Ageing and rejuvenation of Biopol^{TM}, [poly (3-hydroxybutyrate-co-3-hydroxyvalerate)] copolymers: A dielectric study

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Semi-crystalline Biopol^{TM} copolymers are biodegradable materials which are being intensively probed as suitable systems for embossed substrates in tissue regeneration applications. However, it has been shown that an embrittlement process occurs on storage at room temperature which places restrictions as to their application possibilities. In order to study this process we have made use of Biopol^{TM} systems which have aged for 3 years since extrusion as thin films, and subsequently rejuvenated at elevated temperatures. Utilising varying techniques we have attempted to shed light on the mechanisms responsible for the rejuvenation, with particular emphasis on the observed dielectric properties. We highlight the possibility of on-going secondary crystallisation on ageing and attempt to rationalise the rejuvenation in terms of release of amorphous material from the rigid amorphous phase of semi-crystalline systems. © *2004 Kluwer Academic Publishers*

1. Introduction

There have been many publications [1–3] highlighting the potential use of biodegradable polymers as suitable materials in medical applications. One such class of polymers, the polyhydroxyalkanoates marketed under the Biopol^{TM}. trademark, has been intensively studied due to their inherent flexibility and ductility [4]. However, it has been shown that on ageing these materials exhibit severe embrittlement. In a previous paper [5] we highlighted the differences between compression moulded and extruded films of two copolymers of Biopol^{TM}. We observed that various characterisation techniques highlight either the amorphous or crystalline regions specifically. However, dielectric techniques were able to probe the amorphous/crystalline interphase, thus emphasising the effect of the processing conditions on the resultant polymer microstructure and morphology.

Prior to examining the data from this study which deals with rejuvenation of properties in Biopol^{TM} systems, it is relevant at this point to overview the hypothesised mechanisms of embrittlement. Initially we have to consider the morphology of a semi-crystalline polymer. Struik [6] has proposed a model which incorporates three domains; a crystalline phase, an undisturbed amorphous phase, and an amorphous region of reduced mobility caused by 'interactions' close to the crystal boundaries; i.e., a rigid amorphous phase [7].

The main mechanism for embrittlement in amorphous polymers has been attributed to physical age-

ing [8, 9] and, in semi-crystalline systems such as Biopol^{TM}, such processes are suggested [10]. In amorphous polymers cooled below their T_g there is considerable free volume available for subsequent rearrangement of polymer chains at temperatures well below the glass transition temperature. These rearrangements result in a continued reduction of the free volume towards the equilibrium value, with the result in a change in mechanical properties such as a decrease in impact strength and elongation to break, and an increase in modulus [11]. However, these effects can be reversed by heating the sample above its T_g [12].

For semi-crystalline polymers the situation is made more complicated due to the presence of the constrained amorphous phase. This is the case with Biopol^{TM} copolymers. The T_g of the bulk amorphous phase of the Biopol^{TM} copolymers is just below room temperature and, thus, by the simple model, should not undergo physical ageing. Biddlestone *et al.* [13] have argued that the T_g of the bulk amorphous phase is too low for the phenomenon to account for ageing at room temperature. This would be true for the two-phase model of the morphology, but as has already been stated we have to consider the presence of a rigid amorphous phase whose effective T_g may well be above room temperature and, hence, be subject to a physical ageing process [6]. Further, both Biddlestone [13] and de Koning [14] have alluded to another phenomenon which may be ongoing; viz. interlamellar secondary crystallisation. They conjecture that these secondary crystallites underpin

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parts of the amorphous region and reduce the mobility of the chain segments thus raising the modulus and embrittling the material.

The theories put forward to explain embrittlement, however, are dependent on which technique is used to study aged materials. Studies by X-ray diffraction [15] of poly(hydroxybutyrate) (PHB) homopolymer have highlighted the crystalline phase and failed to give observable changes compatible with the changes in mechanical properties. Hurrell *et al.* [16] presented work on thermal expansion data on the microstructural scale and considered that their findings were consistent with the reversal of physical ageing as an aged sample is reheated. De Koning *et al.* [17] agree with the aforementioned findings and whilst concurring that physical ageing does occur, indicate that it cannot account for all the changes seen in the mechanical properties of PHB on ageing.

