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RESEARCH ARTICLE

Ambient Air Ageing Effect on Vapour-Chopped Polyaniline Thin Film Optical Waveguide for Integrated Optics

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ABSTRACT: Polyaniline (PANI) was synthesized initially as a powder in an acidic medium by oxidation polymerization and used for vacuum evaporation on an optical flat glass substrate. This paper reports the effect of ambient air ageing (30 days at room temperature) on optical, mechanical and optical waveguide transmission loss properties of PANI thin film. The vapour chopping technique was successfully used for reducing the optical transmission loss, refractive index, intrinsic stress and increasing adhesion of the waveguide film. Both (as-deposited and vapour-chopped) thin films showed oxime-type PANI structure after ageing. The vapour-chopped film (2.45 - 3.69 dB/cm) showed a small optical transmission loss change as compared to the as-deposited thin film waveguide (3.18 - 5.08 dB/cm) after ageing. The air ageing caused to increase in refractive index, optical transmission loss and a decrease in adhesion and intrinsic stress but the effect was found to be lesser in vapour-chopped PANI thin film.

Keywords: Polyaniline thin film, vapour chopping, Air ageing, Optical transmission loss, Optical properties

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1. INTRODUCTION

Integrated optics stands as the pinnacle of optical technology, amalgamating various optical devices and components onto a single substrate for functions such as signal generation, splitting, coupling, switching, modulation, and detection. In essence, optical waveguides act as the conduits, connecting these components, and collectively, they form the optical counterparts of integrated circuits [1]. The demands of such integrated optical networks necessitate a diverse array of material systems to meet the unique requirements of these constituent optical devices [2]. At the forefront of this pursuit lies the quest for robust materials capable of serving as the foundation for optical signal sources, modulators, switches, waveguides, and receivers.

Polyaniline (PANI), an electroactive conjugated polymer, emerges as a promising candidate owing to its remarkable physical and chemical properties, coupled with its adaptability to tailor these properties to suit the needs of integrated optical devices [3]. Demonstrating properties akin to light-emitting diodes [4], electrochromism [5], and photovoltaics [6], PANI offers the potential to design a gamut of integrated optical devices, ranging from signal sources to modulators, switches, and detectors. However, despite its versatility, the exploration of PANI as an optical waveguide remains relatively uncharted, with scant reports on its optical wave-guiding capabilities [7].

In this context, the present study endeavors to delve into the optical wave-guiding properties of PANI and to enhance them through the innovative application of the vapour chopping technique. The transmission loss within optical waveguide thin films is contingent upon factors such as refractive index, mechanical properties, and environmental influences [8]. Consequently, the synthesis of PANI powder via an oxidation polymerization pathway in an acidic medium lays the groundwork for its deposition via vacuum evaporation onto glass substrates.

Central to this investigation is the exploration of the

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ambient air aging effect on the optical, mechanical, and transmission loss properties of PANI wave-guide thin films. Over a span of 30 days, with measurements taken at 10-day intervals, the impact of ambient air aging is scrutinized, shedding light on its implications for PANI thin film performance. Furthermore, the study extends its purview to evaluate the efficacy of the vapour chopping technique in mitigating the deleterious effects of ambient air aging on PANI thin films, presenting a comprehensive analysis of its outcomes.

This study not only ventures into uncharted territories by exploring PANI as a potential material for optical waveguides but also pioneers novel methodologies to enhance its performance, thus contributing to the advancement of integrated optics and paving the way for the development of more resilient and efficient integrated optical networks.

2. EXPERIMENTAL DETAILS

PANI powder was synthesised by oxidation polymerisation pathway. Here aniline monomer was oxidized by ammonium peroxidisulphate (APS) in an acidic medium which resulted in PANI salt. PANI salt powder was deprotonised in an ammonia solution to get base powder after filtering, washing and drying in a vacuum. This PANI base powder was used for vacuum evaporation (resistive heating using a tantalum boat at 10^{-4} Torr) on a glass substrate.

