<연구논문(Original Articles)>

Preparation of Polymer Thin Films of Pentafluorostyrene via Plasma Polymerization

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Abstract: Polymer thin films of pentafluorostyrene (PFS) were prepared by RF plasma (13.56 MHz) polymerization in continuous wave (CW) mode, as a function of plasma power and monomer pressure. Conditions for film preparation were optimized by measuring the solvent resistance of plasma polymer thin films in DMAc, NMP, THF, acetone and chloroform, as well as by evaluating the optical clarity via UV-VIS measurements. Pulsed mode plasma polymerization was also utilized to enhance the optical properties of the films by varying the period of on-time and duty cycle. Finally, the films were subjected to refractive index measurements and analyzed by α-step, TGA and FT-IR.

1. Introduction

During the past decade, polymer thin films have received great attention in the area of electronics, optics, sensors, and molecular devices due to their easy processing and low cost[1-3]. For optical application, such as optical waveguides and optical interconnections, critical properties are tunability of refractive index (1.6~ 4) and low absorption loss at the telecommunication wavelength of 1.3 and 1.55 µm, along with good thermal properties [4]. Since the optical loss of polymeric materials at near-infrared wavelengths is caused by absorption from vibrational overtones of the carbon-hydrogen (C-H) bond, fluorinated and deuterated polymers have been investigated. To date, a number of fluorinated polymers have been prepared[5-7] and their application in the field of optics has been studied[8-9].

For optical application, polymers are utilized as thin films that are generally prepared by spin casting from polymer solution, which is considered a very convenient method among the wet processes, such as Langmuir-Blodgett, dipping, or solvent casting[10]. Using this process, however, it is virtually impossible to remove the solvent completely upon drying, and at times, finding the proper solvent for the polymer poses a difficult problem. Furthermore, solvents utilized, for the most part, are hazardous to health and cause damage to the base material of devices. Therefore, attempts have been made to utilize a dry process such as plasma polymerization, which does not involve a solvent and can provide pinhole free thin polymer films upon *in situ* reaction of monomers via plasma energy[11-13]. Moreover, this technique provides excellent adhesion of films to various substrates, as well as good solvent resistance, due to their cross-linked nature.

Such advantages have led to plasma polymerization being utilized for the preparation of polymer thin films for optical application[14,15], along with microelectronics [16,17], coatings for corrosion protection[18], modification of membranes[19], and adhesion enhancement of carbon fibers[20] and silica[21]. However, the plasma polymerization technique mostly utilizes a continuous wave plasma source, which could result in significant monomer fragmentation[11,12]. Consequently, the resulting polymers have very different chemical structures compared to their monomers, and thus very different properties from the linear polymers prepared from the same monomer. To overcome such drawbacks, pulsed mode plasma polymerization has been introduced, which minimizes monomer fragmentation by on-time and off-time control. Recently, a comparison study was also carried out on the continuous wave plasma polymerization and pulsed mode plasma polymerization[22,23].

To date, a number of monomers have been utilized to afford polymer thin films for optical application by plasma

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polymerization[15,16,24-27]. However, only a few fluorine-containing monomers have been utilized[17,26-27], and their optical properties were not thoroughly investigated. In this study, therefore, a fluorine containing monomer, pentafluorostyrene, was selected for plasma polymerization in order to prepare polymer thin films for optical application. Plasma polymerization was carried out using RF (13.56 MHz) plasma in a continuous wave (CW) mode, as a function of plasma power and monomer pressure. First, conditions were optimized by measuring the solvent resistance of plasma polymer thin films in DMAc, NMP, THF, acetone, and chloroform, followed by the measurement of their optical clarity via UV-VIS. Next, pulsed mode plasma polymerization was also utilized in order to enhance the optical properties by varying on-time and duty cycle. Finally, the films were characterized by TGA and FT-IR, and their refractive indices and thickness analyzed.

