

FTIR SPECTROSCOPY OF DRAGLINE SILK OF *Cyrtophora citricola* (FORSKAL, 1775) FROM FAMILY ARANEIDAE**Satyavijay S. Dhande**

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Abstract

The ability of spiders to synthesize and use silk for a variety of purposes makes them unique. Since spider silks are known for having superior tensile strength, extensibility, and biodegradability, factors influencing their structure need to be investigated. This attempt was made to investigate the functional groups in the stretched and unstretched dragline silk fiber of spider *Cyrtophora citricola* (Forsk., 1775) from the family araneidae. The silk samples were periodically collected from the leaves and branches of herbs, shrubs and plants of residing fences close to the agro-ecosystem in and around Akola district, Maharashtra. A number of well-defined peaks were obtained in the range of 600-4000 cm^{-1} . All the silk types show protein peaks in the Amide I (1600-1700 cm^{-1}).

Keywords: Spider dragline silk, Araneidae, FTIR spectroscopy, agro-ecosystem.

Introduction

The family Araneidae include 198 genera and 3160 number of described species (world spider catalog, 2025). The spider from family araneidae weave orb web consists of silk polymeric protein. Silk proteins (Spidroins) produced by the six different spider silk glands and generally have relatively high molecular weights of 200 K to 350 K (Susan K. Robinson, Utah state university). The spider silk has an elastic nature and higher tensile strength due to presence of proteins like Spidroin I and Spidroin II. The Spidroin I and Spidroin II protein contains repetitive sequence of amino acids like Glycine (40%) and Alanine (29%). The Glycine provides elasticity to the spider silk. The spider produces silk is used for different purposes like spinning web, catching of flying insect, and for self-protection. The exact composition of these Spidroin proteins is depends on the type of species, diet and its environment. The spider silk gland are acquired to produces different type of silk that perform different functions like resting, hiding, feeding, protection of egg sacs (Foelix, 2011). The spider spinnerets silk fiber performs important function to carry the weight of spider and paralyze the pray by wrapping it with the help of silk fibers at the time of feeding. Spiders are evolved to constructs horizontal web that help them to catch insect flying in horizontal direction. Silk fibers are very sensitive to movement. When the flying insect hit the silk web the spider must be able to reach it quickly before it escapes. Spider can run fast downwards than upwards, hence orb web has more area down to the hub and central disc so that top-down asymmetry is found. The hub is present in the centre of the upper part of the web (Vollrath *et al.*, 1997). Many of the spider species construct cease in the web to keep killed pray and feed on the insect in starvation. The silk used for cease protect the killed insect. The protein Spidroins in the silk are composed of polypeptide molecules containing

alpha helices and beta sheets that provide more elasticity and extensibility than rubber and provide more tensile strength and make more stronger than steel. The increase in temperature or change in the P^{H} can denature the protein folding that intern changes the three-dimensional structure and function of the protein in the silk. Environmental conditions such as reeling speed can affect silk properties (Madsen *et al.*, 1999; Riekel *et al.*, 1999). In FTIR (Fourier transform infrared) spectroscopy the molecules once interact with the infrared radiations, the incident radiations are absorbed by a molecule in the silk fiber in particular wavelength. The molecules give vibrations that intern produces absorption spectrum. The absorption spectrum provides information of different functional group present in the spider silk fiber. Humidity is the important factor responsible to alter the mechanical properties of spider silk. Dew and rain will lead spider dragline fibers to shrink significantly (up to 50 % of its initial length) and restrained silk generates stresses in excess of 50 MPa (Work 1981; Bell *et al.* 2002; Pérez-Rigueiro *et al.*, 2003; Boutry and Blackledge 2010). This process is known as super contraction (Work 1977, 1981).