The vapour chopping technique consists of a circular metallic vane of 10 cm diameter with a V-cut (1550) shape. This circular metallic vane is connected to the shaft of a 6 V DC motor having a broad base by the aluminium rod. The variable power supply of 0-6 V (DC) was used to vary the voltage using which the speed of rotation can be controlled and hence the chopping speed [9]. The rate of chopping in this study was ~5-6 rot\s. The structural, optical and mechanical properties of as-deposited and vapour-chopped fresh PANI (acidic) thin film have been reported in previous papers [10].

For the air ageing study, the films were kept in an air atmosphere for 30 days at room temperature and measured optical, mechanical and transmission loss properties for 10 days. The optical transmission loss was measured by the prism coupling technique [11]. The set-up consists of a He-Ne laser (632.8 nm), spectrometer, polarizer, two special right-angled prisms (refractive index 1.717), prism mount and detector. The prisms were kept at 1.5 cm from each other. Only the lowest mode m=0 has been studied. Precise adjustment of the angle of incidence for obtaining m=0 mode was done. The input light intensity was measured at the region of the coupling spot where the actual launching into the waveguide takes place. The output intensity was measured in terms of current through a photodiode.
The thickness of the film was ~150 nm as measured by the Tolansky interferometer method [12]. The refractive index was measured by Abele's method [13]. The adhesion was measured by the direct pull-off method and intrinsic stress by interferometer technique [14].

3. RESULTS

3.1. Structural properties

Figure 1 shows the FTIR spectra of fresh and air-aged (30 days) as-deposited and vapour-chopped PANI thin films. The FTIR spectra of both (as-deposited and vapour-chopped) fresh thin films have been reported in previous reports [10]. It is seen that both the films show a peak at 1650 cm^{-1} but the peak intensity is more prominent in as-deposited films as compared to vapour-chopped films. In as-deposited films after ageing, the peak intensity ratio of 1590 to 1500 cm^{-1} is increased as compared to fresh film which is not observed in vapour-chopped thin films. The as-deposited fresh film showed a peak at 1105 830 with 749 cm^{-1} more prominent in as-deposited films. The vapour-chopped film shows less change in FTIR peak as compared to as-deposited films.

3.2. Refractive index

Table 1 shows the refractive index values of as-deposited and vapour-chopped thin films after ageing. Both (as-deposited and vapour-chopped) thin films showed high refractive index values with an increase in ageing time. The as-deposited film showed an increase in refractive index from 1.823±0.003 to 2.052±0.003 whereas the vapour-chopped film showed from 1.717±0.005 to 1.874±0.004. It is seen that the refractive index of the vapour-chopped thin film is comparatively smaller than the as-deposited films.

As we have seen above, all the films showed an increase in the refractive index but to know the trend of increase in refractive index is also important. Figure 2 shows the graph of variation in refractive index (Delta 'n') with respect to ageing time for both (as-deposited and vapour-chopped) PANI thin films.

It is seen that both the film (as-deposited and vapour-chopped) show a gradual negative increase in "Delta 'n'" values with an increase in ageing time which is due to the films after ageing have higher refractive index values as compared to fresh films. Delta 'n' value was gradually increased up to 20 days but then it tends to remain constant. The ageing effect was found comparatively lesser in vapour-chopped PANI waveguide thin films.

3.3. Mechanical properties

The durability of the film mainly depends on the adhesion and intrinsic stress properties of the film. The adhesion and intrinsic stress values of as-deposited and vapour-chopped PANI thin film is tabulated in Table 2. The values in the table are the average of five samples.

