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BADANIA MIESZNEK POLIKAPROLAKTON/ŻELATYNA POD WZGLĘDEM MIESZALNOSCI
INVESTIGATIONS OF POLYCAPROLACTONE/GELATINE BLENDS IN TERMS OF THEIR MISCIBILITY

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Addition of some peptides like collagen or its denatured form - gelatin, 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. 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. Quantitative analysis of miscibility between the polymeric components in such systems is critical for understanding physical properties in this type of mixtures.

The aim of the work is to analyse miscibility of polycaprolactone and gelatine. There is a lack of literature data on this topic.

Materials

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

Methods

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. Sample mass ranged between 7-9 mg were used. Polarizing-interference microscope MPI 5 was used for the analysis of morphology.

Results

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

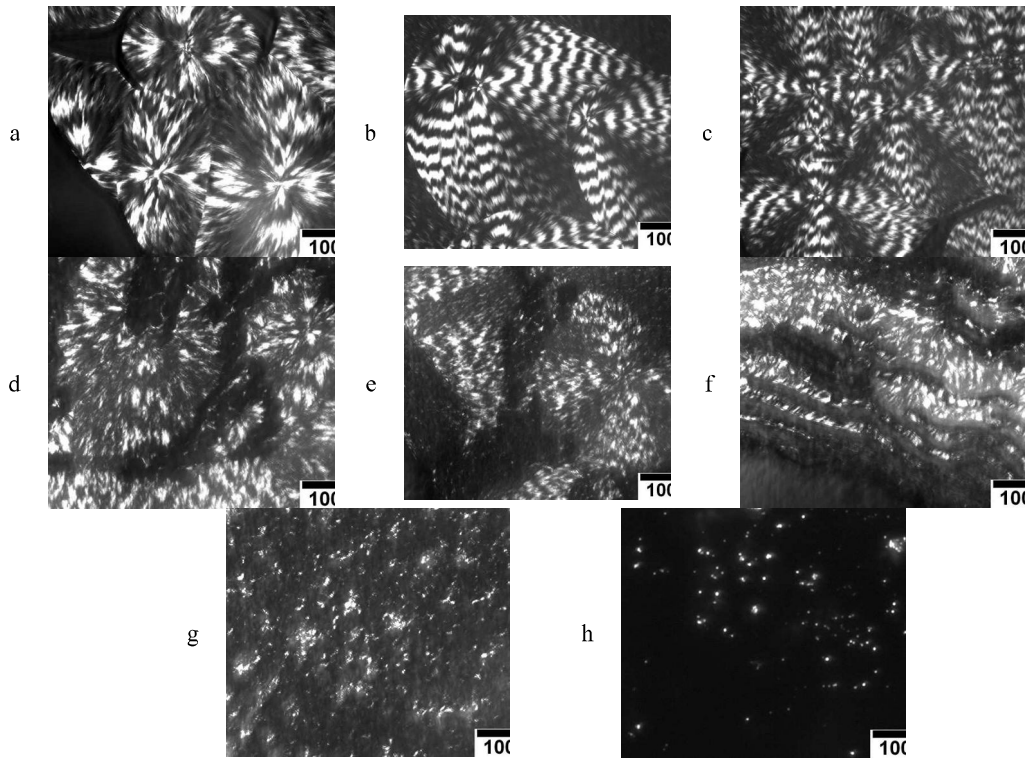

Fig. 1. Optical micrographs at crossed polarizers of PCL/Ge blends. PCL/Ge: (a) 100/0, (b) 95/5, (c) 90/10, (d) 80/20, (e) 70/30, (f) 60/40, (g) 50/50, (h) 20/80

It is evident from Fig. 1 that addition of Ge changes the morphology of spherulites into ring-banded structure compared to non-ringed spherulites in pure PCL. According to Woo et al. [1], 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 gelatin molecules into a structure of PCL spherulites. It is known that gelatin remains amorphous while PCL is a crystallizing component. At higher Ge content there is phase separation (Fig. 1f, g), most probably into two phases, PCL reach phase and Ge reach one. At very high Ge content (above PCL/Ge 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 gelatine with PCL molecules scattered within amorphous gelatin without or very weak formation of crystallites.

Fig. 2 shows the dependence of T_g from DSC measurements on PCL/Ge ratio for samples U. This type of dependence as seen in Fig. 2 indicates the there is no molecular miscibility of both substances which should be manifested by more or less linear dependence of measured Tg on blend content. Instead of this nonlinear dependence is seen, typical for compatible systems [2], e.g. there are two Tg values which depend in a specific way on composition. Compatibility, being intermediate state between miscibility and immiscibility is caused by sufficiently strong interactions between the components. The analysis of T_g for E samples is not so informative in terms of miscibility because of complex effect of external fields during solvent evaporation during electrospinning.

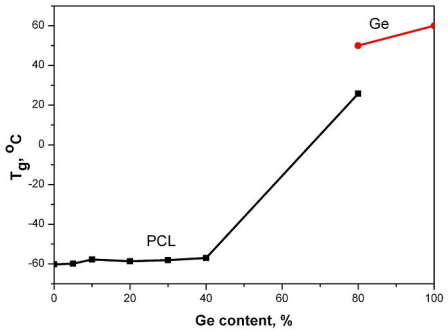

Fig. 2. DSC glass transition temperatures for PCL/Ge blends (U samples)

Additional conclusions regarding miscibility can be drawn from the analysis of PCL crystal melting. Both types of samples (U and E) in the range of composition up to 70/30 PCL/Ge ratio show during heating one endothermic peak related to melting of PCL crystals; the changes of melting temperatures are rather small. For higher Ge content endothermic effect splits into two peaks. At the content of Ge>80% there is practically no traces of PCL crystallinity as observed during DSC heating. The existence of two endothermic peaks can be interpreted at the moment as an evidence of formation of two phases, differing in PCL content and hence in size and perfection of crystals.

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

Conclusions

The data obtained recently indicate that the system of PCL/gelatin belongs to type of s.c. compatible system, being intermediate between miscible and immiscible systems. Strong molecular interactions between PCL and gelatin which are responsible for existence of compatibility are evidenced by FTIR results [3]. In terms of morphology, it is concluded that the phase separation occurs in the range of gelatin content between ca. 30 and 80%.

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