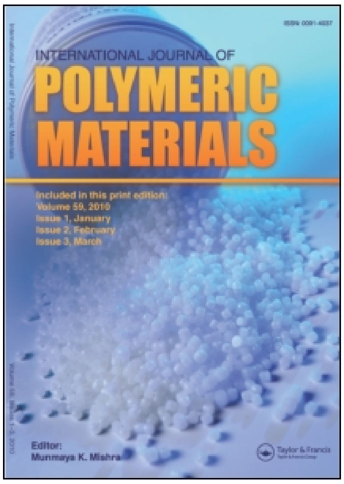

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A Totally Bioresorbable Fibrillar Reinforced Composite System: Structure and Properties

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The structure and properties of a new biodegradable fibrillar reinforced composite system have been studied. The focus of the material investigated was set on blends of different Polyhydroxyacids. According to the microfibrillar composite processing procedure, the samples were prepared in the following sequences: blending, drawing and finally annealing. Thermal (DSC), microscope (SEM) and static mechanical tests of the samples were carried out. The microscope observations on the fracture surfaces of the samples proved the feasibility of the MFC procedure for these blends, *i.e.*, small oriented fibrils embedded in an isotropic matrix could be observed. The mechanical properties of the samples were increased nearly twice by this processing route. The results also showed that overheating the system in the final processing step can produce recoiling of the oriented fibrils.

Keywords: Polyhydroxyacid; Biodegradable; Resorbable; Microfibrillar; Composite

INTRODUCTION

There is an increasing interest in the use of resorbable polymers for the preparation of internal fixation devices. Many such devices produced from various polyhydroxyacids are available in the market at present, mainly used for the treatment of small fractures. The advantage of

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such resorbable implants is that they do not have to be removed from the implantation site after fracture healing is completed. One limitation on the broad use of these resorbable implants in bone fracture treatment relates to their relatively poor mechanical properties. While the latter still seem to be sufficient when the implants are used in areas of restricted load, they are inadequate, however, to allow for the use of implants in high-load situations [1].

Various techniques are applied to produce resorbable internal fixation devices with enhanced mechanical properties [2–11]. For example, compression moulding of reinforcing fibres embedded in a matrix of the same or a different polymer is such a technique. Orientrusion, a cold- or hot-drawing process above the glass transition temperature and below the melting temperature, is another technique for enhancing the mechanical properties. However, many problems of these techniques, like delamination between the matrix and the reinforcing component or high crystallinity of the polymer, have not been solved yet.

In this aspect, a new type of polymer–polymer composites is of interest. It was developed in the polymer materials laboratory of the Sofia University and is satisfying the demand for high strength and high modulus of polymer blends [12–15]. These composites are called microfibrillar reinforced composites (MFC) and are prepared from polymer blends of immiscible partners having different melting points. In the case of MFC, the reinforcing elements (*i.e.*, the fibrils) and the completely isotropic matrix are created during processing *via* special thermal treatment conditions. In earlier investigations carried out by Fakirov *et al.* [16, 17] it was shown, that Young's moduli and tensile strengths of MFC, made of nonbiodegradable materials like PET and PA6, can be increased by 30–50% in comparison to the weight-average values of the components and are comparable to those of short glass-fiber-reinforced composites having the same matrix.

This paper reports the examination of a bioresorbable fibrillar reinforced system. The aim is to develop a strong material while avoiding massive crystallinity. The difference from other techniques is the in situ processing of the composite and the nearly short fibre reinforcement through one of the blend components, which can be of advantage regarding the degradation behaviour. In this study small rods were produced which can be processed further into internal fixation devices with more complex shapes and enhanced mechanical properties.

EXPERIMENTAL

Materials

Various types of Polyesters based on Polyhydroxyacids from Boehringer Ingelheim KG (Ingelheim, Germany) were used. The raw materials were blended and injection moulded into cylindrical bars using a technology at Aesculap GmbH (Tuttlingen, Germany). The samples were then dried and stored in a desiccator prior to the beginning of the MFC-processing procedure.

