

Investigations of polycaprolactone/gelatin blends in terms of their miscibility

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Abstract. Synthetic and natural polymers blends represent a new brand of materials with application in wound healing, scaffolds or drug delivery systems. Polycaprolactone/gelatin (PCL/Gt) blends were analyzed in terms of their miscibility. The PCL structure was investigated as a function of Gt content. Changes in the PCL spherulitic structure with Gt content were investigated by a polarizing-interference microscope. The analysis of the glass transition temperature (T_g) of both components as a function of PCL/Gt ratio by differential scanning calorimetry indicates that the system of polycaprolactone/gelatin belongs to a type of s.c. compatible system, being intermediate between miscible and immiscible systems. There is possibility of very limited miscibility of both components. Supplementary wide angle X-ray scattering results are presented.

Key words: blends, compatibility, miscibility, polycaprolactone, gelatin.

1. Introduction

The synthesis of new polymers is usually much more expensive and needs more effort than forming composites or mixtures from known and described materials. Mixtures of two polymers combine properties characteristic of both of them. Addition of some peptides like collagen (Col) or its denatured form – gelatin (Gt) to synthetic polymers like polycaprolactone (PCL) is a well-known route for improving cell adhesion in tissue engineering through introduction of amino-acid RGD sequence (Arginine-Glycine-Aspartic acid). A lot of papers describe electrospinning of nano- and submicron fibres from a mixture of synthetic polymers with biopolymers, most of them focusing on the practical aspects of scaffold effectiveness for cell cultures in vitro conditions [1–6]. Some of the papers show unexpected results related to phase content and hence some properties of such blended fibers without any attempt of physical interpretation. The quantitative analysis of miscibility between the polymeric components in such systems is critical for understanding physical properties in this type of mixtures. Miscibility corresponds to a precise thermodynamic description of the system and strongly influences crystallization and therefore properties.

Properties of polymer blends are closely associated with their structure on several scale levels, such as crystallinity and supermolecular structure. Thus, a series of methods that enable one to characterize these different structure parameters can be employed, including for instance differential scanning calorimetry for analysis of glass transition temperature (T_g) of both components, allowing thus deduction on miscibility, Fourier Transform Infrared Spectroscopy (FTIR) for analysis of interactions between various chemical groups, Transmission Electron Microscopy (TEM), Wide Angle X-ray Scatter-

ing (WAXS) and selective leaching. However for polyester – gelatin/collagen blends there is no answer if they are miscible or not.

In poly(lactic-co-glycolic acid)/collagen (PLGA/Col) blends, slight shift in the ester carbonyl peaks of PLGA from 1747 to 1754 cm^{-1} and also slight shift in other characteristic peaks of PLGA to a higher wave number was observed with increasing Col concentration and is interpreted as sign of miscibility of those polymers [6]. According to Sionkowska [7], slight shift in the amide I peak suggests conformational changes in the collagen molecule. Overall, these shifts suggest limited interactions between PLGA and Col.

According to the theory of Flory – Huggins, the miscibility and compatibility of two polymers depend on their ability to form specific interaction between them, which contributes to diminish or make negative the mixing enthalpy. By this theory it was evaluated that Col and polyvinylpyrrolidone (PVP) are miscible due to the strong interactions between the synthetic and biological component, mainly by hydrogen bonds [7]. Moreover, it was found that collagen and polyethylene oxide (PEO) are immiscible as there is a lack of strong interactions between the synthetic and biological component. Poly(ethylene glycol) PEG and Polyvinyl alcohol (PVA) were partially miscible with Col. Results were confirmed by FTIR and viscosimetry investigations [7].

There are also some papers which suggest immiscibility of polyester/natural polymer blends. In PCL/Gt blends segregation component was determined during leaching samples in polybutylene succinate (PBS). After few days, Gt was dissolved, and holes appeared [8]. Lack of the shift of position of peaks (110) and (200) of orthorhombic PCL crystal in PCL/Gt blends was observed by WAXS suggesting immiscibility [9]. According to the results of uniaxial tensile tests of

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PCL/Gt samples, additive of Gt can lead to increase of tensile strength. It is suggested that this phenomenon is likely due to the immiscibility and microphase separation which leads to easier slip-page of chains under loading because of less entanglements and weak physical interactions among the chains of mixed polymers [10]. TEM figures suggest segregation of polymers in polylactic acid/gelatin (PLLA/Gt) fibres also. The ribbons of Gt are deployed along fibres direction [11].

