Solutions of Mixtures of Cellulose and Synthetic Polymers in $N$-methylmorpholine-$N$-oxide


Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninskii pr. 29, Moscow, 119991 Russia
e-mail: glk@ips.ac.ru

Received November 21, 2007;
Revised Manuscript Received July 14, 2008

Abstract—Phase state and morphological features of solutions of cellulose blends with rigid-chain thermotropic LC copolymers and isotropic poly($m$-phenyleneisophthalamide) in the highly polar donor solvent $N$-methylmorpholine-$N$-oxide are studied by DSC and polarization microscopy. The ternary phase diagram for the cellulose–copolymers–$N$-methylmorpholine-$N$-oxide system is constructed. Rheological characteristics of the prepared solutions are studied using capillary and rotary rheometers under the regimes of continuous and periodic shear deformation. Rheological characteristics of cellulose solutions with copolymers in $N$-methylmorpholine-$N$-oxide with their different phase states are shown to change in accordance with the traditional mechanism of flow for solutions with high specific interactions between their components. However, the character of the rheological behavior of mixtures of cellulose with poly($m$-phenyleneisophthalamide) in $N$-methylmorpholine-$N$-oxide primarily stems from structural–morphological transformations in solutions taking place upon deformation.

DOI: 10.1134/S0965545X09030079

INTRODUCTION

At the present time, numerous mixed composites based on synthetic polymers have been developed, and these systems have found wide practical application in various areas. However, despite evident advantages of such systems, their preparation and utilization have encountered many serious problems related to ecological requirements.

Natural cellulose should primarily be considered a promising polymer that allows efficient solution of ecological problems for composite materials, since this material is known to be inexpensive and easily reproducible in nature. This polymer can readily be subjected to biodegradation. In addition to the above advantages, cellulose is characterized by sufficiently high mechanical characteristics and relatively high hygroscopicity. Therefore, this polymer can be used for the preparation of various household and technical materials with good service characteristics (fibers, films, sponges, etc.).

Good grounds for the development of biodegradable cellulose-based composites are a new ecologically safe process of processing cellulose from its solutions in the highly polar donor-type solvent $N$-methylmor-

1 This work was supported by the program of Fundamental research, Division of Chemistry and Materials Sciences, Russian Academy of Sciences “Preparation and study of new-generation macromolecules and macromolecular structures” (project “Development of Principles for the Preparation of Nanocomposites Based on Natural Polysaccharides”).
ious polymers from the solutions of their mixtures in MMO. Preparation of mixed solutions in which cellulose and polymers are compatibilized at the molecular level, offers wide opportunities for the control over cellulose structure and development of new composites with desired characteristics by combining in one material the advantages of both polymers.

However, despite high dissolving potency of MMO, preparation of mixed solutions of cellulose with various polysaccharides and synthetic polymers requires the use of mixed dissolving systems and, hence, multicomponent precipitating agents. For example, cellulose–base composites with poly(vinylpyrrolidone) were prepared from the mixed MMO–DMSO solvent [8]. Solutions of cellulose with PA-66 were prepared by mixing of homogeneous cellulose solutions in MMO and PA-66 in the MMO–phenol mixtures (80 : 20); upon mixing, the system undergoes phase separation [9]. For the preparation of mixed solutions of cellulose with PAN, PEO, PVA, and PET, mixed solvents based on MMO with DMAA–LiCl or DMSO–n-formaldehyde were used [10].

Depending on the nature of the polymer additive, the resultant cellulose-based composite fibers show different service characteristics. For example, the addition of carboxymethylchitine, chitosan, and poly(ethylene imine) is shown to improve the fungicidal and antibacterial characteristics of the mixed fibers [11–13]. Addition of poly(ethylene imine) is known to improve dyeability of the composite fibers with respect to acid dyes. Therefore, even though there is evident progress in modifying the service characteristics of the composite cellulose-based fibers, problems related to controlling their stress–strain characteristics remain unsolved. In this connection, the results presented in [14] seemed unexpected: according to this study, composite systems prepared from single-phase mixed solutions of cellulose with aromatic polyamide, poly(2,6-dichloro-1,4-phenyolphthalimide) in MMO are characterized by the same mechanical characteristics as individual cellulose fibers. Furthermore, when composites contain less than 10% of PA, their mechanical characteristics remain unchanged; as the content of PA is increased above this level, the tendency toward fibrillization appears to even improve.

Earlier studies showed that the genesis of cellulose structure upon processing represents a very important factor that controls the structural features of cellulose and, correspondingly, the characteristics of the resultant fibers. In other words, the character of structural rearrangements upon cooling and precipitation of the polymer phase from solutions is governed by the structural features of their solutions [6, 15].

In this connection, the objective of this work is a detailed investigation of the mutual dissolution of cellulose, rigid-chain thermotropic alkylen aromatic LC copolyesters (CPEs), and isotropic aromatic PA in MMO, as well as characterization of the rheological characteristics and structural morphological features of the mixed solutions.

**EXPERIMENTAL**

In this work, we used Baikal softwood cellulose with a degree of polymerization of 600. Cellulose contains 8% water, and this level corresponds to its equilibrium sorption under normal conditions. The dissolving system was a high-melting hydrate form of MMO with $T_m = 120–160^\circ C$ (water content was 8–10%).

Other components were polar rigid-chain LC thermotropic alkylen aromatic homopolysters with mesogenic triads based on fumaric and oxybenzoic acids with hexa- and decamethylene spacers (HP-6, HP-10) and copolysters (CPE-I, CP-II) with a different content of elementary units of initial homopolysters (HP-6 and HP-10) as well as those based on terephthalic and oxybenzoic acids (PDTOB).

Along with LC polymers, we also studied the mutual solubility of cellulose and isotropic aromatic PA, poly(m-phenylene isophthalamide) (PMPIA), in MMO. Synthesis, characteristics, and temperatures of the main phase transitions of CPEs have been described in [16–18].

All mixed solutions of cellulose with synthetic polymers in MMO were prepared according to a well-known procedure involving preliminary solid–phase activation of the cellulose–MMO system in a laboratory grinder, further addition of polymer, and homogenization of the resultant three-component mixture by mechanical stirring. To inhibit thermooxidative degradation of MMO and cellulose, this system was modified with 0.5% propyl gallate. Under the parallel action of temperature and deformation (on passing through an MV-3M capillary viscometer at 120°C), solid-phase composites melt down and pass into their flow state [19, 20]. The completeness of dissolution of components in MMO was controlled by observations with a polarization microscope.

Rheological characteristics of solutions were studied on an MV-3M capillary viscometer [21] under constant stress and measurements of volume flow, as well as on a PIRSP-2 rotary viscometer [22] under continuous and dynamic deformation regimes in a uniform shear field (a cone—plate working unit). This procedure made it possible to cover a wide interval of shear rates $\dot{\gamma} = 10^{-3}$–$10^3$ s$^{-1}$ and shear stresses $\tau = 10–10^6$ Pa. The use of capillaries with a (length $L$)-(diameter $D$) ratio of 5–40 showed that the correction for input effects is small (1.0–1.5) and, for capillaries with a high $L/D$ ratio, it can be neglected. Viscosity was measured at 120°C.

To visualize the morphology of the flow of a solution during its loading and deformation, the rotary viscometer was equipped with an optical plate–plate unit.