2. Experimental

2.1. Materials
The monomer 2,3,4,5,6-pentafluorostyrene (PFS, Aldrich) was used for plasma polymerization without any purification. The silicon wafer and glass slides were washed with acetone and dried completely before being used as substrates for plasma polymerization coatings.

2.2. Plasma Polymerization of Pentafluorostyrene
Polymer thin films were prepared in a RF (13.56 MHz) plasma reactor equipped with manual impedance matching, Pyrex chamber (d=30 cm, h=30 cm), thermocouple pressure gauge, rotary pump, mass flow controller (MFC) and liquid monomer inlet, along with a pulse function generator (Yokogawa, Model FG110). First, the reactor was cleaned with acetone, followed by oxygen plasma etching (100 W, 30 min, 30 mTorr), and then a silicon wafer or glass slide was placed on the sample stage in the Pyrex chamber.

Next, the reactor was vacuumed to 1 mTorr and monomer vapor of pentafluorostyrene (PFS) was introduced. After purging for 10 min, plasma polymerization was carried out as a function of plasma power (5, 10, 30, 60 W), and monomer pressure (40, 60, 80 mTorr) at a fixed time of 10 min in the continuous wave mode. The conditions were optimized by measuring the solvent resistance and optical clarity of the plasma polymer films. Pulsed mode plasma polymerization was also utilized to maximize the optical properties of the plasma polymer films. The conditions for the pulsed mode were optimized by measuring the light transmittance with UV-VIS as a function of on-time (1, 10 and 30 ms) and duty cycle (10, 30 and 70%) at the optimum conditions of continuous wave plasma

polymerization.

2.3. Characterization of Plasma Polymer Films
The polymer thin films prepared were subjected to solvent resistance tests, since oligomer type polymer films would be soluble in solvents such as NMP, DMAc, CHCl$_3$, THF and acetone, while crosslinked films are insoluble. Therefore, plasma polymer coated glass slides (2 cm × 2 cm) were immersed in solvents (10 mL) for three days under slow stirring, after which solvent resistance was evaluated based on the residual polymer film on the glass slide and solvent clarity.

The samples that passed the solvent resistance test were subjected to transparency measurements via UV-VIS spectroscopy (Cary 1E, Varian), in order to evaluate the optical clarity. The baseline was corrected with a blank glass slide and transmittance was measured in the 250～800 nm range. The thickness of plasma polymer films was measured by α-Step 500 (Tencor) with a scan length of 500 μm at 2 μm/second. Prior to the measurements, a step was made by scraping off a portion of the film with a razor blade, and the results of 3 measurements were averaged.

Plasma polymer films were analyzed by FT-IR (IR 2000 Series, Perkin Elmer) with 64 scans taken of samples prepared on a silicon wafer at a resolution of 4 cm^{-1}. The plasma polymer film on the Si wafer was scraped off with a razor blade and approximately 10 mg was used for TGA analysis (TA-2050) at a heating rate of 10°C/min in air. Some samples were also subjected to annealing at 100, 200, or 300°C for 1 hr prior to the TGA analysis. The refractive index of plasma polymer films was measured by ellipsometer (Auto EL-Ⅱ Rudolf) at 632.8 nm and then by prism coupler at 632.8, 830, 1310 and 1550 nm. Refractive indices at T_E and T_M modes were measured and birefringence was also calculated.