Sample Preparation

According to the MFC technology, the blends were stretched between the glass transition temperature and the melting temperature of the lower melting phase (fibrillization step), so as to create at first a fibrillar structure in both phases. The last step was to anneal and isotropize the stretched samples within a window between the melting points of the two components (isotropization step). The samples obtained after cooling were cylindrical in shape and had a geometry of approximately 50 mm in length and 4 mm in diameter.

Thermal Analysis

A Mettler-Toledo differential scanning calorimeter (Type "DSC 821") calibrated with indium was used for evaluation of the samples' thermal characteristics. The specimens had an average weight of roughly 10 mg and were scanned in aluminium pans at a heating rate of 10°C/min under dry nitrogen flowing at a rate of 30 ml/min.

Mechanical Tests

To measure bending modulus and bending strength of the samples, a Zwick universal testing machine (Type 1474) was used. The measurements were carried out at room temperature and ambient condition (approximately 50% humidity) in a three point bending mode. The span of the two bottom support was 40 mm, the diameter of the support was 5 mm and the cross-head speed amounted to 1 mm/min.

Scanning Electron Microscopy (SEM)

Jeol models "JSM 5400" and "JSM 6300" SEM allowed to characterise the morphology of the samples. The instrument was operated at 20 kV.

RESULTS AND DISCUSSION

Thermal Characteristics by DSC Study

Figure 1 shows typical DSC thermograms for (i) the blended samples, (b) the samples after orientation (fibrillisation step), and (iii) the annealed samples (isotropisation step). The samples show three major

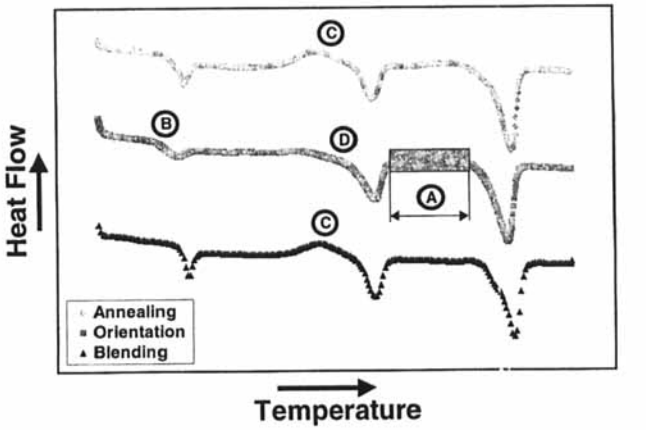

FIGURE 1 Representative DSC thermograms (obtained during heating) for the samples subjected to various processing steps.

phase transitions, a glass transition in the lower temperature range and two melting peaks in the upper temperature range. According to the DSC curve the investigated blend is miscible in the amorphous phase, only one glass transition can be observed. While heating the system, the components crystallize, both components of the blend show separate melting points in the system. Due to this fact the blending of both components chosen permits the preparation of a polymer composite according to the MFC technology. The tagged region (A) refers to the processing window for the final isotropization step.

This figure shows also the effects of different cooling rates during processing of each sample. The glass transition of the oriented (*i.e.*, fully fibrillized) material is shifted to the left, as shown by mark (B). The blended and the annealed samples show a glass transition superimposed by an endothermic peak. This endothermic peak is a result of the additional crystallisation of both blends components due to thermal treatment.

Another difference can be seen by the exothermic peak (C). Both samples, the blended and the annealed one, show a cold crystallisation during the DSC-measurement. This effect can be proven by a second measurement to exclude prehistory-influence on the measurement. It is a result of the incomplete crystallisation of the processed samples. This peak is missing from the thermogram of the oriented material (D), but it appears in a second measurement again. In this case, crystallisation cannot be observed during the first run due to the high orientation of the molecules.

