, a', a'': parameters of Eq 15a for real time t (data in italic)

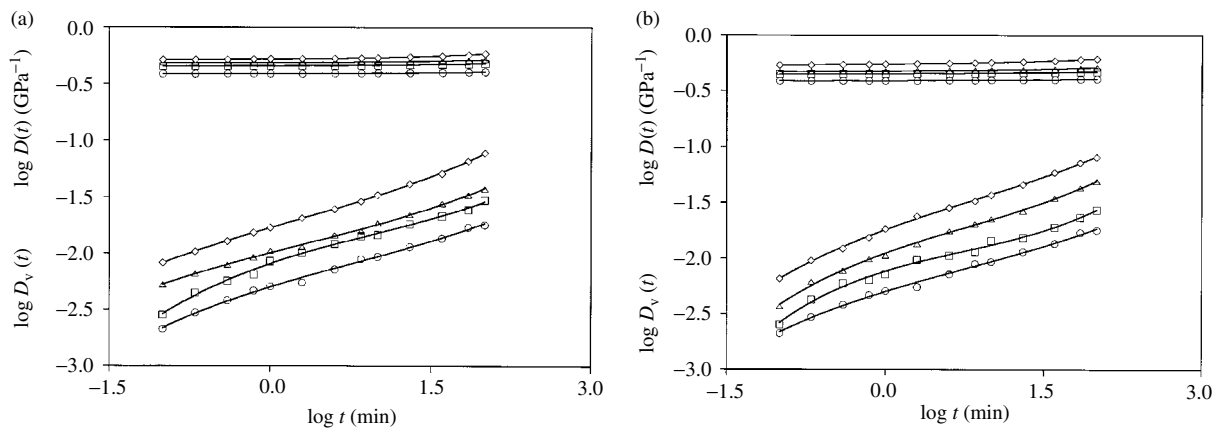
C\*, a\*', a\*'': parameters of Eq 15b (M = 1) for "internal" time t\* (data in italic)

R: correlation coefficient





**Figure 3.** Short-term tensile creep: effect of stress on compliance  $D(t)$  (upper plots) and its viscoelastic component  $D_v(t)$  (lower plots). (a) PET – applied stress (MPa): (○) 7.07; (□) 14.14; (△) 21.21; (◇) 28.27. (b) PET/Lucalen = 85/15 – applied stress (MPa): (○) 7.35; (□) 14.69; (△) 22.04; (◇) 29.39. (c) PET/Paraloid = 85/15 – applied stress (MPa): (○) 6.90; (□) 13.80; (△) 20.71; (◇) 27.61.



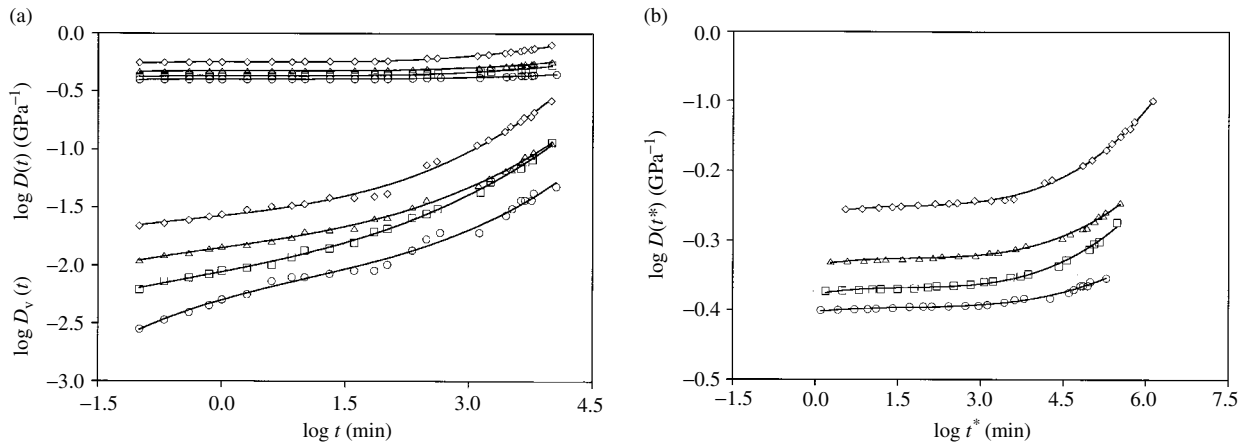
**Figure 4.** Short-term tensile creep of PET/IM blends: effect of IM fraction on compliance  $D(t)$  (upper plots) and its viscoelastic component  $D_v(t)$  (lower plots). (a) Weight fraction of Lucalen and applied stress (MPa): (○) 0 %, 28.47; (□) 7 %, 28.73; (△) 10 %, 25.95; (◇) 15 %, 29.39. (b) Weight fraction of Paraloid and applied stress (MPa): (○) 0 %, 28.47; (□) 7 %, 27.79; (△) 10 %, 28.18; (◇) 15 %, 7.61.