3. Results and Discussion

3.1. Condition Optimization for Continuous Plasma Polymerization
The conditions for plasma polymerization were first optimized by measuring the solvent resistance of the films, as shown in Table 1. The films prepared at 10, 30 and 60 W were insoluble in NMP, DMAc, CHCl$_3$, THF, and acetone, irrespective of the monomer pressure used, demonstrating good chemical resistance, likely resulting from crosslinking. However, the films prepared at 5 W were partially soluble in NMP and DMAc, but insoluble in CHCl$_3$, THF and acetone, possibly due to light crosslinking. Consequently, the samples prepared at 10, 30
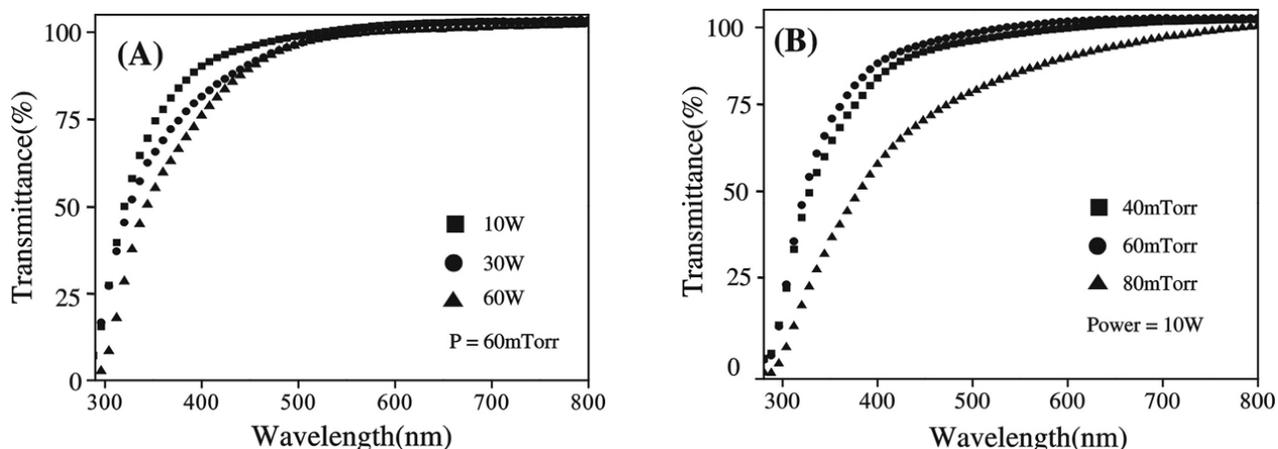
Figure 1. Optical transmittance of pentafluorostyrene plasma polymer films in continuous mode, (A) as a function of plasma power at 60 mTorr, (B) as a function of monomer pressure at 10 W.
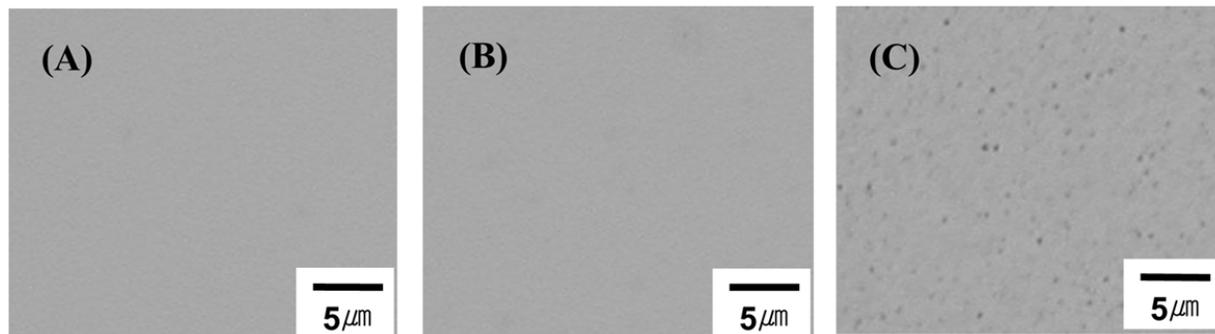
Figure 2. Optical microscopy of plasma polymerized pentafluorostyrene films in continuous mode at 10 W, (A) 40 mTorr, (B) 60 mTorr and (C) 80 mTorr.