The aim of the work is to investigate miscibility of PCL and Gt. There is a lack of literature data on this topic. Part of the results were obtained for electrospun fibers, taking into account that electrospinning is a very popular method of formation of bicomponent PCL/Gt fibers for tissue engineering applications.

2. Materials

Polycaprolactone (PCL) ($M_n = 80.000$) and gelatin (Gt) type A from porcine skin were used. Blends were prepared by making solutions using common solvent – hexafluoro-2-propanol (HFIP) at room temperature. Total concentration was 5% and the ratio of PCL/Gt was varied. After complete mixing, a solvent was evaporated. During solvent evaporation, solutions remained either undisturbed (evaporation under vacuum, samples U) or were electrospun (samples E).

3. Methods of investigation

Differential Scanning Calorimetry (DSC) was applied for investigations of glass transition temperature (T_g), and melting temperature (T_m), for PCL amorphous phase and crystals, respectively. Melting temperature was determined at the maximum of the peak. DSC Pyris-1 (Perkin-Elmer) and DSC Q2000 (TA Instruments) calorimeters were used. A sample mass ranged between 7–9 mg. The polarizing-interference microscope MPI 5 was used for the analysis of morphology. Wide angle X-ray scattering (WAXS) investigations were performed using X-ray Bruker D8 Discover diffractometer with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54059 \text{ \AA}$).

4. Results and discussion

The analysis of superstructures by MPI for samples U indicates clearly spherulitic structure without any traces of phase separation up to PCL/Gt ratio of 70/30 (Fig. 1).

It is evident from Fig. 1 that low content of Gt as additive (5–10%) leads to more clear and regular ring-band pattern of spherulites compared to pure PCL. According to Woo et al. [12], formation of ringed spherulites in PCL blends is an evidence of miscibility. In our opinion, this observation can be only treated as an evidence of incorporation of Gt molecules into a structure of PCL spherulites. It is known that Gt remains amorphous while PCL is a crystallizing component. At higher Gt content there is phase separation (Fig. 1f,g), most probably into two phases, PCL rich phase and Gt rich one. At very high Gt content (above PCL/Gt 20/80), there is again one phase structure. On the contrary, this structure is practically not birefringent or very weakly birefringent, being an

evidence of dominating amorphous Gt with PCL molecules scattered within amorphous Gt without or very weak formation of crystallites.

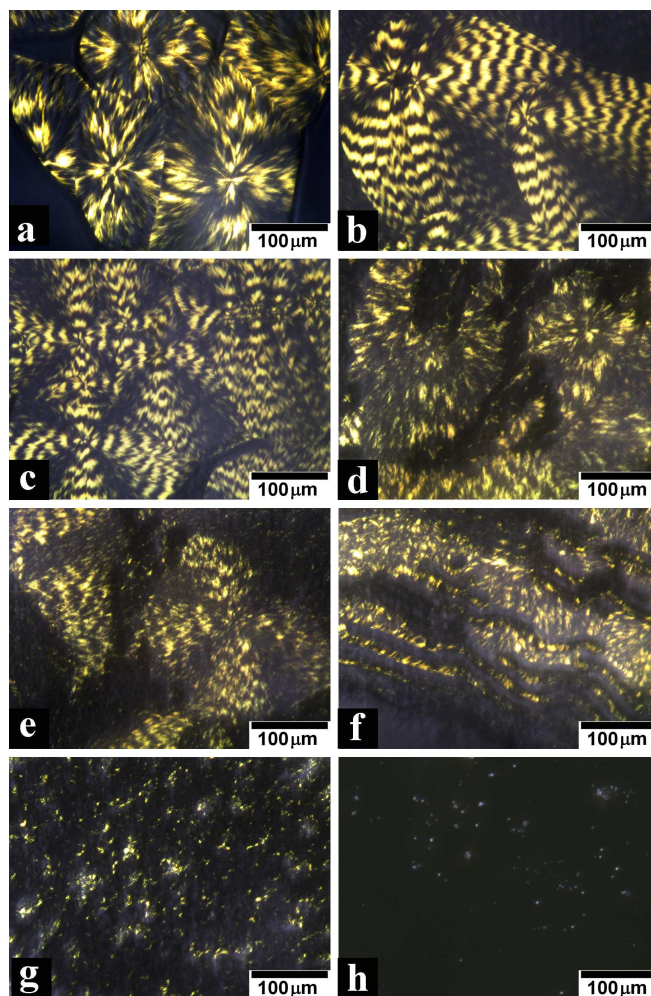


Fig. 1. Optical micrographs at crossed polarizers of PCL/Gt blends. PCL/Gt: a) 100/0, b) 95/5, c) 90/10, d) 80/20, e) 70/30, f) 60/40, g) 50/50, h) 20/80