It would seem, therefore, that the embrittlement, and subsequent rejuvenation, processes contain elements due to both physical ageing and some other phenomena, which involves the presence of the rigid amorphous phase, and possibly the development of secondary crystallisation processes.

In this communication we have made use of samples, previously described elsewhere, which have been ageing for over three years. Subsequent rejuvenation of the samples at an elevated temperature have been undertaken and examined most specifically by dielectric techniques. The resultant data highlights the considerable changes in the dielectric properties upon rejuvenation.

2. Experimental
The preparation of extruded films of Biopol polyester copolymers containing 8% (D400G) and 12% (D600G) of hydroxyvalerate component has been adequately described in a previous publication [5]. The samples have been ageing for three years prior to the present study. The deageing/rejuvenation process was undertaken by placing the extruded films in an oven at 140°C for 1 h. The samples were analysed within 1 h of the rejuvenation procedure. Other rejuvenation profiles have been utilised and will be defined in the text.

The tensile properties of extruded, aged and rejuvenated, films were evaluated with a Lloyd's LRX Tensile Tester at a crosshead speed of 100 mm/min. Films 100 mm long, 10 mm wide and ca. 0.4 mm thick were prepared and the resultant stress/strain curves obtained.

Differential Scanning Calorimetry (DSC) was used to assess the melting points and crystallinity. Analyses were carried out using a Mettler-Toledo FP84Ht DSC hot stage with a FP90 processor. All runs were performed at a ramp rate of 10°C/min under nitrogen. The stage was calibrated with indium (T_m, 156.64°C; ΔH_m, 28.4 Jg^{-1}) and benzophenone (T_m, 48.1°C). An average sample size was between 5 and 10 mg.

A Polymer Laboratories Dynamic Mechanical Thermal Analyser MKIII operating at a frequency of 1 Hz, a strain of ×8 and a scanning rate of 3°C per minute was used to analyse samples of film approximately 0.4 mm

thick. Measurements were performed from −50° to 100°C and the resultant changes in E′, E″ and tan delta recorded.

X-ray diffraction (XRD) measurements were performed using a Siemens X-ray diffractometer with a Cu K_α ($\lambda = 0.154$ nm) radiation source, and a curved graphite crystal monochromator was used to analyse the samples. XRD experiments were performed directly on the films and the data analysed using the Xfit software package [18].

The a.c. dielectric properties were obtained using the apparatus described elsewhere [19]. Electrodes (aluminium) were evaporated onto the samples using an Edwards High Vacuum coating facility.

3. Results and discussion
3.1. Mechanical properties
The tensile properties of the aged and rejuvenated sample of D400G were evaluated at room temperature (Fig. 1). For the aged sample a maximum stress of 33.9 MPa and 3.2% extension with no yield point was observed. On rejuvenation the sample yielded to an ultimate extension of 19%, with a maximum stress of 18.5 MPa. This data is consistent with other studies and exemplifies the rejuvenation process occurring in the Biopol^{TM} copolymers.

To further exemplify the changes upon thermal treatment of the aged sample we conducted a study whereby rejuvenation was again carried out using smaller temperature intervals. To this end we rejuvenated a series of samples at 40, 50, 60, 70, 80, 100 and 120°C respectively for a period of one hour. Fig. 2 shows the stress-strain plots for a series of temperatures. It is clear that the rejuvenation process is starting to show above 60°C where the plots are showing classical rejuvenation behaviour; i.e., decrease in maximum stress, decrease in modulus, an increase in elongation to break and yielding behaviour.

These observations are particularly interesting in respect of the mechanisms conjectured for the embrittlement process. Secondary crystallization [13] has been mooted as such a mechanism, and the melting of such entities in the temperature range of the stress-strain
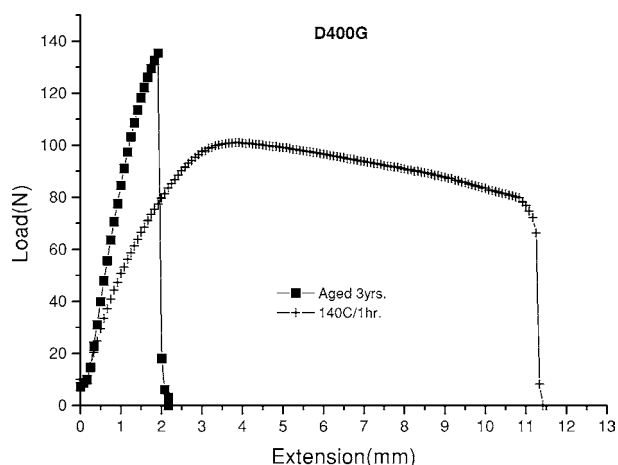