Table 1. Solubility of pentafluorostyrene plasma polymer films from continuous plasma polymerization

Power \ Pressure (mTorr)	DMAc			NMP			CHCl$_3$			THF			Acetone		
	40	60	80	40	60	80	40	60	80	40	60	80	40	60	80
5 W	P	P	P	P	P	P	I	I	I	I	I	I	I	I	I
10 W	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
30 W	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
60 W	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I

I: insoluble, P: partially Soluble

and 60 W, which showed good chemical resistance, were subjected to UV-VIS measurements in the range of 250～800 nm, in order to evaluate their optical transparency.

As shown in Figure 1-A, the film transmittance was approximately 100% at 800 nm, and then slowly decreased to 95% (at 500 nm), followed by a sharp drop to 0% at 300 nm. It was noted that the samples prepared at 10 W provided slightly better transmittance than those prepared at 30 and 60 W. The small difference in the transmittance can be attributed to the increased cross

linking density of the polymer films as the power increased, possibly resulting in more scattering. Upon varying the monomer pressure at 10 W, the transmittance of the films followed a similar trend as the samples prepared at 6 mTorr under varying plasma power (Figure 1-B), exhibiting a gradual decrease in the 800～)0 nm range and then a sharp drop in the 400～)0 nm range.

The optical transmittance at 40 mTorr was slightly inferior to that at 60 mTorr, but far superior than that at 80 mTorr, resulting in a descending transmittance order of
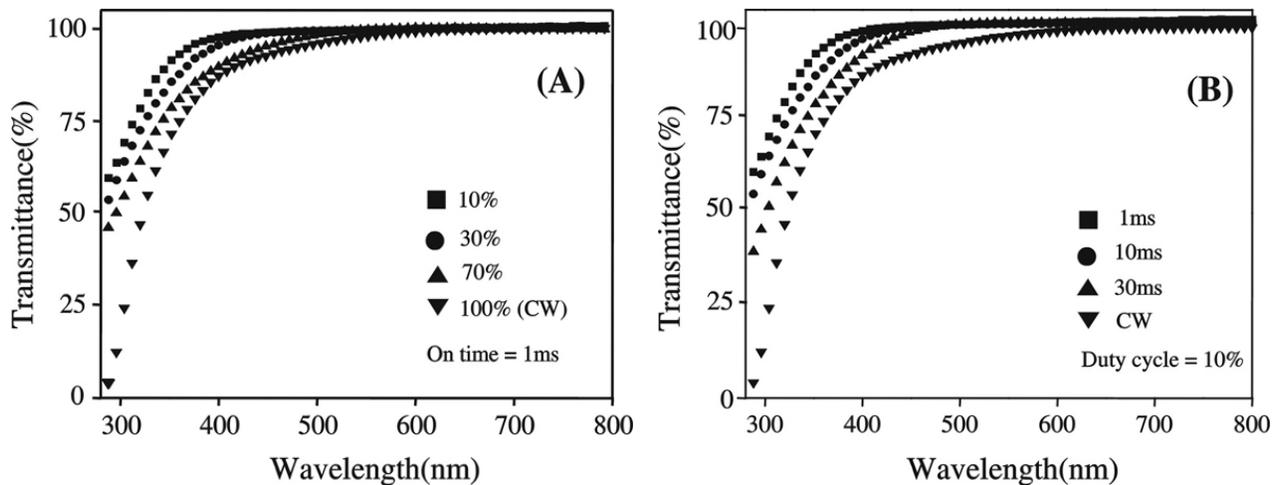
Figure 3. Optical transmittance of pentafluorostyrene plasma polymer films in pulsed mode, (A) as a function of duty cycle at 1 *m*s, (B) as a function of on-time at 10% duty cycle.

60 > 40 > 80 *m*Torr, thus indicating that there is no correlation with monomer pressure. However, this can be explained by the energy input level (W/FM; W: power, F: flow, M: molar mass), which is high enough at 60 *m*Torr to activate all the monomers to form a homogenous, crosslinked polymer film, resulting in high transparency. The input energy was also more than enough at 40 *m*Torr to form a highly crosslinked film, thus leading to low transmittance. At 80 *m*Torr, the input energy level may not have been high enough to activate all the monomers, resulting in a mixture of lightly crosslinked polymer and low molecular weight oligomers.

