INTRODUCTION

Modification of polymers to obtain materials with new or improved properties has attracted constant interest from researchers because the starting materials often do not possess the set of properties required for definite practical applications. One of these materials is molecular collagen. It has a set of unique properties such as biodegradability and biological compatibility, which make it preferable and occasionally indispensable in many fields of science and technology.

Filling with nanosized ceramic corundum particles obtained by mechanochemical activation is suggested in this study as a method for preparing materials from molecular collagen with increased performance. The chief advantage of the use of the suggested modifier is its bioinertness. In addition, corundum is an ecologically safe, accessible, and inexpensive material.

EXPERIMENTAL

The molecular mass of water-soluble molecular collagen is 90 kDa, which corresponds to a single polypeptide chain. Nanodisperse ceramic corundum particles were obtained by mechanochemical treatment (MT) of the starting powder with a specific surface of $1.1 \pm 0.1$ $m^2/g$ in an AGO-2 centrifugal planetary mill [1]. The specific surface of the ceramic filler after MT was determined by thermal desorption of argon [2]. The size of ceramic particles was calculated from their specific surface [3]. According to the specific surface data, the average particle size of corundum after MT for 3 min with a water addition (2% of the mass of the powder being treated) was $\sim 40$ nm.

The size distribution of ceramic corundum particles was determined on an LS13320 particle size analyzer (Beckman Coulter). The yield of particles with a size of $\leq 100$ nm was $\sim 60\%$ (Fig. 1). Composite materials based on molecular collagen and corundum were prepared in the form of polymer films by coating from 10% aqueous polymer solution. The degree of filling of polymer films with ceramic particles was varied from 0.01 to 0.3 wt %. The agglomerates of disperse particles were decomposed and uniformly distributed in the polymer matrix by ultrasonic treatment of a filled solution of a binder (50 mL) using an UZD2-0.1/22 disperser at ultrasound power 50 W for 2.5–5 min.

Fig. 1. Size distribution ($D$) of corundum particles after mechanochemical treatment for 3 min.
The density of polymer composites with different degrees of filling was determined by hydrostatic weighing according to [4]. The tear strength of the films was determined on a ZWICK/Roell-Z005 tension tester. The strength was measured with an Xforce HP stress sensor (500 N). The tear strength was measured at a rate of 500 mm/min under ambient conditions [5].

The changes that took place in the structure of polymers after their modification were studied with an optical microscope. An XRD analysis was performed on a DRON-4 diffractometer under the following conditions: CuKα radiation, λ = 1.5418 Å, diffraction angle 2θ = 10°–70°, rate 2 deg/min. The Raman spectra were recorded on a Bruker RFS 100/S spectrometer.

RESULTS AND DISCUSSION

The experimental dependences of density and tear strength on the corundum content for films based on molecular collagen are presented in Fig. 2. The strength characteristics of the modified collagen films exceeded those of the starting film (by more than 25%) only at low degrees of filling (0.01–0.3 wt %). Further increase in the amount of the modifier led to a decrease in the characteristics most probably because of the aggregation of particles when their number is large. These aggregates can act as structure defects, thus weakening the material.

The film density and strength can increase as a result of structural changes in the polymer in the presence of ceramic nanoparticles. The character of changes can be determined from the micrographs of the film samples. Figure 3a shows that the grain size of the unmodified polymer is ~5 µm. The addition of corundum (dav ~ 40 nm) in an amount of 0.05 wt % led to grains diminished to 1 µm and less (Fig. 3b). The formation of a more perfect polymer structure can be explained by the fact that highly disperse polymer-insoluble substances can act as artificial seed-forming agents (structure-forming centers), whose high concentration leads to a decrease in the polymer grain size because they restrict growth of one another.

At higher degrees of filling (1 wt %), the grains are again enlarged (Fig. 3c) because the ceramic particles approach one another and form aggregates at increased amounts of modifiers. As a result, the structure-forming centers are enlarged and their number...