Figure 1 Stress-strain curves for aged and rejuvenated D400G at room temperature.
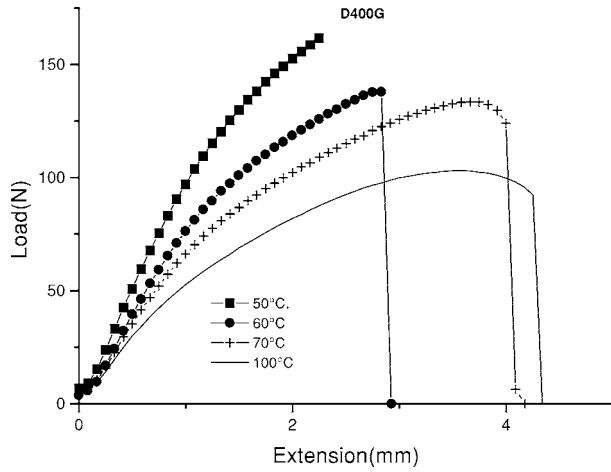
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Figure 2 Stress-strain curves for aged D400G as a function of rejuvenation temperature.

measurements we have conducted could give rise to significant changes in the ultimate mechanical properties as a consequence of changes in the relative amorphous/crystalline compositions.

3.2. Dynamic mechanical properties (DMTA)

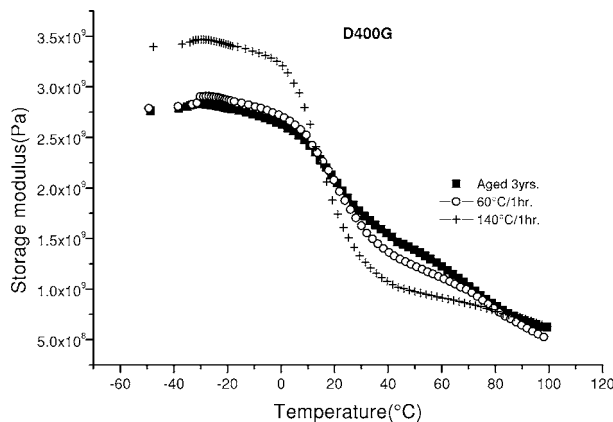Figs 3 and 4 highlight the dynamic mechanical properties of an aged and rejuvenated copolymer (viz.

Figure 3 Storage modulus as a function of temperature for aged and rejuvenated D400G (60°C and 140°C).
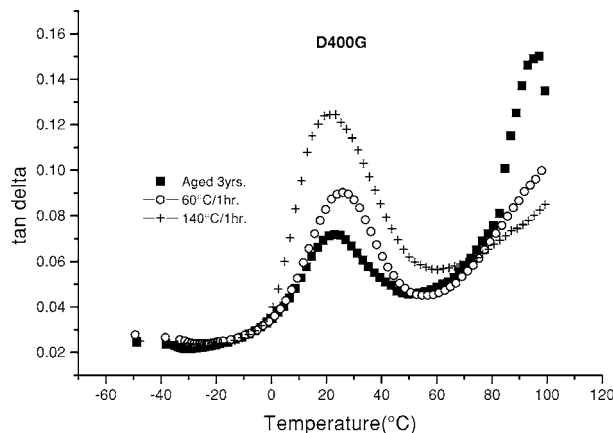

Figure 4 Loss modulus as a function of temperature for aged and rejuvenated D400G (60°C and 140°C).

D400G). In addition, a rejuvenation was carried out at 60°C for 1 h. The storage modulus data shows significant differences from below T_g of the copolymer up to the premelt region.

This data is consistent with an increased rubbery nature brought about by changes in the effective amorphous/crystalline composition. In a previous paper [5] we have inferred that changes in the processing conditions can affect the amount of amorphous/crystalline interface. Also, in two-phased systems such as polycarbonate/ABS blends, it is known [20, 21] that the degree of intermixing at the phase boundaries plays the major role in defining the ultimate mechanical properties. This is further exemplified by observing the change in tan delta on rejuvenation. The magnitude of the tan delta peak from DMTA [10] has been correlated with an increase in the elongation upon heat treatment. Even at temperatures as low as 60°C the increase in tan delta is evident and, as in the case of the aforementioned stress-strain analysis, is evidence that some significant release of mobile amorphous phase, possibly from the rigid amorphous phase, may have occurred.