In order to explain the low transmittance of the samples prepared at 80 *m*Torr, the films were analyzed by optical microscopy. As shown in Figure 2, the plasma polymer films prepared at 40 and 60 *m*Torr were transparent when analyzed with an optical microscope, while those formed at 80 *m*Torr exhibited dark second phases. Consequently, it is believed that the dark phases were formed by the condensation of low molecular weight species due to the low input energy level. Based on the solvent resistance data and the UV-VIS and optical microscopy results, the optimum conditions for plasma polymerization of penta-fluorostyrene (PFS) were determined to be 10 W and 60 *m*Torr at 10 min.

3.2. Condition Optimization for Pulsed Mode Plasma Polymerization

In the utilization of pulsed mode plasma polymerization, the duty cycle and on-time were optimized by measuring the optical transmittance via UV-VIS measurements under the optimum conditions determined for continuous wave mode plasma polymerization (10 W and 60 *m*Torr). As

shown in Figure 3-A, the transmittance of plasma polymer films from pulsed mode provided a similar trend as that observed in the continuous mode; a very slow decrease in the 800~)0 *n*m range, followed by a rather sharp decline in the 500~)0 *n*m range. At 1 *m*s of on-time, the transmittance does not vary much in the 800~)0 *n*m range, regardless of the duty cycle (10, 30, 70 and 100%). In the 500~)0 *n*m range, however, the duty cycle of 10% provided the best transmittance, followed by 30, 70 and 100%, but the difference was rather small.

Upon varying the on-time from 1 *m*s to 30 *m*s at 10% duty cycle, the transmittance decreased very slowly in the 800~)0 *n*m range, but rather sharply in the 500~)0 *n*m range, exhibiting a similar behavior as that observed with duty cycle variation (Figure 3-B). The samples prepared at 1 *m*s exhibited the best transmittance, followed by those at 10 and 30 *m*s, but again the difference was small. The highest transmittance at lowest duty cycle (10%) can again be attributed to the decreased fragmentation of mon-omers and thus decreased crosslinking density, resulting in less scattering of light. This is also true for the highest transmittance with the shortest on-time (1 *m*s). Therefore, for the pulsed mode plasma polymerization, the duty cycle of 10% and on-time of 1 *m*s were selected as optimum con-ditions, based on the transparency of plasma polymer films.

3.3. Thickness of Plasma Polymer Films

The film thickness was measured as a function of plasma polymerization time, under the optimum conditions of pulsed mode plasma polymerization. As reported previously[19], the film thickness increased with time, as shown in Figure 4. At 5 min, the film thickness was approximately 0.08 *n*m and linearly increased to 3.8 μm

Figure 4. Thickness of plasma polymer films as a function of time.

Figure 5. Variation of refractive index as a function of duty cycle and on-time.

Figure 6. Comparison of T_M and T_E refractive indices of PFS films (10 W, 60 mTorr, 1 ms and 10% duty cycle) as a function of wavelength.

duty cycle, with similar trends also observed at 30 and 70% duty cycles. On the other hand, the refractive index of 1.520 was observed at 10% duty cycle, which further increased to 1.528 (30%) and 1.562 (70%) at 1 ms of on-time. The increased refractive index with on-time and duty cycle can be explained by the increased fragmentation of PFS monomers and thus increased crosslinking, which resulted in the formation of dense films. Consequently, it was found that it is possible to control the refractive indices of polymer thin films by varying plasma polymerization conditions such as on-time and duty cycle without changing the chemical structure of monomers.