Materials and Methods

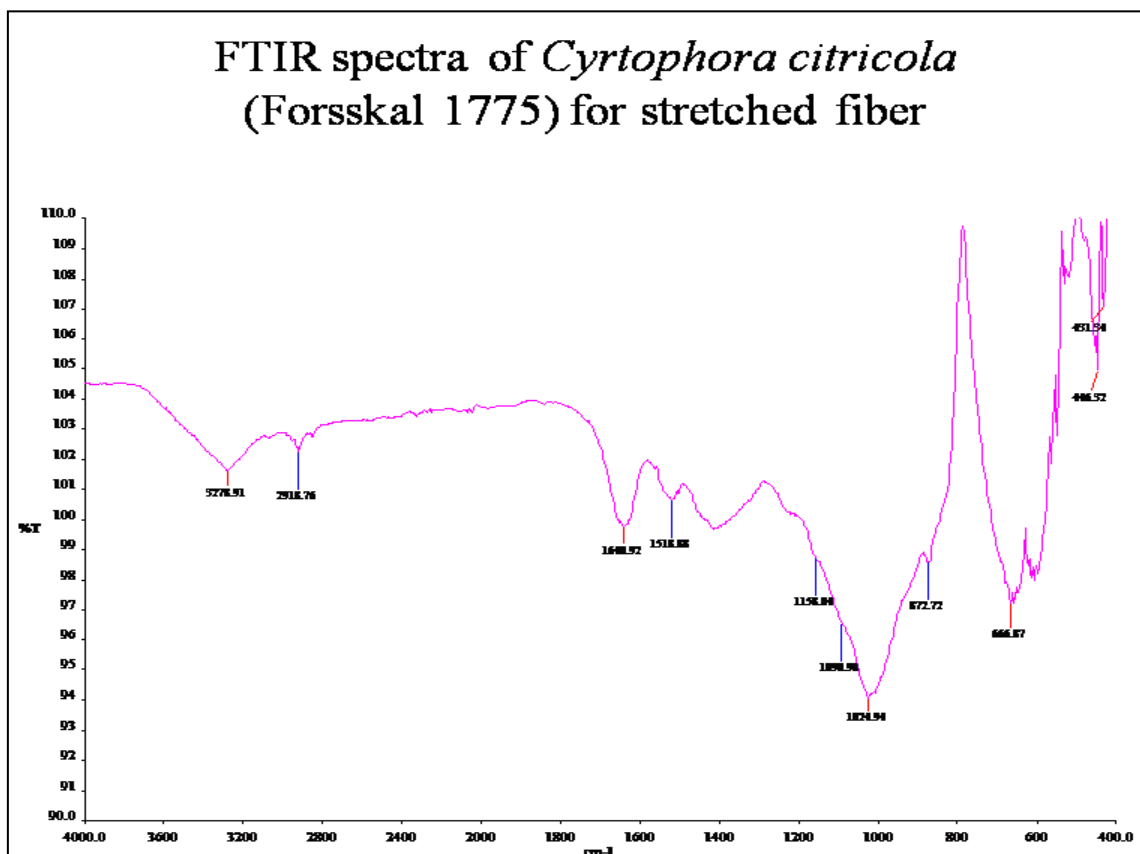
The dragline silk samples were periodically gathered from the leaves and branches of shrubs, herbs and plants of living fences near the agro ecosystem in and around Akola district, Maharashtra. The spider specimen from the web were also collected and identified by under Carl-Zeiss Stemi 2000c stereo zoom microscope referring to the morphological descriptions and illustration given by Levi (1997) and Gajbe (2007). The genital your dissected in 10% KOH solution until get clear and observed under microscope. All the identified spider species with their silk type were grouped and later on Fourier transmission

infrared spectroscopy (FTIR) of the clean and strong silk fiber were done at National chemical laboratory Pune India. They have rimmed all the

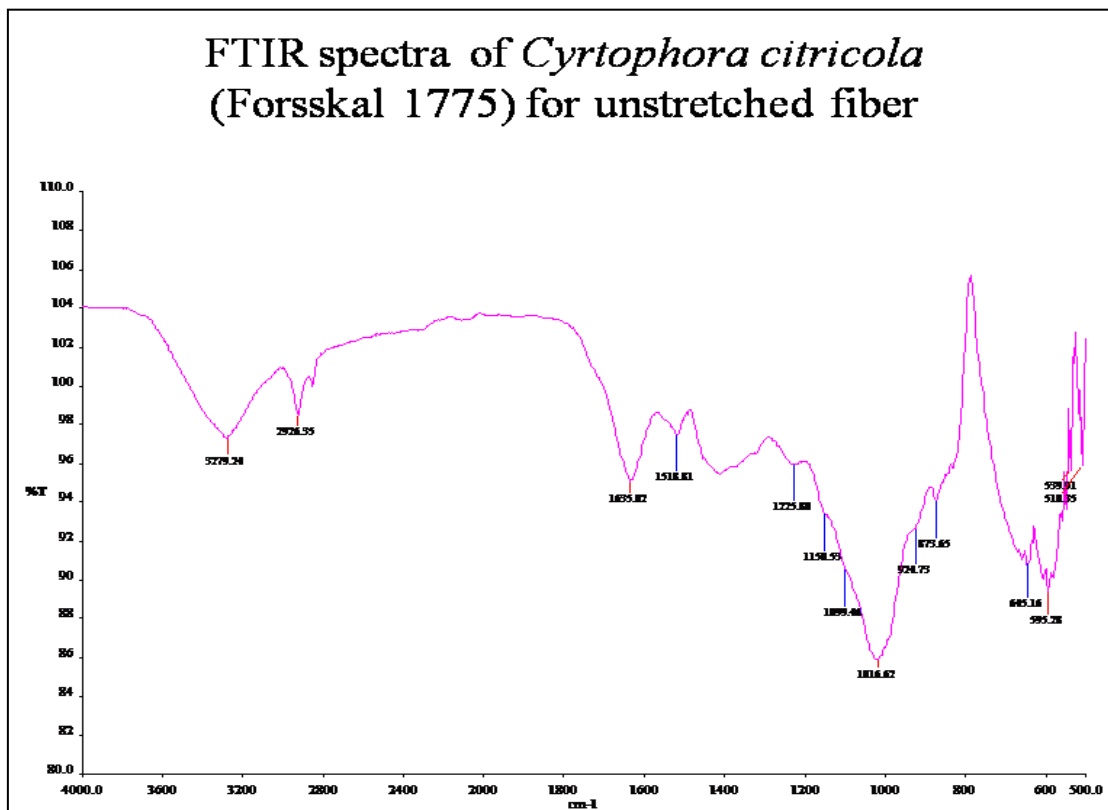
silk samples on ATR attenuate transmittance resonance mode. The FTIR instrument were spectrum GX from Pe Perking Elmer.