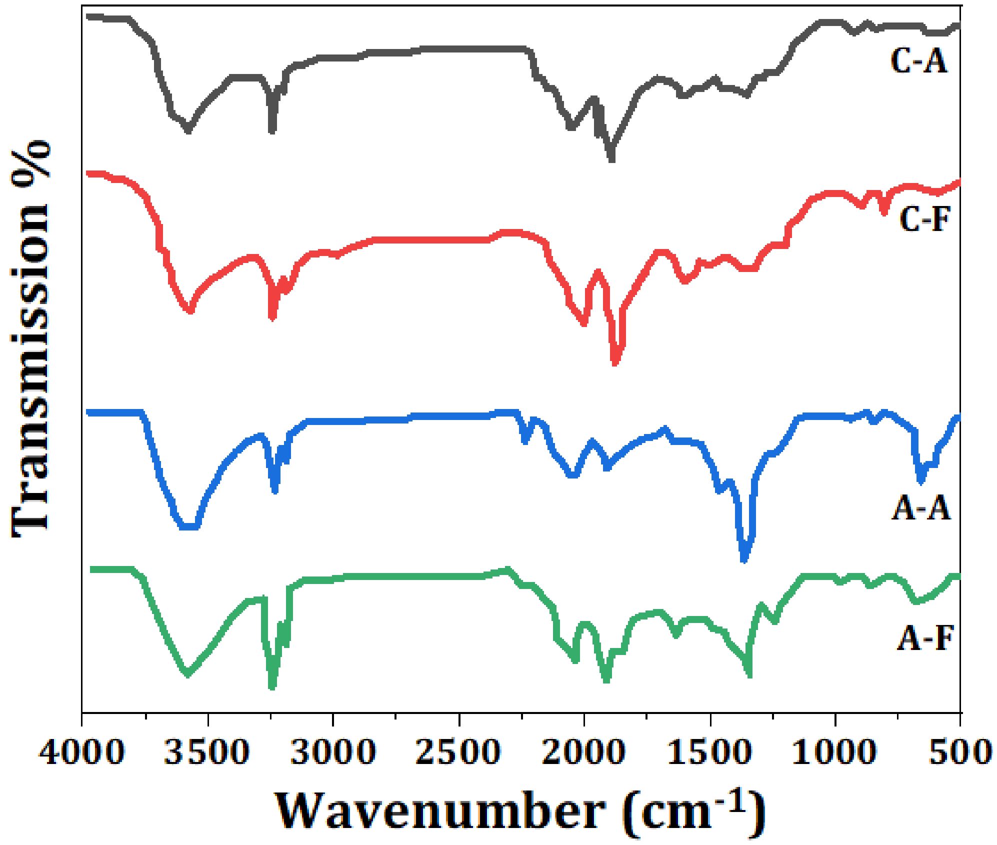

Fig. 1. FTIR spectra of both the fresh (A-F and C-F) and air-aged (A-A and C-A) as-deposited and vapour-chopped thin films.

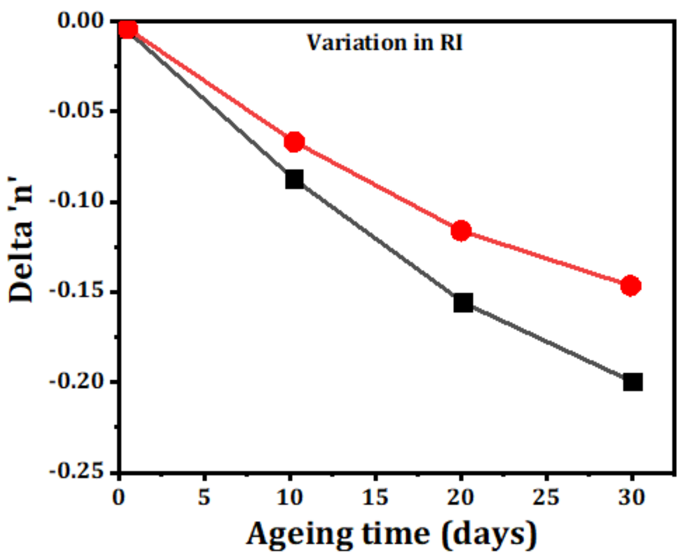

Fig. 2. Variation in refractive index Vs ageing time of both as-deposited (●) and vapour-chopped thin films (■).