Figure 2 shows the change in the thermal characteristic of the samples, when annealed at different temperatures. The annealing temperatures are chosen within the processing window illustrated in Figure 1. The lower annealing temperature is on the left side of the window, the higher temperature is more to the right side. After annealing at the lower temperature, the thermogram shows a rounded edge (E) for the higher melting component. This can be assigned to the partial melting of the higher melting component. Maybe it reflects the existence of a material with a low degree of crystal perfection produced during annealing. Annealing the samples at a temperature near to the melting point of the higher melting component leads to a sharp edge of the endothermic peak (see mark (F)). It is assumed, that the temperature is too high for the formation of small crystals.

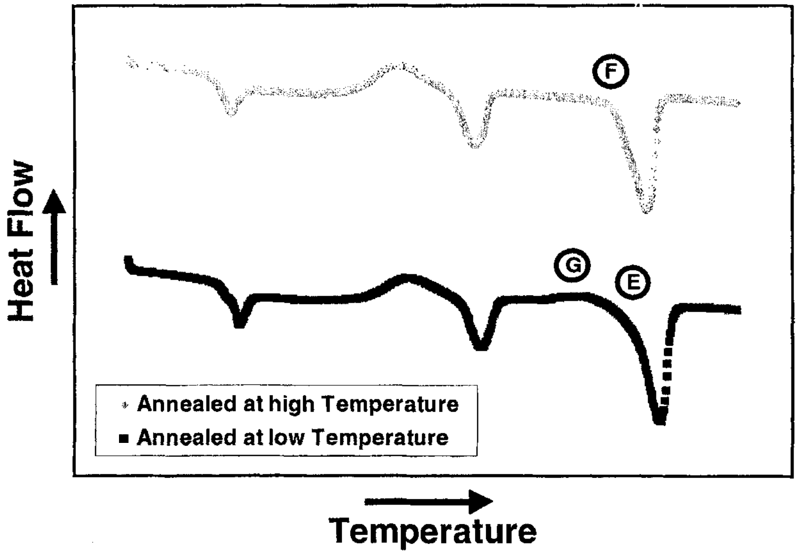

FIGURE 2 Typical DSC scan (obtained during heating) for differently annealed samples.

In addition small relaxation effects can also be observed. All thermograms in Figures 1 and 2 show a small exothermic peak (G) before melting of the second component, except the sample annealed at a high temperature. After a second verification run it can be ensured that these exothermic peaks are a result of relaxation of the higher melting component. If the annealing temperature is too high, the material loses its internal stresses, thus the peak at (G) disappears. As a result of this observations it can be stated, that especially the higher melting component has to be preserved during the annealing process. The latter statement is also verified by the mechanical test results.

Sample Morphology

MFC-processing of the biodegradable blends leads to the formation of a typical fibrillar structure, as pointed out in the following series of SEM pictures. At first, the MFC process starts with a blending the raw material components. Figure 3a shows a scanning electron micrograph of the fracture surface of the blended material. It can be seen that both components are not miscible, and that the phases are arranged