Figure 2 shows the dependence of T_g from DSC measurements on PCL/Gt ratio for samples U. This type of dependence as seen in Fig. 2 indicates that there is no molecular miscibility of both substances which should be manifested by more or less linear dependence of measured T_g on blend content. Instead of this, nonlinear dependence is seen, typical for compatible systems [13], e.g. there are two T_g values which depend on composition in a specific way. Compatibility, being intermediate state between miscibility and immiscibility is caused by sufficiently strong interactions between the components. According to basic concepts, compatible blends refer to immiscible blends that exhibit macroscopically uniform physical properties. Sometimes the term of compatibility is identified with partial solubility [e.g. 15]. The analysis of T_g for E samples cannot be unequivocal in terms of miscibility because of an effect of external field acting additionally on a system during electrospinning. An external electric field

may affect interactions between components of the system, hindering possibility to draw clear conclusions on molecular miscibility.

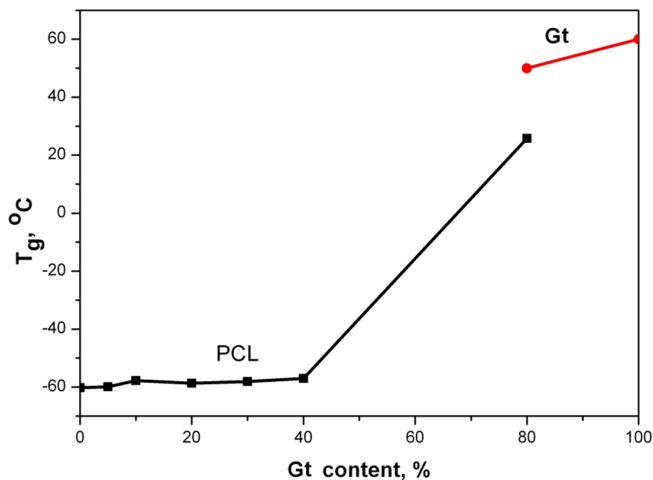


Fig. 2. DSC glass transition temperatures for PCL/Gt blends (U samples)

Additional conclusions regarding miscibility can be drawn from the analysis of PCL crystal melting (Fig. 3). Both types of samples (U and E) within the range of composition up to 70/30 PCL/Gt ratio show, during heating, one endothermic peak related to melting of PCL crystals; the changes of melting temperatures are rather small. For the higher Gt content the endothermic effect is much broader or even splits into two separated peaks with extremum at 40°C and at 52°C. This very broad peak is most probably a result of overlapping of two peaks. At the content of Gt >80% there is practically no traces of PCL crystallinity as observed during DSC heating. The existence of two endothermic peaks can be interpreted as an evidence of formation of two phases, differing in PCL content and hence in size and perfection of crystals.

The additional result which needs further physical explanation is related to changes of PCL crystallinity. It was observed that PCL crystallinity in samples both U and E containing relatively small content of Gt (up to 10%) increases over the value for pure PCL samples.

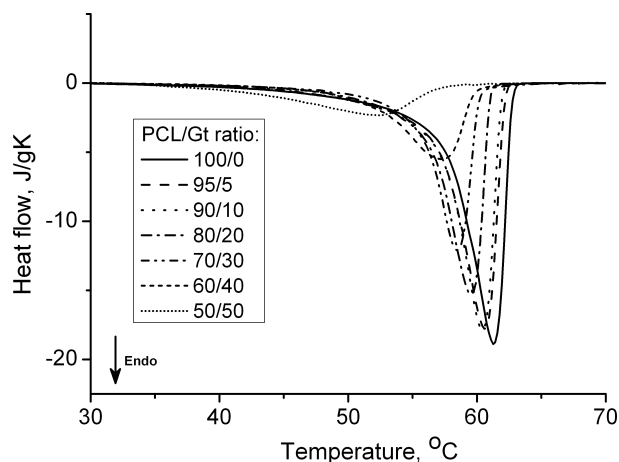


Fig. 3. DSC scans for heating of PCL/Gt blends with various ratio of PCL to Gt (indicated in legend; U samples)