3.3.1 Adhesion

From the table, it is seen that all the films showed a decrease in adhesion with an increase in ageing time. The vapour-chopped film showed an increase in adhesion from 907±3 × 10^2 to 878±4 × 10^2 (N/m^2) whereas in as-deposited film from 635±4 × 10^2 to 590±4 × 10^2 (N/m^2). The vapour-chopped film showed small adhesion as compared to as-deposited films and also showed small change with an increase in ageing time.

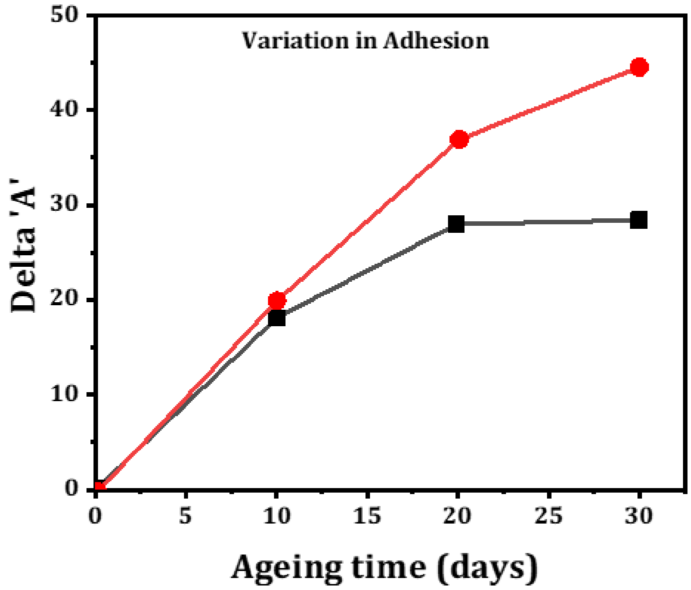

Fig. 3. Variation in Adhesion values (Delta ‘A’) Vs ageing time of both as-deposited (●) and vapor-chopped thin films (■).

Figure 3 shows the variation in adhesion (Delta 'A') as a function of ageing time for as-deposited and vapour-chopped thin films. It is seen that both (as-deposited and vapour-chopped) the film showed a gradually positive increase in "Delta 'A'" with an increase in ageing time. The adhesion was found higher in fresh films than in air-aged films hence the graph showed a positive change in "Delta 'A'" values. Initially both the films (as-deposited and vapour-chopped) showed very small differences in Delta 'A' values but the difference increased considerably with an increase in ageing time. After 20 days, the vapour-chopped film showed very negligible change as compared to as-deposited films. The ageing effect was found comparatively very small in vapour-chopped thin films.

3.3.2. Intrinsic stress

Table 2 shows the intrinsic stress values of both the as-deposited and vapour-chopped PANI thin films after ageing. Both the films (as-deposited and vapour-chopped) showed an increase in intrinsic stress value with an increase in air ageing time. The intrinsic stress value of as-deposited film increased from 16.64±0.08 × 10^8 to 16.37±0.07 × 10^8 N/m^2 whereas in vapour-chopped films it increased from 13.25±0.06 × 10^8 to 13.18±0.07 × 10^8 N/m^2 with increase in ageing time. The ageing effect was found lesser in vapour-chopped films.

Figure 4 shows the graph of variation in intrinsic stress (Delta 'S') for air ageing time. Both the films (as-deposited and vapour-chopped) showed an increase in Delta 'S' value with an increase in ageing time. Delta 'S' values are positive because the fresh film has higher intrinsic stress. The vapour-chopped thin films showed very small values of Delta 'S' which is nearly equal to the experimental error of measurement. The as-deposited films showed an increase in Delta 'S' value with an increase in ageing time. But after 20 days it remained constant. The vapour-chopped film showed lesser change than those in as-deposited film.