Further, to gain a quantitative appreciation of the amount of amorphous phase present we can make use of the modulus temperature curves [22]. Let us assume that in the case of the Biopol^{TM} systems we have a morphology that essentially consists of a rigid continuous phase (the crystalline region) and a dispersed, occluded phase (the amorphous region). [This assumption is obviously crude since we have already stated that in semicrystalline materials a rigid amorphous region is also present.]

Nevertheless, making use of the modified Kerner [23] composite modulus equation we can calculate the mechanically effective volume fraction of the occluded material (Equation 1).

$$\phi_{\text{eff}} = \frac{(E_m - E_c)}{(E_m + \alpha_m E_c)} \tag{1}$$

where, E_m and E_c are the elastic moduli of the matrix and composite phases, α_m is a function of the Poisson's ratio and φ_{eff} is the effective volume fraction of the occluded phase. For the data presented in Fig. 3 the effective volume fractions calculated for the aged, 60° and 140°C rejuvenated samples were 0.21, 0.26 and 0.42 respectively. These data will be discussed later in conjunction with the dielectric properties.

3.3. Differential scanning calorimetry (DSC)

The DSC data for the aged and rejuvenated samples are listed in Table I. As has previously been observed [25], the polyhydroxyalkanoates can exhibit bimodal melting endotherms, which are attributed to such as: heterogeneous distribution of crystal compositions, distinct pre-existing crystalline morphologies and the melting of thin, unstable crystals. The most significant observations are twofold. Although there is a relatively small change in the calculated level of crystallinity, the number and positions (i.e., melting points) of the endotherms indicate that there are subtle changes of the texture and morphology of the crystalline phase.

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TABLE I DSC data for aged and rejuvenated samples

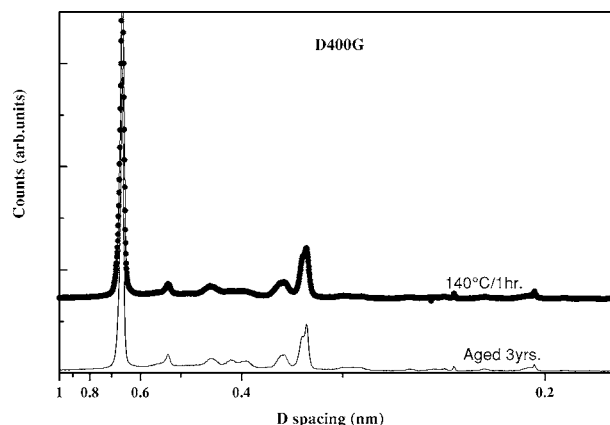| Sample	History	Remarks	Peak endotherm (°C)	ΔH (Jg^{-1})	Crystallinity (%)
D400G	Aged 3 yrs	Bimodal	154/161	69.5	58.6
D400G	Then, 140°C/1h	Single melt	155	66.8	56.3
D600G	Aged 3 yrs	Bimodal	138/151	63.5	56
D600G	Then, 140°C/1h	Single peak + shoulder	150	65	57.8

Figure 5 XRD spectra for aged and rejuvenated D400G.

3.4. Wide angle X-ray diffraction

The differences in the XRD for the 3-year aged and rejuvenated samples are negligible (Fig. 5). Indeed analysis of the crystalline content using the XFit program (obtained from CCLRC Daresbury Laboratory) gave a value of crystallinity of 70% for both systems. This again suggests that the overall level of crystallinity is unaffected by the rejuvenation process.