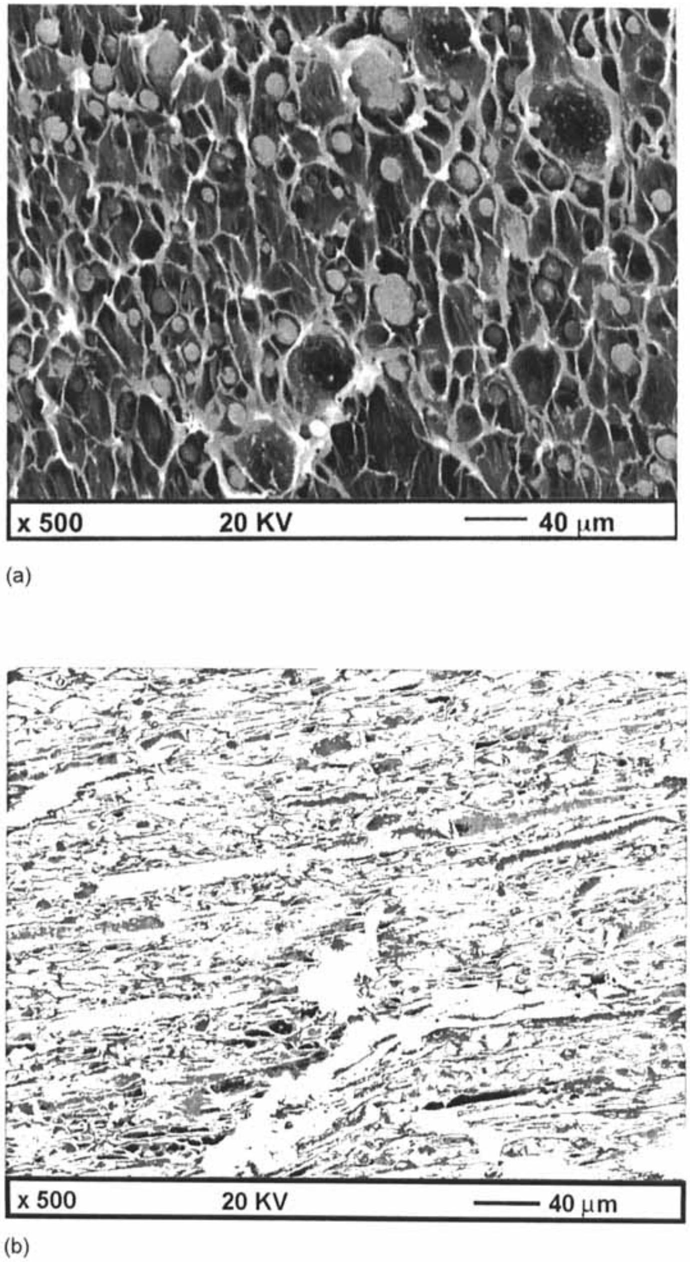

FIGURE 3 Scanning electron micrographs of the split surface after different processing steps. (a) after blending step; (b) after the orientation step; (c) after the isotropisation step.

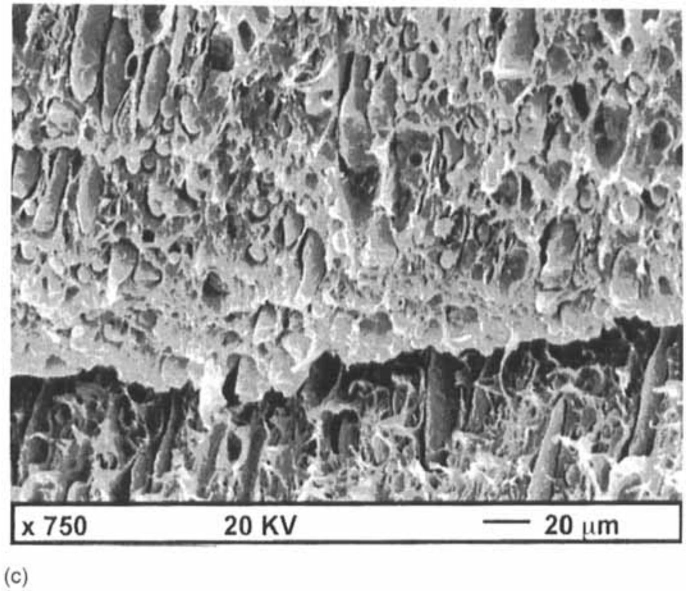

FIGURE 3 (Continued).

separately. In particular, the blending resulted in a system of small spheres of the higher melting component, embedded in a cellular structured matrix of the lower melting one.

A different structure can be seen after the second processing step, the fibrillization. Figure 3b illustrates the changes in the material which have lead to an increase in strength; both components have been transferred into an oriented state. The fibrils of the higher melting component possess a diameter of roughly 10 µm and are uniformly stretched within the surrounding matrix. The latter has also experienced a certain degree of orientation, as evidenced by the oriented, stretched matrix tips formed during fracture of the oriented blend structure transverse to the fibrillization direction.