WAXS experiments were performed to estimate the effect of gelatin on interplanar spacing in PCL crystal structure. Figure 4 shows the WAXS patterns of PCL, PCL/Gt: 95:5, 90:10, 80:20.

Neat PCL shows two strong diffraction peaks at $2\theta = 21.597$ degree and $2\theta = 22.224$ degree corresponding to (110) and (200) planes. Pure Gt does not show any narrow peak from the crystal structure – it is fully amorphous indicating only broad halo which is related to coil conformation of Gt molecules.

There is a small shift of both PCL reflections observed for PCL/Gt 95:5, 90:10 blends in comparison with pure PCL. Those shifts correspond with a small increase in PCL crystal spacing in the presence of small content of gelatin (5–10%).

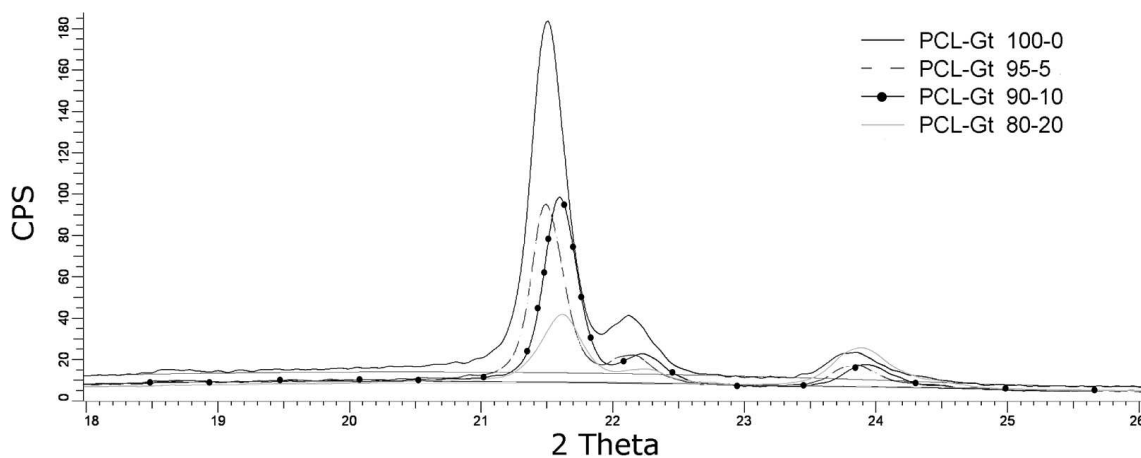


Fig. 4. Typical WAXS radial profiles for investigated blends (E samples)

Table 1
Angular positions 2θ of peaks from (110) and (200) planes of PCL crystals and corresponding interplanar distances, d

	(110)		(200)	
	2 Theta [deg]	d [Å]	2 Theta [deg]	d [Å]
PCL/Gt 100/0	21.597	4.111	22.224	3.997
PCL/Gt 95/5	21.493 ↓	4.131 ↑	22.138 ↓	4.012 ↑
PCL/Gt 90/10	21.503 ↓	4.129 ↑	22.124 ↓	4.015 ↑
PCL/Gt 80/20	21.616 ↑	4.108 ↓	22.245 ↑	3.993 ↓

5. Conclusions

The data obtained recently indicate that the system of polycaprolactone/gelatin belongs to a type of s.c. compatible system, being intermediate between miscible and immiscible systems. According to our results, there is possibility of very limited miscibility of both components. A description of miscibility only from the analysis of glass transition temperature (T_g) results are not fully possible because T_g in gelatin depends on water sorption [14]. In terms of morphology, it is concluded that the phase separation occurs in the range of gelatin content between ca. 30% and 80%. Changes of interplanar spacing within PCL structure at relatively low content of gelatin registered by wide angle X-ray scattering indicate incorporation of gelatin molecules into the crystal structure of PCL.

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