$a''$  of Equation (15a). Therefore, we will resort to an empirical equation for fitting the experimental data. Despite a relatively large scatter of this data, we can roughly estimate  $a'$  as 0.004 and propose a simple equation for  $a''$ , ie  $a'' = 0.0025 + 0.05v_2$ . Utilizing these input data, we have calculated the time-dependent compliances of the two blends, namely PET/Paraloid = 90/10 and PET/Lucalen 85/15. Figure 7 shows that the predicted curves plausibly fit the experimental data, which means that

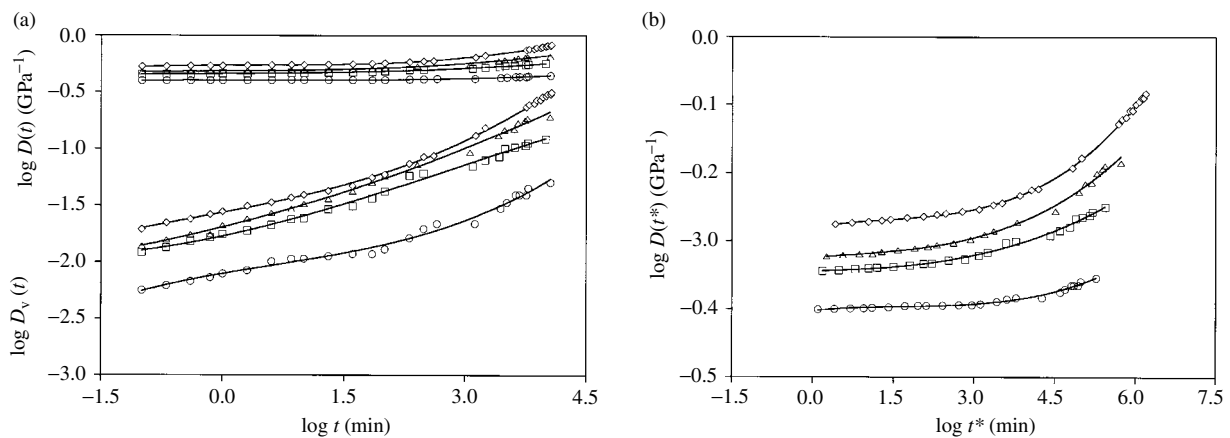
the proposed format can be used for preliminary calculations of the compliance of PET with fully dispersed impact modifiers.