The structure after annealing of the samples is displayed in Figure 3c. The fibrils with an average diameter of 10 µm, formed from the high-melting component, are embedded in the low-melting component. Although an isotropization of the lower melting component has taken place, the fibrillar structure of the higher melting component was preserved.

The following Figures 4 and 5 illustrate the differences in the material as a function of annealing temperature. For low annealing temperatures the formation of a brittle matrix can be detected. High annealing temperatures lead also to a decrease in strength, and two possible reasons can be pointed out for the differences:

(i) Annealing the pins at low temperature yields a material composed of well oriented fibrils embedded in an isotropized matrix (Fig. 4a). Increasing the annealing temperature too much results in a re-coiling of the fibrils, a loss of their strength and a partial transformation into spherical particles (Fig. 4b).

(ii) Annealing the samples can be accompanied by the formation of a rough structure on the surface of the higher melting fibrillar phase, as shown in Figures 5a and 5b. The extent and perfection of this surface structure is affected by the annealing temperature. At low and moderate temperatures, a well pronounced structure can be observed, whereas at rather high annealing temperatures such a structure nearly disappears. Choosing the appropriate temperature for this processing step, such a rough surface can ensure a good bonding between both components, and thus an optimum in the composites' bending strength.

Mechanical Properties

Better mechanical properties be achieved by MFC processing. As shown in Figure 6, the bending strength of the blend can be increased after drawing by up to 36%. The maximum in strength is, however, reached after annealing, where the values increase about two fold. The unexpected relatively low values achieved after drawing are a result of the brittleness of the samples obtained after the orientation process. Furthermore the surfaces of the drawn pins frequently contained numerous cracks. Both, the high brittleness and the cracks disappeared after annealing and isotropization of the lower melting phase. It should be stated, in addition, that the bending modulus too was improved similar to the bending strength.

Figure 7 illustrates the effect of the annealing temperature on the bending strength. According to the DSC study, the x-axis represent the annealing condition chosen. Even at a less optimal annealing