3.5. Dielectric spectroscopy

An example of the dielectric spectra for the aged and rejuvenated sample of D400G is highlighted in Figs 6 and 7. The dielectric loss spectrum (Fig. 6) at 30°C illustrates the change in the intensity and position of the relaxation on rejuvenation. Further, the Cole-Cole plot (Fig. 7) emphasises the effect of the heat treatment. The data extracted from the dielectric plots are summarised in Table II.
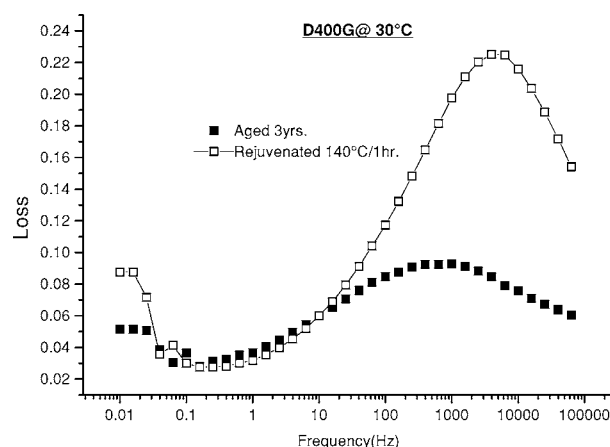

Figure 6 Dielectric loss as a function of frequency for aged and rejuvenated D400G.
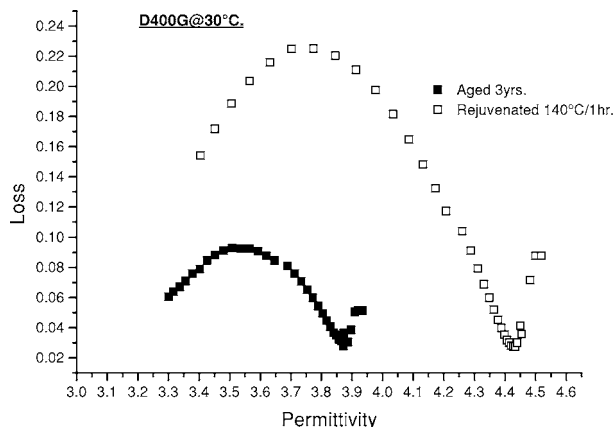

Figure 7 Cole-Cole plots of aged and rejuvenated D400G.

An initial examination of the dielectric properties of the aged and rejuvenated samples is of interest. Table II highlights that the position of the peaks on the frequency scale (a relative measure of the T_g of the amorphous phase) is significantly altered by the rejuvenation process. The rejuvenated amorphous phase transition moves to higher frequencies (at a constant 30°C) indicative of a lowering of the T_g. Concomitant with this observation is the change in the other Havriliak-Negami [24] parameters. The distribution of relaxation times as represented by the α (breadth of the relaxation) and β (high frequency skewness) parameters are indicative of a process which is becoming more amorphous in nature. As was mooted in the DMTA analysis, it may be that on rejuvenation the effect of changes between the true amorphous and the amorphous/crystalline interphase are being highlighted.

Unlike the dynamic mechanical analogue, the dielectric increment ($\varepsilon_0 - \varepsilon_\infty$) is a direct measure of the number of entities (in this case dipoles) taking part in the relaxation process. In the case of the rejuvenation of the copolymers it is clear that there is a significant increase in the amorphous content. This is further exemplified by observing the calculated amorphous content for the D400G sample (Table II). In order to obtain this value

TABLE II Dielectric data for aged and rejuvenated samples

Sample	History	F (Max)	ε''_{max}	$\varepsilon_0 - \varepsilon_\alpha$	α	β	Amorphous content (%)[a]
D400G	Aged 3 yrs	761	0.093	0.81	0.333	0.64	23
D400G	140°C/1 h	5,083	0.225	1.33	0.427	0.90	38
D600G	Aged 3 yrs	2139	0.116	0.90	0.366	0.67	N/A
D600G	140°C/1 h	10,500	0.252	1.34	0.476	0.86	N/A

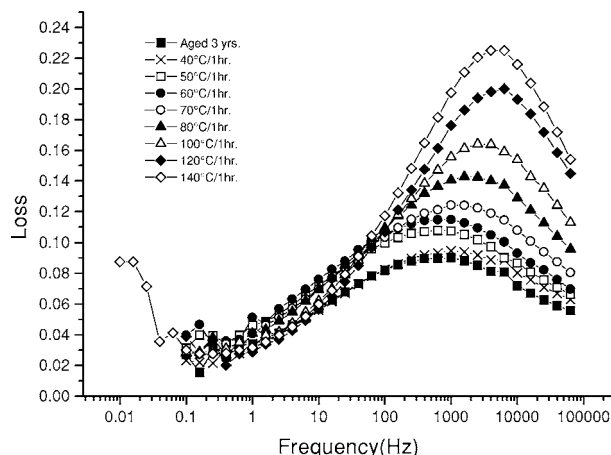[a]Based on a value of $\varepsilon_0 - \varepsilon_\alpha = 3.55$ for a pure amorphous D400G.

