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Shear and extensional rheological characterization of poly(acrylonitrile)/halloysite nanocomposite solutions

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ABSTRACT

The shear and extensional flow properties of polyacrylonitrile (PAN) solution in the presence of halloysite nanotubes (HNTs) were investigated at an industrially relevant concentration of the polymer. In dynamic shear rheology, the elasticity and relaxation time of PAN solutions and the availability of heterogeneous PAN domains were found to increase with HNT content. Extensional flow behavior of PAN solutions were characterized using the capillary breakup extensional rheometry and increasing the amount of HNT content in the solution was found to increase the life-time of the filament and suppress strain hardening at high strains.

1. Introduction

Halloysite nanotubes (HNTs) are hollow tubular nanostructures, made of a naturally occurring silicate. They exhibit high mechanical strength and thermal stability and even small amounts of HNTs can enhance thermal and mechanical properties of the polymeric host material [1,2]. Moreover, HNTs can be used to carry and control the release of protective agents, drugs, and bioactive chemicals in functional materials [3,4]. Due to non-existence of strong tube–tube interactions among HNTs, a uniformly dispersed morphology is usually obtained in polymer–HNT composites [4]. Therefore, they offer a great potential for industrial production of nanocomposites in terms of their processability. Lately, extensive studies on nanocomposites of HNTs with various polymers such as epoxy [5], polypropylene [6], polyamide 12 [7], and nitrile rubber [8] have underscored the use of these nanocomposites for structural and thermal applications.

Poly(acrylonitrile) (PAN), due to its high stability and specific strength, has been widely used in textile industry and fabrication of carbon fiber precursors [9–11]. Dry-jet wet spinning is the most widely used method for the production of PAN fibers [12,13]. In this process, polymer solution is extruded through a spinneret and stretched to the desired diameter in an air gap before a coagulation bath to form a stable spin-line. The filament of polymer solution is then immersed into a non-solvent bath to leach out the solvent and precipitate the polymer under tension. Due to the close relationship between processability and viscoelastic behavior of polymer solutions, understanding the rheological behavior of PAN solutions is an important milestone in processing and fiber forming technologies [9,14,15]. While documenting rheological response of polymer solutions in shear mode enables precise control of flow rates in the extrusion step of the spinning process, it cannot reproduce the behavior of the solution in the spin-line, where there are no confining surfaces and shearing components. Understanding the flow behavior of the solution in the spin-line is critical since the majority of the polymer chains are aligned in this region. Here, elongational flow controls the formation of the filament and thus, mechanical properties of the final product [16]. The flow behavior of the fluid in this region can be simulated by the capillary breakup extensional

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rheometer (CaBER). Absence of external force in the spin-line necessitates utilization of shear-free uniaxial elongational kinematics. Therefore, capillary breakup extensional rheometry can be used to monitor the thinning process and evolution of the extensional characteristics of the solutions. Indeed, qualitative description and quantitative values of extensional viscosity of polymer solutions can be extracted from the dynamics of the necking process in CaBER [17,18].

Here, we studied the effect of addition of HNTs on shear and extensional properties of PAN/dimethylacetamide solution. Since the spinnability of nanocomposites depends on the amount of loading of HNTs and high HNT content may affect the continuity of fibers [4], we focused on rheological behavior of PAN solutions with low HNT content (1–8 wt% relative to PAN content). In the first part, we characterized the rheological properties of the solution in shear mode and demonstrated the enhancement of elasticity and physical structures of these solutions. In the second part, we concentrated on the extensional response of the system. We showed that the increasing amount of HNT content in the solution improves the life-time of the filament and suppresses the strain hardening at high strains.

2. Materials and methods

2.1. Starting materials

HNT powder with a tube diameter of 20–40 nm, length of 200–600 nm, and typical specific gravity of 2.5 g/cm^3 was provided by ESAN Eczacibasi A.S. Dimethylacetamide (DMAc, $\geqslant$99%) was purchased from Merck Schuchardt, Germany. PAN powder with comonomer content of 93% acrylonitrile and 7% vinyl acetate, average molecular weight of 2.7×10^5 g/mol and molecular weight distribution (M_w/M_n) of 3.17 received by the courtesy of a fiber-manufacturer company, AKSA. HNT powder and DMAc were used without further purification; PAN powders were vacuum-dried at 70 °C for 3 days and sealed to avoid adsorption of humidity.

2.2. Sample preparation

PAN powder was initially dissolved in DMAc to obtain 1 wt% PAN solution. Different amounts of HNTs were then added to this dilute solution. These solutions were stirred for 2 h at 80 °C in sealed containers. Subsequently, polymer concentration was increased to 20 wt% by gradual addition of PAN powder to the system at 80 °C in 6 h. Finally, the mixture was subjected to additional 6 h of stirring to produce optically homogenous HNT–PAN/DMAc solutions. The solutions contained 1, 2, 4, and 8 wt% HNT (compared to PAN powder); and they are hereafter named as HNT1, HNT2, HNT4, and HNT8, respectively. The neat polymer solution is referred to as HNT0.

2.3. Characterization methods

The linear and nonlinear rheological measurements in shear mode were conducted in Anton-Paar MCR 302 rheometer with cone-plate geometry of 50 mm/2° and a gap size of 0.208 mm. After loading each sample, a thin layer of low-viscosity paraffin oil was employed around the outer edge of the platens to protect the sample from adsorption of humidity. Temperature was set to 25 °C and all samples remained uninterrupted for 60 s before starting the measurement. In steady state tests, the shear rate ranged from 0.1 to 100 s^{-1}. In dynamic regime, frequency was set to 10 rad s^{-1} and strain was changed from 0.01% to 1000% to find the range of linear viscoelastic region. For the frequency sweep tests, strain was maintained at 10% and frequency was swept from 0.1 to 100 rad s^{-1}. A new sample is used for each test.

The extensional properties of PAN–HNT solutions were assessed by using a capillary breakup extensional rheometer (HAAKE CaBER 1, Thermo Scientific, Germany) with two 6 mm-diameter plates. A fluid drop ($\sim$0.06 ml) was placed between two plates and then exposed to an extensional step strain. After establishment of the liquid bridge, the midpoint diameter ($D(t)$) was monitored as a function of time using a laser micrometer. Plate separation was changed from $L_0 = 1.99$ mm to $L_f = 12$ mm within 50 ms. Therefore, the extension rate ($\dot{\varepsilon}$) was set to 35.93 s^{-1} according to the relation $L_f = L_0 \exp(\dot{\varepsilon}t)$, where t is time (s). In order to minimize the gravitational sagging, initial separation of 1.99 mm was chosen to be less than the capillary length $L_{cap} = (\sigma/\rho g)^{1/2}$, where σ (mN m^{-1}) and $\rho = 0.99$ g cm^{-3} are the surface tension and density of polymer solution, respectively; and $g = 9.81$ m s^{-2} is the standard acceleration due to gravity. Surface tension of polymer solutions was measured to be $\sigma = 40$ mN m^{-1} in a KSV Sigma 701 tensiometer; thus, L_{cap} was calculated as $\sim$2.03 mm.

The nuclear magnetic resonance (NMR) spin–spin relaxation (T2) test was performed in a Varian Unity Inova 500 MHz spectrometer at room temperature. All measurements were performed using the pulse spacing of 5–20 ms and 23 data points were collected by sampling the echo maxima.

3. Results and discussion

3.1. Shear rheology

Dynamic strain sweep measurement was first carried out to quantify the viscoelastic nature of samples and determine the crossover strain (γ_c) from linear to nonlinear viscoelasticity. As shown in Fig. 1a, all samples showed a plateau region