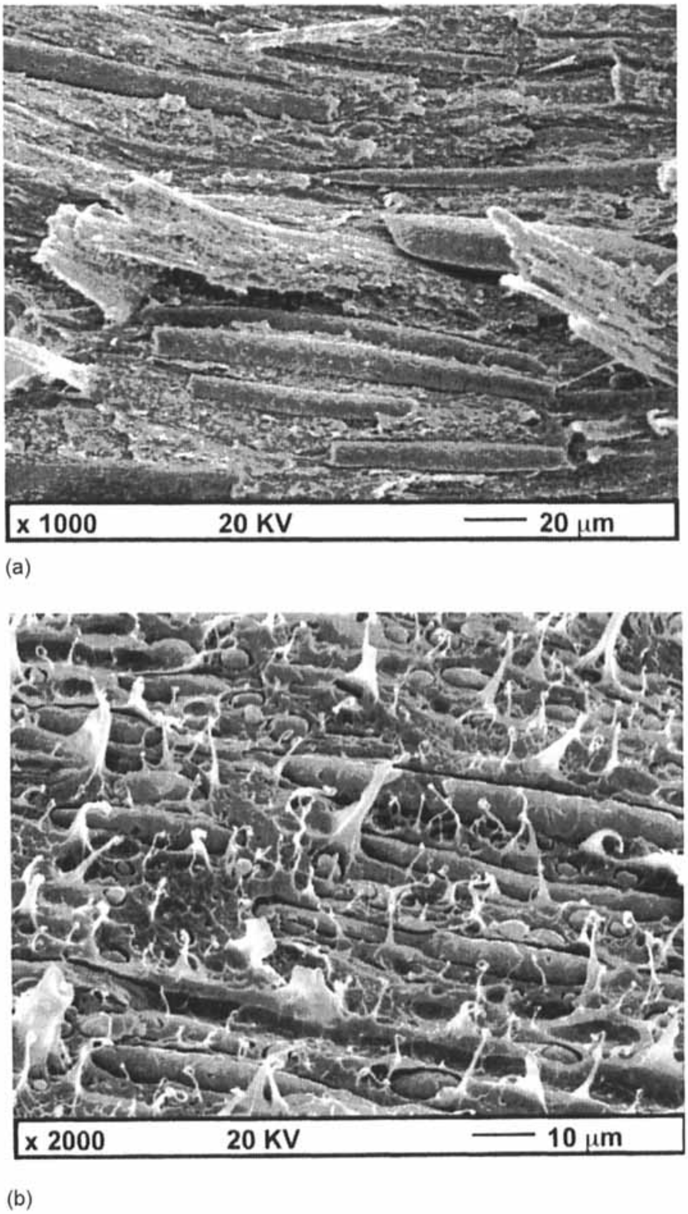

FIGURE 4 Scanning electron micrograph of the fracture surface of samples annealed by different temperatures. (a) annealed at low temperature; (b) annealed at high temperature.

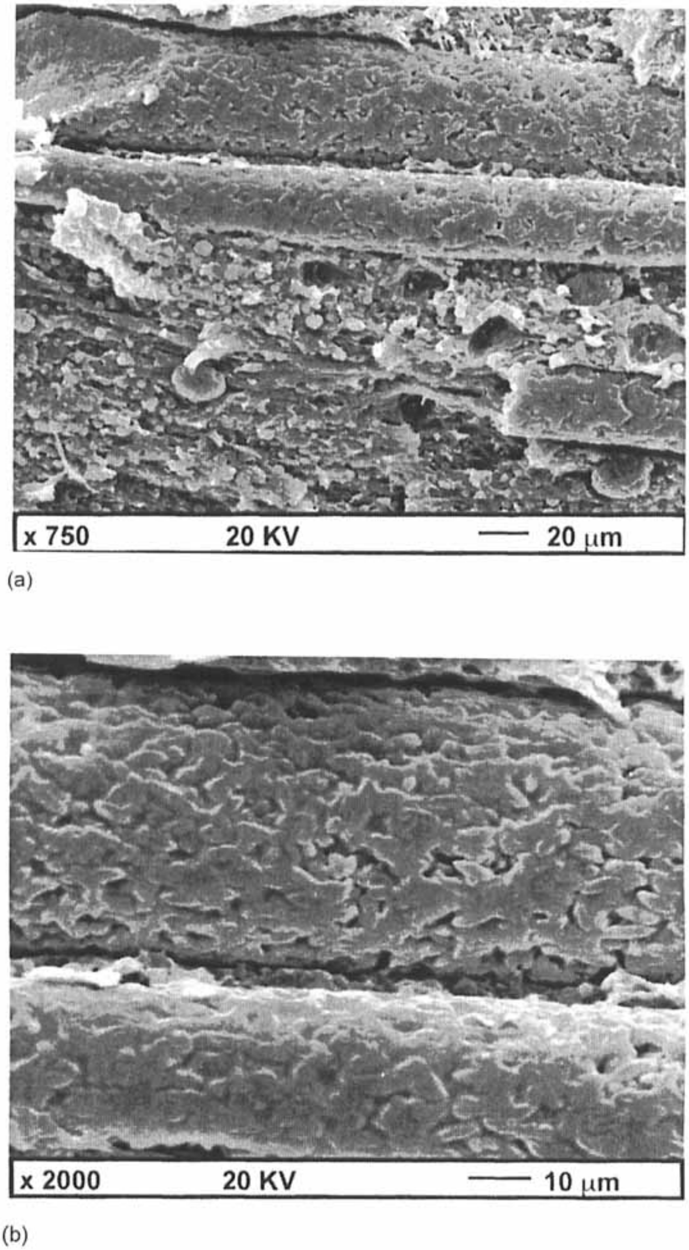

FIGURE 5 Scanning electron micrograph of a sample annealed at low temperature. (a) overview; (b) detail in higher magnification.