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Figure 8 Effect of rejuvenation temperature on the dielectric loss as a function of frequency for D400G.

we ran a sample of a quenched D400G to obtain a totally amorphous system. We can see immediately that the values obtained (viz. 23% for the aged and 38% for the 140°C rejuvenated sample) compare very well with the effective volume fractions obtained from the modulus/temperature curves.

As with previous techniques (stress-strain measurement and DMTA), we can speculate that this additional amorphous material has been released from the rigid amorphous phase. As with the stress-strain experiments we carried out a similar procedure dielectrically whereby an aged sample of D400G was annealed from 40°C for one hour to the rejuvenation at 140°C for one hour. This data is highlighted in Fig. 8. We clearly see that there is a progressive increase in the loss maximum (and subsequently, the dielectric increment) on ageing.

This consistency between the effects seen from the stress-strain and dielectric measurements is highlighted in Fig. 9. It is clear that the increase in elongation is consistent with consequence 'introducing' more rubbery material into the matrix as seen from the increase in the dielectric increment.

3.6. Mechanism for rejuvenation

The data explored thus far has highlighted that the aged sample undergoes major changes on application of a
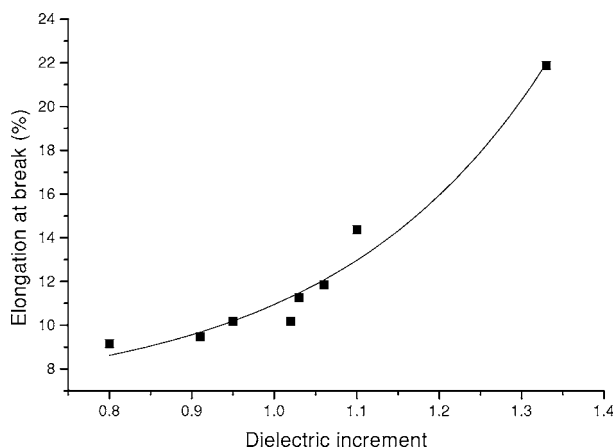

Figure 9 Relationship between elongation at break and the dielectric increment for D400G.

thermal treatment. There is no doubt that the lack of a significant change in the overall crystalline properties as measured by DSC and WAXS indicates that the underlying cause of the rejuvenation is as a result of considerable changes to the overall amorphous phase content. We propose that upon rejuvenation the polymer regains mobile amorphous material from the rigid amorphous phase. This leads to the conclusion that the crystal element (i.e., that part of the rigid amorphous phase which may be being constrained by crystalline elements), which is indeed underpinning and restricting the amorphous entity, has undergone considerable change; e.g., melting. From the stress-strain and dielectric studies we have shown that these changes start to occur at relatively low temperatures and continue up to the primary crystallisation region.

To examine this hypothesis we carried out a dielectric study whereby we subjected the aged D400G to a series of temperature scans as a function of time. Initially the sample was ramped to 70°C for 10 min then cooled to 30°C, equilibrated, then the dielectric spectrum obtained. The same schedule was repeated 6 times. The same was done at temperatures of 100° and 140°C respectively, and the data highlighted in Figs 10 and 11, showing both the permittivity and loss data. It is evident that at each temperature there is no change in the spectra as a function of time of rejuvenation. Further
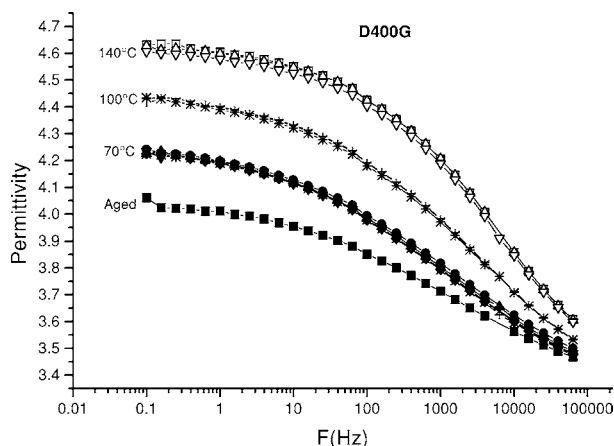