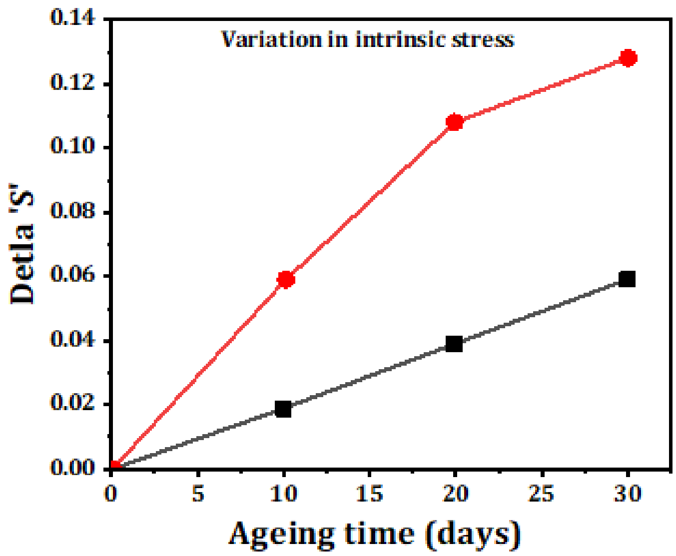

Fig. 4. Variation in intrinsic stress values (Delta 'S') Vs ageing time of both as-deposited (●) and vapour-chopped thin films (■).

3.4. Optical transmission loss

Table 3 shows the optical transmission loss values of deposited and vapour-chopped PANI thin films after ageing. Both the films (as-deposited and vapour-chopped) showed an increase in optical transmission loss with an increase in the air ageing time. The as-deposited film showed an increase in optical transmission loss from 3.18 to 5.08 dB/cm and that of vapour-chopped films from 2.45 to 3.69 dB/cm. The vapour-chopped film showed lesser change.

Figure 5 shows the optical transmission loss (Delta 'TL') of as-deposited and vapour-chopped thin films with respect to air ageing time. It is seen that both the films (as-deposited and vapour-chopped) show a negative increase in the "Delta 'TL'" value and an increase in ageing time. The negative Delta 'TL' indicates that the air-aged film have a higher value of optical transmission loss than the fresh films. The vapour-chopped film showed lesser change.

Table 1. Refractive index of deposited and vapour-chopped thin films after ageing.

Ageing time (days)	Refractive index	
	As-deposited	**Vapour-chopped**
Fresh	1.823±0.003	1.717±0.005
10	1.938±0.004	1.786±0.003
20	1.987±0.005	1.834±0.003
30	2.052±0.003	1.874±0.004

Table 2. Adhesion and intrinsic stress of as-deposited and vapour-chopped PANI thin film after ageing.

Ageing Time (Days)	Adhesion ($\times 10^2$ N/m^2)		Intrinsic Stress ($\times 10^8$ N/m^2)	
	As-deposited	Vapour-chopped	As-deposited	Vapour-chopped
Fresh	635±4	907±3	16.64±0.08	13.25±0.06
10	615±4	889±4	16.58±0.06	13.23±0.05
20	598±5	879±5	16.55±0.07	13.21±0.05
30	590±4	878±4	16.37±0.07	13.18±0.07

Table 3. Optical transmission loss of as-deposited and vapour-chopped thin films after ageing.

