Polymer 135 (2018) 39–49

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Positronium probes free volume to identify *para*- and *meta*-aramid fibers and correlation with mechanical strength

R. Ramani [a, *], T.M. Kotresh [a], R. Indu Shekar [a], F. Sanal [a], U.K. Singh [a], R. Renjith [b], G. Amarendra [b]

[a] Defence Bio-Engineering and Electromedical Laboratory (DEBEL), ADE Campus, C.V. Raman Nagar, Bangalore, 560 093, India
[b] Materials Science Group, Indira Gandhi Centre for Atomic Research, Home Bhabha National Institute, Kalpakkam, 603 102, India

ARTICLE INFO

Article history:
Received 31 August 2017
Received in revised form
20 November 2017
Accepted 23 November 2017
Available online 28 November 2017

Keywords:
Kevlar
Nomex
Nomex IIIA
Fiber
Free volume
Positron lifetime

ABSTRACT

We adopt here a novel approach to identify the *para*- and *meta*-aramid fibers using the available free volume in them. Positron Annihilation Lifetime Spectroscopy (PALS) has been employed to characterize the free volume in these fibers. The free volume content in the *para*-variety (Kevlar) is less and the free volume distribution is narrow as compared to its *meta*-counterpart (Nomex). The results are further validated by characterizing the free volume content in Nomex IIIA fibers, which is a blend composed mainly of *para*- and *meta*-aramid fibers. The free volume results are in good correlation with the mechanical properties of these fibers obtained by Universal Testing Machine (UTM), structural studies by X-ray diffraction (XRD) and storage modulus using Dynamic Mechanical Thermal Analysis (DMTA). The thermal decomposition temperature (T_d) of the fibers is characterized by thermo gravimetric analysis (TGA). We also show here the first results of an appreciable glass transition temperature (T_g) not only for the Nomex fibers but also for its blend Nomex IIIA using the combined results of Differential Scanning Calorimetry (DSC) and DMTA.

1. Introduction

Aramid fibers are a class of synthetic polymers in which the fiber forming substance is a long chain polyamide with at least 85% of the amide linkages are attached directly to two aromatic rings [1,2]. They possess excellent thermal and thermo-oxidative stability, flame resistance, superior mechanical properties and are used mainly for the preparation of ultrahigh strength materials and personal protective clothings [3–5]. The discovery, development and commercialization of such high strength and high modulus aramid fibers have attracted polymer researchers to explore their use in potential high performance applications. The poly(*para*-phenylene terephthalamide) (PPTA) is the *para*-variety of aramid fiber and differs from its *meta*-variety poly(*meta*-phenylene isophthalamide) (PMIA) in the chemical structure only in phenyl-nitrogen and phenyl-carbonyl linkage positions. This minor change in linkage position introduces significant differences in their structure and properties [6]. However, the influence of this change in linkage position on the free volume properties of these fibers has not been attempted so far, and is the nucleus of this study.

The PPTA was synthesized and its liquid crystalline properties were discovered by Stephanie Kwolek [7,8]. The lyotropic behavior of PPTA allowed the development of ultrahigh orientation fibers with outstanding tensile properties and therefore, this high temperature resistant fiber has raised considerable attention [8–10]. The PPTA fibers show specific strength that are superior to their inorganic counterparts like glass and carbon fibers and are marketed by M/s. Du Pont in the name 'Kevlar' [1]. Microstructural investigation of PPTA fibers has revealed that on account of intermolecular interactions between sequential phenyl and amide segments in the chain, free rotations around the phenyl-carbonyl and phenyl-nitrogen bonds are absent [11]. This particular nature of the chain essentially accounts for its structural rigidity and hence they are regarded as rigid rods. This makes it difficult for the polymer chains to form a folded structure and thus exists in the form of stacked sheets [1,12,13]. The increased strength of PPTA is also attributed to its greater degree of conjugation, more linear geometry of the *para*-linkages together with greater chain orientation derived from high crystallinity [13]. Because of their outstanding

* Corresponding author.
E-mail address: ramanir70@rediffmail.com (R. Ramani).

https://doi.org/10.1016/j.polymer.2017.11.064
0032-3861/

mechanical properties, these fibers find increased use in the field of structural composites for aerospace and other reinforcement applications (predominantly in defence sector), where performance to weight ratio is a concern [1,14,15].

The *meta*-aramid is marketed by M/s. Du Pont as 'Nomex' and plays a vital role in the field of thermal and electrical insulation [1,12,16]. The PMIA is also a fibrous polyaramid that has excellent thermo-oxidative stability, high strength and high radiation resistance but has much lower tenacity and modulus compared to PPTA [1,12,16]. Also, physically, they are softer and more textile-like than PPTA fibers. As mentioned earlier, they differ from PPTA in their molecular structure by having benzene-amide linkages in the skeletal chain at the *meta*-position. This small difference in molecular structure changes the optimal bond angles of phenyl-nitrogen and phenyl-carbonyl bonds resulting to a 'crumpled' chain structure that cannot be crystallized into stacked sheets. This causes the *meta*-variety to take a 'jungle-gym' structure, with randomly stacked polymer chains, and thus results to lower crystallinity compared to *para*-aramid [12,17]. More importantly, the high temperature integrity of *meta*-aramid results from a unique mechanism of flame resistance in the fiber [16,18].