FTIR absorption values for spider silk samples				
Peak range cm ⁻¹	Assignments	Spider silk		Remark
		stretched	unstretched	
643-967	-	666.87	645.16	Absorption due to vibration of alpha helix structure
1015-1032	-	1024.94	1016.62	Absorption due to bending
1140-1492	N-H amide II	1158.04	1150.53	Absorption due to bending vibrations
1500-1600	Tyr-OH	1518.88	1518.81	Absorption due to tyrosine ring -OH vibrations
1600-1700	Protein amide	1640.92	1635.02	Frequency peaks or (wave number peak) due to beta sheet
2941-2946	O-H, C-H	2918.76	2926.35	O-H bond formation/ salt formation and C-H stretching
3297-3300	O-H, N-H	3278.91	3279.24	Hydroxyl group/ N-H Stretching

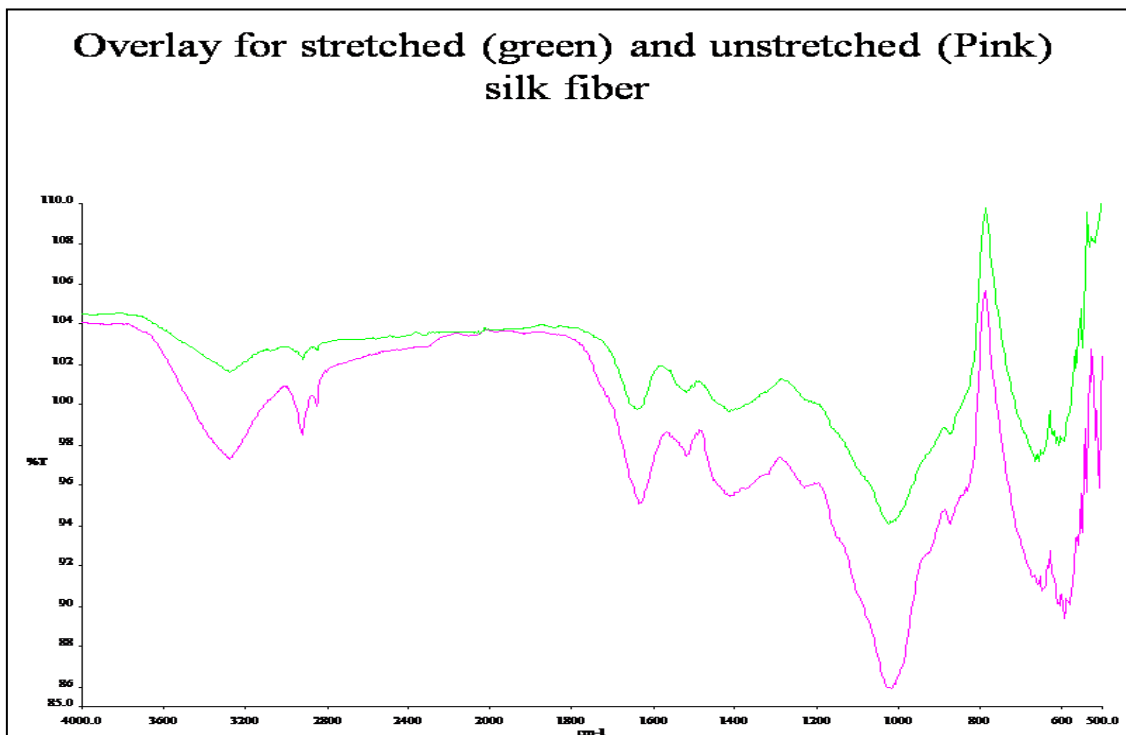
Table 1. FTIR absorption values for spider silk samples