Figure 10 Permittivity as a function of frequency for varying rejuvenation schedules (6 consecutive runs at each rejuvenation temperature).
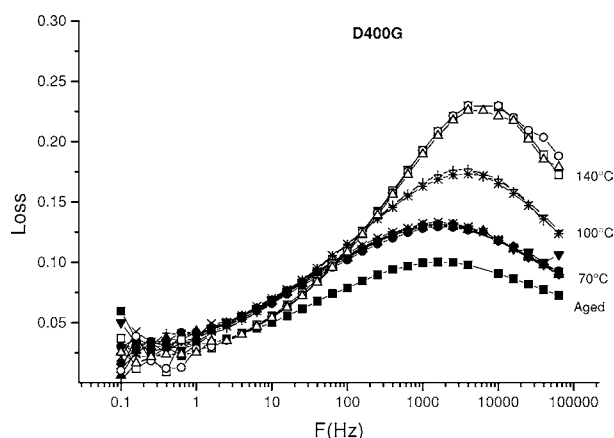

Figure 11 Loss as a function of frequency for varying rejuvenation schedules (6 consecutive runs at each rejuvenation temperature).

in a purely physical ageing process [13] we would expect a time-temperature superposition relationship to be observed whereby successive temperature ramps at each temperature to change the observed properties as a function of time. It is clear from the data that some instantaneous phenomenon has occurred upon rejuvenation at each temperature to increase the dielectric loss (and increment) and enhance the amorphous phase. The simplest explanation could be due to the melting of secondary crystals, which consequently release the constricted amorphous regions. The increase in dielectric properties as a function of temperature would, then, be a consequence of the increase in the amount of secondary crystals melting with a concomitant increase of amorphous material becoming available from the rigid amorphous phase.

In order to follow up the observations made from the dielectric technique further DSC experiments were initiated. The initial DSC experiments have shown that there is little difference in the melting points and enthalpies of the aged and rejuvenated Biopol[TM] copolymers. However, we have shown that the mechanical and dielectric properties are greatly changed on rejuvenation. The question we now want to consider is: are there any other DSC procedures we can utilise to probe the rejuvenation phenomenon?

There is evidence from the DSC scans that an endothermic event begins to occur at a temperature greater than 50°C. This event, which is not thermo-reversible, is assumed to be first order melting process. To probe this further we carried out a DSC scan of an aged D400G copolymer, which was compared to another sample rejuvenated at 100°C. The scans were then superimposed (Fig. 12). The area between the two curves is indicative of the absorbed heat on rejuvenation. This area corresponded to a value of $16.4 \pm 3 \text{ Jg}^{-1}$.

Unfortunately, this procedure was more difficult to follow at lower rejuvenation temperatures since the low endotherm values made superimposition of the traces difficult.

To overcome the above-mentioned restriction, we utilised a partial integration technique to obtain information on any endotherms which may be occurring at lower rejuvenation temperatures. This t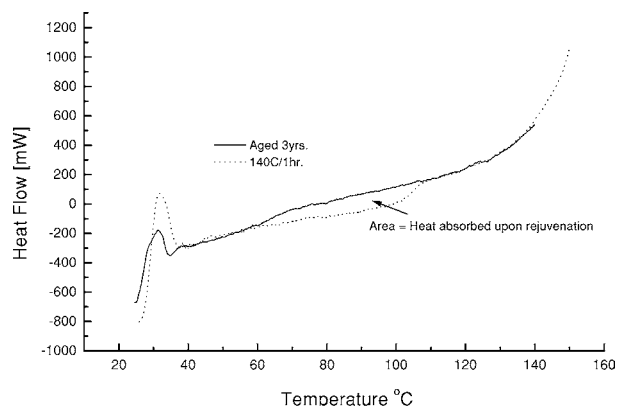echnique allowed us to compensate for sample-to-sample variations in the packing and other experimental considerations such as sample-pan contact, which can cause changes in the baselines; this latter restriction is the reason that superimposing of the curves becomes difficult.