**CONCLUSIONS**

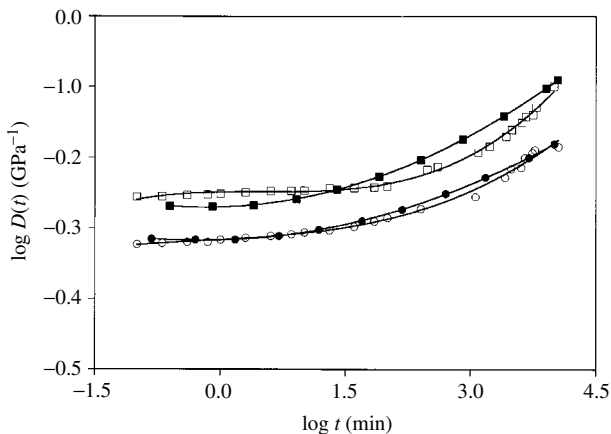
Photomicrographs obtained by various techniques, concurrently provide evidence that impact modifiers form particles, which are evenly distributed in the matrix of recycled PET. Their adhesion to the PET



**Figure 5.** Long-term tensile creep of PET/Lucalen blends: effect of Lucalen fraction on: (a) compliance  $D(t)$  (upper plots) and its viscoelastic component  $D_v(t)$  (lower plots); (b) compliance  $D(t^*)$  for  $M = 1$  on an extended scale (weight fraction of Lucalen and applied stress (MPa): (○) 0 %, 21.21; (□) 7 %, 22.71; (△) 10 %, 21.12; (◇) 15 %, 21.88).



**Figure 6.** Long-term tensile creep of PET/Paraloid blends: effect of Paraloid fraction on: (a) compliance  $D(t)$  (upper plots) and its viscoelastic component  $D_v(t)$  (lower plots); (b) compliance  $D(t^*)$  for  $M = 1$  on an extended scale (weight fraction of Paraloid and applied stress (MPa): (○) 0 %, 21.21; (□) 7 %, 20.16; (△) 10 %, 20.49; (◇) 15 %, 20.99).



**Figure 7.** Comparison of experimental (open symbols) and calculated (filled symbols) compliance dependencies for PET/Paraloid = 90/10 (○ and ●) and PET/Lucalen = 85/15 (□ and ■).

matrix is relatively high, because the fracture surfaces (produced in liquid nitrogen) do not proceed along the interface. The tensile compliance of PET is virtually independent of the applied stress, which indicates linear viscoelastic behaviour. An essential part of the strain of PET and PET/IM blends produced

by an applied load corresponds to the elastic time-independent component, which occurs immediately after loading. The viscoelastic component of the compliance is low, representing only a few percent of the compliance, even if relatively high stresses (up to 28.3 MPa) are applied. PET/IM blends (93/7, 90/10, 85/15 (by weight)) have somewhat higher compliances than PET because of the ‘diluting’ effect of the IM. The produced creep grows with the IM content and its time-dependence becomes more visible. The effects of the two types of IMs seem to be practically identical from the viewpoint of dimensional stability of the blends. The logarithm of the compliance rises with  $\log t$  faster than linearly and this tendency becomes more evident with the rising fraction of IM. The time-dependent component of the compliance grows with creep time, especially for  $t > 100$  min, and at  $t = 10\,000$  min may correspond up to 50 % of the compliance.

Even if corrections for the strain-induced free volume are introduced, the dependence of  $\log D(t^*)$  on  $\log t^*$  still perceptibly deviates from linearity. A noticeable upswing of the compliance for longer creep periods ( $t > 1000$  min) cannot be interpreted

as a consequence of the plastic flow, because the recovery following the creep has proved a complete reversibility of the previous strain. Experimental data are fitted much better if a time-dependent exponent is introduced into Equation (15). Despite a relatively large scatter in the experimental data, a simple empirical relationship has been proposed, which makes possible a plausible prediction of the creep behaviour of PET blends with dispersed impact modifiers.

## ACKNOWLEDGMENTS

This work was carried out under the financial support of the 'Ministero dell'Istruzione dell'Università e della Ricerca' (MIUR—Italy), COFIN 2000, Grant No.1 MM09012922-005.

One of the authors (JK) is greatly indebted to the Grant Agency of the Academy of Sciences of the Czech Republic for financial support of this work (Grant A4050105).

The authors are very much obliged to Dr Miroslav Slouf of the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, for preparation and analysis of the photomicrographs.

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