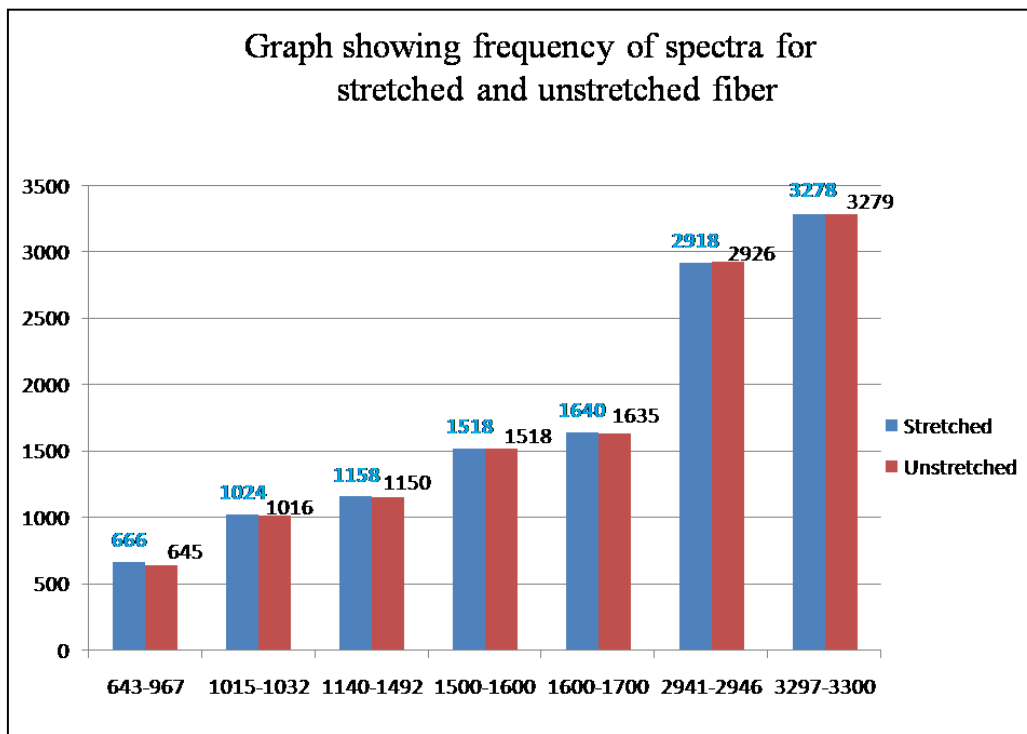
Graph-1 FTIR spectra of *Cyrtophora citricola* (Forsskal, 1775) for stretched fiber



Graph-2 FTIR spectra of *Cyrtophora citricola* (Forsskal, 1775) for unstretched fiber



Graph- 3 Overlay for stretched and unstretched silk fiber



Graph-4 Graph showing frequency (cm⁻¹) of spectra obtained from stretched and unstretched spider silk fiber.

Results and Discussion

FTIR spectroscopy of spider *Cyrtophora citricola* (Forskal, 1975) was recorded for stretched and unstretched silk fiber. As detailed in Table 1, a number of well-defined peaks are obtained in the range of 600-4000 cm⁻¹. All the silks show protein peak in the Amide I (1600-1700 cm⁻¹) and Amide II (1500-1600 cm⁻¹) range. The amide group in protein and polypeptides give specific vibration band in UV spectra. The spider silk (in unstretched sample) shows a peak at around 1635 cm⁻¹ due to presence beta sheet. The frequency peak (in stretched sample) is at around 1640. This frequency peak (in the stretched sample) is due to unordered secondary structure of protein. Below 1200 cm⁻¹, spider silk fiber exhibit frequency peak at 1024 cm⁻¹ (stretched), 1016 cm⁻¹ (unstretched), 1158 cm⁻¹ (stretched) and 1150 cm⁻¹ (unstretched) due to bending vibrations. In addition, spider silk exhibits a frequency peak at 1518 cm⁻¹ due to tyrosine ring -OH vibrations (according to Venyaminov and Kelnin, Biopolymers 1990). The spider silk fiber exhibit frequency peak at 2918 cm⁻¹ (stretched) and 2926 cm⁻¹ (unstretched) for salt formation and C-H stretching. The spider silk fiber exhibit frequency peak at 3278 cm⁻¹ (stretched) and 3279 cm⁻¹ unstretched for N-H stretching. It has observed that the spider *Cyrtophora citricola* (Forskal, 1975) have rich protein content according to the FTIR assignments. It can also be concluded that Hierarchical structure and greater properties of

natural fibers can give significantly varying responses depending on spider species, their feeding, feeling, natural environment and conditions, etc.

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