The experimental procedure involves rejuvenation of the sample at a particular temperature, subsequent cooling to room temperature then monitoring the DSC trace as normal. The partial integral of the melt endotherm as a function of temperature gives us a measure of the percentage melting complete as a function of temperature (Fig. 13). A knowledge of the enthalpy of melting for the 100% crystalline polymer allows us, from the graph, to estimate the degree of enthalpy change for each of the rejuvenation temperatures. This data is listed in Table III.

Now we have to conjecture as to the source of the endotherms. It is clear from the XRD data that there is no change in the overall crystallinity on full rejuvenation at 140°C. The data presented above suggests that if the process at hand were due to a crystalline melt then at 100°C the crystallinity would change by around 15%. There is absolutely no evidence for this in the XRD experiment. Hurrell [18] has found that on ageing of Biopol systems there is little change in the wide angle XRD crystallinity. However, data from small angle experiments has indicated that there may be a secondary crystallisation ongoing. The difficulty with the secondary crystallisation hypothesis, however, is that any new crystals forming will be very thin, hardly thick enough to be called crystals at all [15]. Further, Rule and Liggat [25] noted a rapid, continuous rise in

Figure 13 % Endotherm complete as a function of temperature for varying rejuvenation cycles.

Figure 12 Heat flow as a function of temperature for aged and rejuvenated D400G (integrated area between curves gives absorbed heat).
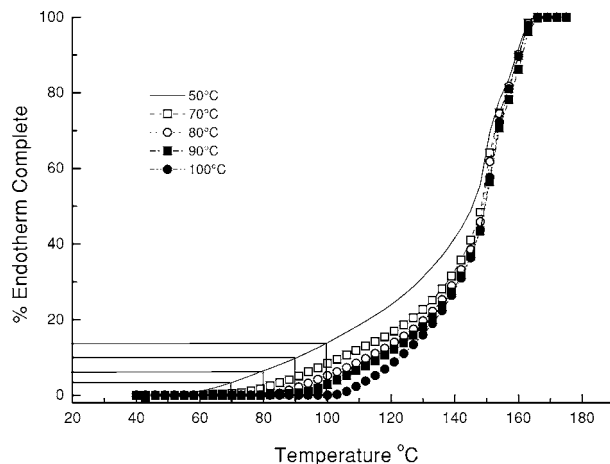
TABLE III DSC data for D400G as a function of rejuvenation temperature

Rejuvenation temperature (°C)	Absorbed heat Jg^{-1}	% Apparent crystallinity from absorbed heat data)
50	N/A	N/A
70	4.3	3.6
80	7.8	6.6
90	12.9	10.9
100	17.6	15

the *d*-spacing during melting, consistent with the disappearance of thinner, unstable crystals from stacks of lamellae possessing a broad distribution of thicknesses. The conclusion would seem to be that if such lamellar insertion is occurring, it could only play a minor role in the overall morphological change and presumably only a minor role in the embrittlement process.

From our study we hypothesise that the amorphous material residing in the rigid amorphous phase is, indeed, restricted by the secondary crystals. When they melt we then observe a glass to rubber type transition manifested by the subsequent endotherms at each rejuvenation temperature. This hypothesis further manifests itself as a change to a more rubber type behaviour as seen via the increase in elongation to break and higher dielectric increment.

4. Conclusions

The rejuvenation of aged Biopol^{TM} copolymers leads to substantial changes in the mechanical, dynamic mechanical and dielectric properties. Indeed, probing via techniques such as DSC (melting) and XRD which highlight the pure crystalline region have shown that the changes in this region are negligible upon rejuvenation. The DMTA and dielectric techniques have shown that the amount of amorphous phase in the copolymers is significantly altered after thermal treatment. Also, the position of the dielectric peaks and the associated distribution parameters give evidence as to changes in the glass transition temperature of the amorphous phase and also highlight subtle changes as to the interaction of the amorphous phase with its surrounding environment. We have conjectured that the nature of the rejuvenation involves release of mobile units from the rigid amorphous phase. Further DSC analysis would suggest that melting of secondary crystals would provide the mechanism whereby restricted amorphous regions are released from the rigid amorphous phase. The nature of the secondary crystals, however, must be such that their size and texture result in no significant contribution to the overall level of crystallinity. The change in enthalpies noted as a result of the rejuvenation point to the presence of a glass/rubber transition emanating from changes in the rigid amorphous phase. This study has focused on one particular Biopol^{TM} copolymer (viz. D400G) but work is on-going to extend this for a series of other copolymers.

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