Ageing Time (days)	Optical transmission loss (dB/cm)	
	As-deposited	Vapour-chopped
Fresh film	3.18±0.05	2.45±0.03
10	4.14±0.04	3.04±0.04
20	4.59±0.02	3.34±0.03
30	5.08±0.05	3.69±0.04

4. DISCUSSION

The FTIR spectra of both (as-deposited and vapour-chopped) films after ageing showed a peak at 1650 cm^{-1} which indicates the presence of oxime-type PANI structure [15]. The growth mechanisms in vacuum-evaporated PANI thin films and inorganic thin films are different. In vacuum-evaporated PANI thin films, it is difficult to evaporate chain segments with more than five or six aromatic rings but in thin films, they are observed as supermolecules of high molecular weight. The evaporated chain segments when reached on the substrate undergo cross-linking and thus increase the molecular weight [16]. However, some of these active oligomers remain as it is in the film. These active oligomers interact with the environmental active gases which causes them to change the film properties. The oxime-type PANI structure is the result of the interaction of active oligomers in the film with environmentally active gasses. However, the peak was observed more prominent in deposited film hence it has a more oxime-type structure as compared to vapour-chopped films.

The vapour-chopping technique gives more time for evaporated oligomers to interact with each other and settle uniformly on the substrate which causes a reduction in voids and achieves a highly compact film structure. Thus, the film gets a minimum surface area open to the environment and also less number of active oligomers to interact. Hence the vapour-chopped film showed a small change in film properties as compared to as-deposited films.

Both the as-deposited and vapour-chopped PANI thin films after ageing showed an increase in adhesion, and intrinsic stress and a decrease in refractive index and optical transmission loss. The film properties were found to diverge due to the interaction of the film material with environmentally active gasses.

The peak at 1590 cm^{-1} was observed for nitrogen quinone (Q) and 1500 cm^{-1} for benzoid (B) deformation. The intensity ratio of peaks 1590–1500 cm^{-1} gives quantitative information about the oxidation state of the PANI. The decreased intensity of 1500 cm^{-1} in as-deposited film (after ageing) indicates the presence of a more oxidized PANI structure [17].

According to Dillingham et. al. [18] the vacuum-evaporated film undergoes oxidation in between leucoemeraldine and emeraldine state in the air atmosphere, which causes to change in optical absorption spectra. The refractive index of the film depends on the difference between the experimental optical wavelength (wavelength at which the refractive index is measured) and the minimum absorption wavelength of the film [19]. The experimental optical wavelength is 590 nm and the minimum absorption wavelength of PANI thin film is around 340 nm. Due to the oxidation, the peak shifts towards the higher wavelength. Thus the wavelength difference is reduced and causes to increase in the refractive index. The refractive index was found to be higher in as-deposited film due presence of the more oxidized structure as compared to vapour-chopped thin films.

The optical transmission loss was found to increase with ageing time. The increase in refractive index and scattering of the beam as it passes through the guided structure at the interface is also another reason for to increase in optical transmission loss. The vapour-chopped films showed lesser optical transmission loss as compared to the as-deposited film which is due to less oxidized structure, uniform surface morphology and less number of voids present in the waveguide structure. The vapour-chopped film showed uniform surface morphology. The effect of vapour chopping on the adhesion, intrinsic stress and optical transmission loss has been also reported for oxide thin films [11, 20-21].

The adhesion and intrinsic stress was found to be decreased with increase in air ageing time. This might be due to the interaction of air molecules with film material which causes the decrease in intermolecular bonding between PANI oligomers present in the film and also decreases the bonding in-between film and substrate at the interface. In as-deposited films, the presence of more voids and uneven surface morphology gives more surface area to interaction with environmental gasses hence showing more change in mechanical properties as compared to vapour-chopped films.

4. CONCLUSION

PANI powder was synthesized in an acidic medium and vacuum evaporated for a thin film optical waveguide and studied air ageing effect on film properties. Both films showed oxime-type PANI structure after ageing but it was found more in as-deposited film as compared to vapour-chopped thin films. Due to air ageing the refractive index, and optical transmission loss were found to be increased while adhesion and intrinsic stress were decreased. The vapour chopping technique was successfully used to reduce the air ageing effect on film properties. This method is an inexpensive and very simple technique to produce high-quality films for optical waveguiding purposes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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