But when used in protective clothing applications, the Nomex fiber would shrink upon experiencing temperatures above its glass transition temperature (T_g, the details of which are provided in sections 3.5 and 3.6) threshold causing it to tear [1]. This would expose the wearer to direct flames causing serious injuries. With decades of extensive studies on structure, morphology, strength as well as structure property relationship on PPTA and PMIA aramids, M/s. Du Pont has also introduced 'Nomex IIIA' which is a blend of 93% Nomex, 5% Kevlar and 2% Antistatic fiber (Belltron) [16]. Fabrics made of Nomex IIIA are thermally stable and extremely durable, especially when compared to other flame retardant (FR) materials such as flame retardant treated (FRT) cotton fabrics, FR viscose and FR nylon. With the unique combination of textile and thermal properties, Nomex IIIA fiber has gained significance and is used in a broad range of thermal protective apparel applications, primarily in defence sectors, wherever the risk of fire or electric arc exposures is present [16]. Since Nomex being the major constituent of this blend, this fabric can also tear when exposed to temperatures above its T_g threshold. However, the presence of low shrinkage *para*-aramid (5%) as one of the constituents in the blend provides improved structural stability for Nomex IIIA as compared to Nomex and prevents it to tear [1,16].

It is an established fact that the physical properties of macromolecules depend on their structural characteristics and available nano-voids (free volumes) at the molecular level [1,19]. The microstructure of aramid fibers have been studied in the past using microscopy techniques such as TEM [20], SEM [3,20], STM [6,21], AFM [3,6,22], as well as using diffraction methods like X-ray [5,8,23,24] and Neutron diffractions [25], methods such as X-ray photoelectron spectroscopy [21] and more recently using Solid State NMR [4]. The density of PPTA fiber is 1.44 g/cm^3 as against its crystalline density of 1.48 g/cm^3 and the absence of amorphous phase in the fiber gives the first indication for the possible presence of voids [26]. In case of ordered structures such as PPTA fibers, the defect points at the end of the molecular crystallites that are vulnerable to mechanical damage may probably constitute free volumes [27,28]. Techniques like TEM directly identified the nanovoids using the stains of AgS deposition into these voids [20]. Small angle X-ray Scattering (SAXS) also indicated the presence of nanovoids in aramid fibers [26].

Only few of the techniques like X-ray diffraction (XRD) [5,8,13,14,29,30], Thermogravimetric Analysis (TGA) [3,6,31–33] and Universal Testing Machine (UTM) [1,30] are commonly being employed to distinguish the *para*- and *meta*-varieties of fibers. Based on the structures of *para*- and *meta*-varieties of aramid fibers briefed above, it is anticipated that their different geometries and the structure might lead to different molecular packing and hence different free volumes in them. Additional motivation towards this work stems from the distinction of *para*- and *meta*-varieties reported in polyimides and other polymers based on the free volume changes in them [34–37].

It is now widely recognized that molecular mobility of a polymer is primarily dependent on the available free volumes in them. The free volumes in polymers arise due to irregular packing and topological constraints [19,38]. In the past three decades, Positron Annihilation Lifetime Spectroscopy (PALS) has extensively been used to probe the nanostructure of polymers in terms of free volume size, fractions and distributions [19,39,40]. The unique nature of the Positronium (Ps) probe and its specific localization in the free volume holes of polymers can provide useful information in this domain that is otherwise unachievable using conventional methods [19]. PALS has also been successfully used in the past for the study of different polymers [19], polymer blends [39], composites [40], liquid crystalline materials [41] and fibers [42,43]. Doppler broadening of the annihilation radiation (DBAR) gives the electron momentum distribution at the site of annihilation and serves as a supplementary tool to PALS in free volume characterization [19,39]. Herein, we have used PALS together with DBAR technique to characterize the free volumes in *para*- and *meta*-aramid fibers and their blend. More details regarding PALS and DBAR techniques can be found from literature [19,44]. The free volume results of the fibers obtained in the present studies have been correlated with their mechanical properties obtained by UTM and the fiber structures are studied using XRD method.

Another interesting aspect of the present work is that although many thermal studies have been reported on the Nomex fibers [6,18,45] and to a less extent on its blend [46], surprisingly no clear thermograms were shown to unequivocally prove the obtained glass transition temperature (T_g). The results reported herein using the combined Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA) will throw more light on the T_g behavior of these fibers.

2. Experimental

2.1. Sample details

The fibers used in this study were of commercial grade PPTA (Kevlar-29), PMIA (Nomex-430) and Nomex IIIA (Nomex type 462; herein after referred to as N-IIIA). PPTA and PMIA are obtained from M/s. Du Pont in the form of continuous filament yarns while N-IIIA is a spun yarn also from M/s. Du pont. The N-IIIA blend has a composition of *meta*-aramid fiber 93%, *para*-aramid fiber 5% and Belltron 2% (organic conductive polyamide fiber that provides antistatic property). The Belltron has a composition of carbon black (3–4 wt%) as core and Nylon 6 (96–97 wt%) on the outer cover. They were washed with methanol (for 12 h) and distilled water (12 h) at room temperature to remove fiber lubricants and impurities, if any. The samples were first air dried for 48 h and then dried in vacuum oven at 80 °C for further 12 h. They were kept in a desiccator before their use in experiments. The chemical structure of PPTA and PMIA are shown in Fig. 1.

2.2. Characterization

2.2.1. Universal Testing Machine (UTM)

The breaking strength measurements were conducted by UTM (model Zwick/Roell Z100, Germany) using fabric samples of 500 mm length and 50 mm width and the results reported here are