Since the lowest refractive index was obtained under the optimum conditions of pulsed mode plasma polymerization (10 W, 60 mTorr, 1 ms and 10%), T_M and T_E mode refractive indices were evaluated in the 600～500 nm range, as shown in Figure 6. At 632.8 nm, the refractive index of 1.517 (T_M) and 1.513 (T_E) were obtained, and these values decreased almost linearly to 1.494 (T_M) and 1.492 (T_E) at 1550 nm. Unexpectedly, the T_M mode was higher than the T_E mode, which is contrary to the trends in general polymer thin films. Consequently, very small and negative birefringence values were obtained with -0.0020 at 632.8 nm, -0.0031 at 830 nm, -0.0013 at 1310 nm, and -0.0028 at 1550 nm. The negative birefringence can be explained by the orientation of polymer molecules in the plasma polymer film, where polymer chains are growing out from the substrate surface making them perpendicular to the substrate surface. In contrast, polymer chains in spin-coated films are aligned along the surface making them parallel to the substrate surface.

at 360 min in pulsed mode plasma polymerization (10 W, 60 mTorr, 1 ms and 10%). The results can be compared to the 0.1 nm at 5 min and 6.2 μm at 360 min obtained from continuous mode plasma polymerization (10 W, 60 mTorr). The estimated average deposition rate was 16.8 and 10.6 nm for continuous and pulsed mode plasma polymerization, respectively. As noted, continuous plasma polymerization provided marginally thicker films than mode plasma polymerization, which can be attributed to the difference in actual time of plasma polymerization.

3.4. Optical Properties of Plasma Polymer Films

The refractive index of PFS plasma polymer films prepared via pulsed mode plasma polymerization increased with on-time and duty cycle at 632.8 nm, as shown in Figure 5. As on-time increased from 1 ms to 30 ms, the refractive index increased from 1.520 to 1.541 at 10%

Figure 7. FT-IR spectra of plasma polymer films in continuous mode plasma polymerization (60 *m*Torr and 10 min).
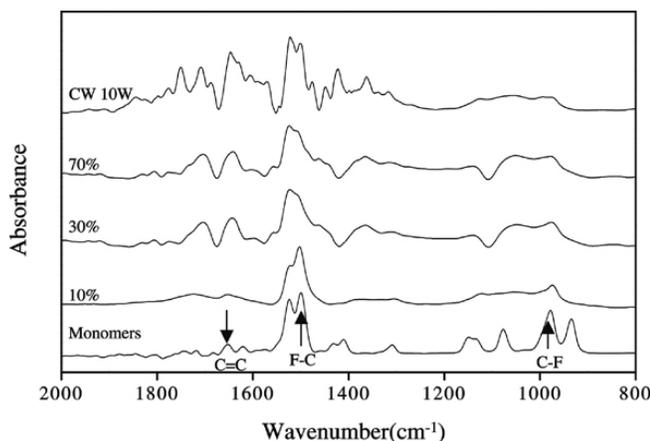
Figure 8. FT-IR spectra of plasma polymer films in pulsed mode plasma polymerization (10 W, 60 *m*Torr, 10 min and 1 *m*s).