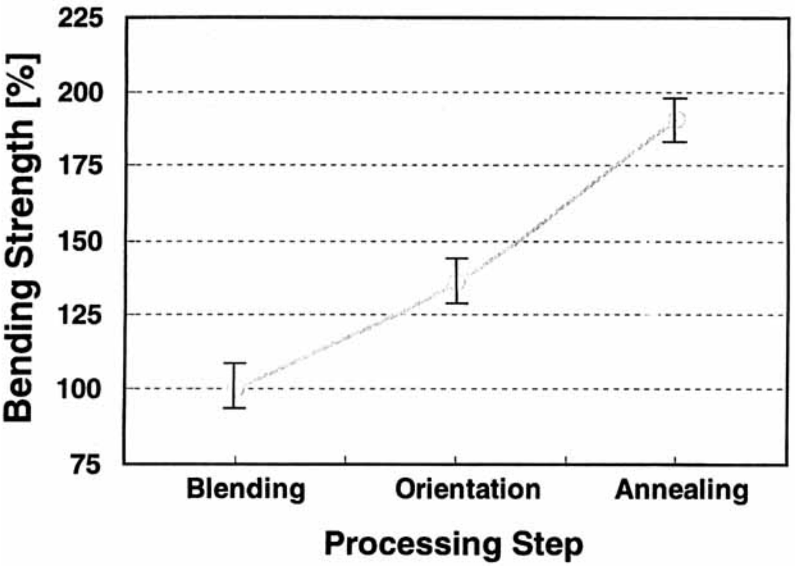

FIGURE 6 The bending strength of a sample for various processing steps.

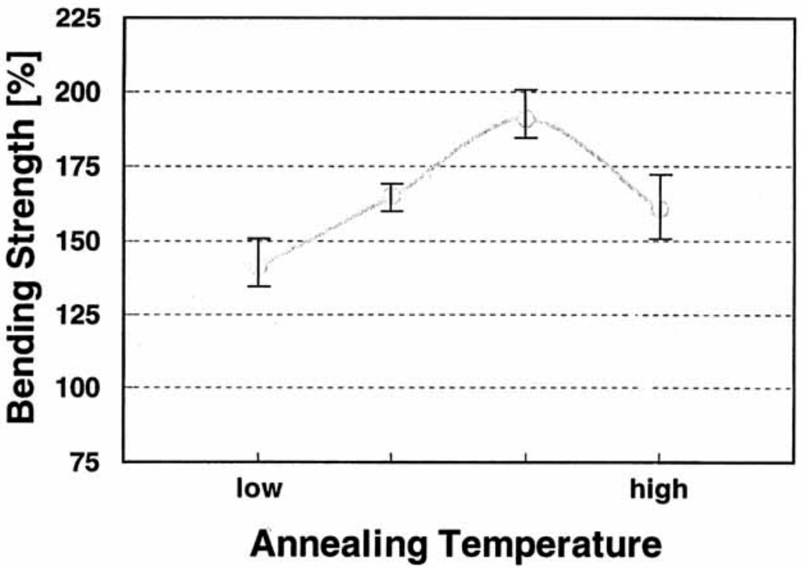

FIGURE 7 The bending strength of a sample for different annealing temperatures.

temperature, the bending strength is about 140% of the blend value, and already higher than the one of the drawn material. With the optimal temperature, the strength increases to a maximum of 190%. One reason for the drop of strength at the very high temperature is the stress relaxation phenomenon, as it was mentioned in conjunction with the DSC-study and was also proven by SEM micrographs.

CONCLUSION

High-strength and high-modulus resorbable composites can be produced by the MFC technique. The rods produced by this technique had a bending strength more than 90% higher than that of the unmodified blend of the two components used. It is assumed, that these properties can be further enhanced after optimising the MFC processing procedure. The manufactured rods can be processed into more complex shapes such as surface structured, bone fixation implant nails, for example by using a subsequent compression-moulding technique. Hence microfibrillar reinforced composites from resorbable polymers are a promising material for the preparation of medical implants parts with enhanced mechanical properties.

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