3.5. FT-IR Analysis of Plasma Polymer Films

The plasma polymer films of PFS prepared in continuous wave mode were analyzed by FT-IR, as shown in Figure 7. As expected, the as-received PFS monomer provided typical IR peaks at 980 cm^{-1} (C-F aromatic stretching), 1500 cm^{-1} (F-aromatic ring vibration) and 1650 cm^{-1} (C=C). The samples prepared at 10W exhibited very different FT-IR results, compared to those from the monomer, exhibiting the disappearance of peaks in the 900～200 cm^{-1} range along with the appearance of new peaks in the 1300～1300 cm^{-1} range. This can be attributed to the recombination and/or crosslinking of radicals from the monomer fragmentation, which in turn, can be correlated to the changes in the chemical resistance and optical properties of plasma polymer films. As plasma power increased from 10 to 30 and 60 W, the peaks in the 1300～1500 cm^{-1} range became bigger, demonstrating more fragmentation
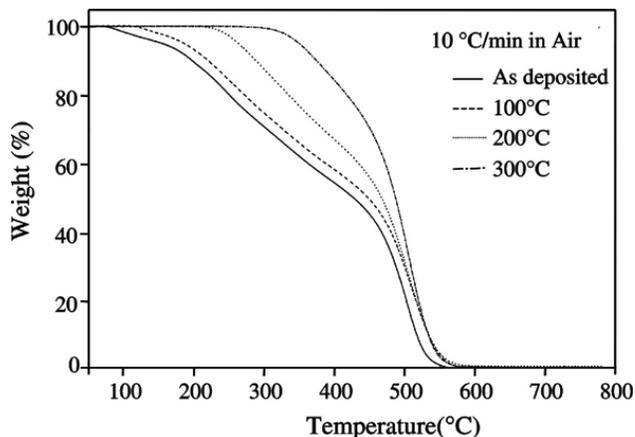
Figure 9. TGA thermograms of plasma polymer films in pulsed mode plasma polymerization (10 W, 60 *m*Torr, 10 min and 1 *m*s).

of the monomers and thus increased recombination and/or crosslinking. This can be correlated to the slight decrease in light transmittance with increased power, as shown in Figure 1-A.

In pulsed mode plasma polymerization (10 W, 60 *m*Torr and 1 *m*s), gradual changes in the chemical structure were observed in the FT-IR analysis (Figure 8). At 10% duty cycle, all the peaks became smaller (smeared), except those around 1500 cm^{-1}, demonstrating a low degree of monomer fragmentation, possibly owing to the low input energy (10% of 10 W). As the duty cycle increased (actual input power increased), peaks at 980 and 1500 cm^{-1} disappeared, while new peaks appeared in the 1300～1800 cm^{-1} range. At 70% duty cycle, the FT-IR spectrum was similar to that from the continuous wave mode (10 W), due to the high fragmentation of monomers. Consequently, it can be said that the fragmentation of monomers was much less in the pulsed mode plasma polymerization, especially at low duty cycles, resulting in low degrees of croslinking, which in turn led to low UV absorption (high transmittance) and low refractive index.

3.6. TGA Analysis of Plasma Polymer Films

The plasma polymer films of PFS prepared in pulsed mode (60 *m*Torr, 10 W, 1 *m*s, 10%) were subjected to TGA analysis in air, as shown in Figure 9. As expected from the literature[23], the polymer thin films exhibited very poor thermal stability, providing 5 wt% loss at 150°C. Such poor stability can be attributed to monomer fragmentation occurring during plasma polymerization, which resulted in low molecular species even after recombination and/or crosslinking reaction of those fragments. Therefore, the films were annealed at 100, 200 and 300°C for 1 hr under nitrogen atmosphere, which increased the thermal

stability dramatically with 5 wt% loss at temperatures of 187, 259, 259 and 352°C. Therefore, it can be said that thermal annealing at high temperatures induced additional chemical reaction(s) of unreacted fragments from plasma polymerization.

4. Conclusions

The plasma polymerization of PFS was carried out as a function of plasma power and monomer pressure in continuous wave plasma polymerization and also in pulsed mode plasma polymerization. Major findings are summarized as follows:

1) The conditions for continuous wave plasma polymerization, optimized by solvent resistance tests and transmittance measurements via UV-VIS, were 10 W and 60 mTorr at 10 min.

2) In a pulsed mode plasma polymerization, the optical transparency of plasma polymer films was evaluated by varying the period of on-time and duty cycle, which resulted in the best transmittance at 10% duty cycle and 1 ms on-time.

3) The refractive indices of the films increased as on-time and duty cycle increased, which can be attributed to the increased crosslinking density of plasma polymer films. Negative birefringence was also observed.

4) The FT-IR analysis demonstrated chemical reactions involving recombination and/or crosslinking of radicals resulting from the fragmentation of monomers, which affected solvent resistance as well as optical properties. This was also supported by the TGA analysis.

Acknowledgement

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