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Influence of Curry Leaves extract of Poly (vinyl alcohol) Composite Films for Food Packaging Applications

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Abstract

The present work aims to evaluate the effect of curry leaves extract on Poly (vinyl alcohol) blend films. The PVA/Curry leaf extract blend films were prepared by solvent casting method and analyzed with different instrumental techniques. The mechanical, morphological, thermal properties of the blend films were determined by using Universal testing machine (UTM), Scanning electron microscopy (SEM) and Thermo gravimetric analysis (TGA). Meanwhile interaction among the blend films was analyzed with Fourier Transform infrared spectroscopy. The results of the mechanical study confirmed the significant enhancement in the tensile properties, elongation at break and young's modulus. Further SEM micrographs showed complete miscibility among the blend films. The thermogram of blend films showed the slight increase in thermal stability compared to the pure PVA blend films. The improved properties could be due to the strong interaction among the blend films which was confirmed by the FTIR spectroscopy. The films exhibited good physicochemical properties, such films can be commercially explored for prolonged shelf life of food packaging in future.

Key words: PVA, curry leaves extract, mechanical properties, thermal properties, morphology.

Introduction

Over the past few decades, the development of new technology based on the composite films has implemented great interested and excitement among the young researchers. New functional properties offered by the composite films has remarkable outcome and presented new opportunities to enrich traditional product properties. Therefore, such composite films have been considered as an alternative novel material in the food packaging, pharmaceutical industry and biomedical field[1-2]. The ordinary composite films property can be enhanced in terms of biodegradability, durability, biocompatibility, barrier properties, flexibility, and antimicrobial properties. Recently, a widespread concern regarding specific packaging properties for the storage, safety, and quality of foods has led to the drastic changes in the food industry. The limitations of single materials with single functional property can be improved by incorporating the active ingredients like antimicrobial agents, antioxidants or nutrients. Such active compounds can project several functions and activate the packaging system to reduce the health and environmental problems[3-6]. Therefore, the edible composite films have attracted much attention for food packaging industry as they can be replacing traditional plastic films and acts as a eco-friendly material. Such biodegradable composite films can improve food quality and safety by creating barrier to moisture, gas and bacteria. Edible composite films are prepared by using natural biodegradable polysaccharides, proteins, and lipids which are nontoxic in nature and exhibit gas barrier properties. These films can be used as a protective coating material or packaging material to reduce packaging waste and to retain the food quality[7].

Experimental Section

Materials

Poly (vinyl alcohol) (PVA) was used as a matrix in the present study supplied by the Central Drug House (CDH), New Delhi and double distilled water used throughout the experiment. Fresh curry leaves around Dharwad were collected and ethanol and acetone was used as a solvent.

Extraction of Fresh curry leaves

Fresh curry leaves were collected from surrounding Dharwad, located in Karnataka, India. Leaves were washed with distilled water and dried at room temperature. Dried leaves were mechanically powdered and extracted using soxhelet apparatus. 100 g of dried powder was added to the 200 ml of ethanol and acetone as solvent (ratio 1:2). The extraction process extraction was carried out for 6 hours and temperature was maintained at 45°C. Color of the crude extract was dark green and semi liquid in both solvents.

Preparation of Composite films.

PVA composite films were prepared, by incorporating different weight percent of curry leaves extract, by solvent casting method. An exactly weighed amount of PVA was dissolved in distilled water. To PVA solution curry leaves extract (1% solution of curry leaf extract prepared in 100 ml of ethanol) was added in mL wise (i.e. 2ml, 4ml, 6ml and 8ml). The mixture of PVA and curry leaf extract solution was stirred for 3-4 hour.

Table 1. Total weight taken- 2.0 g (100 %) Composition table of PVA/Curry leaf extract

Sample code	PVA (%)	Curry leaves extract
A-PVA	100	00
B	100	2 mL
C	100	4 mL
D	100	6 mL
E	100	8 mL

Later, definite amount of clear and homogeneous solution of PVA/curry leaf extract solution were poured onto previously cleaned and dried petri dishes and solvent was allowed evaporating at room temperature. Finally, the petri dishes containing films were dried in hot air oven at 45^{o}C to remove trace amount of solvent present in the films. After complete evaporation of solvent, films were peeled off from the petri dishes and stored in desiccators until further use.

Result and Discussion

Mechanical Properties

Table 2. Mechanical properties of pure PVA and PVA/PCL blend films.

Sample code	Tensile Srength MPa	Young's Modulus MPa	Elongation at break %
PVA (A)	26.21	2099.6	7.0
PVA + 2 mL CLE (B)	17.36	1541.3	9.0
PVA+ 4 mL CLE (C)	30.42	2298.2	6.3
PVA+ 6 mL CLE (D)	31.01	2292.6	25.4
PVA+ 8 mL CLE (E)	24.86	1842.7	29.9

The mechanical properties pure PVA and PVA/PCL blend films were summarized in Table (2). Addition of different volume of curry leaf extract to the PVA has presented significantly increased mechanical properties compared to pure PVA. The pure PVA has tensile strength of 26.21 MPA, young' modulus 2099 MPa and elongation at break 7.0. With increase in curry leaf extract in the PVA film presented increased tensile strength from 17 MPa to 31 MPa, young's modulus 1541.3 MPa to 2292.6 MPa and elongation at break 9.0 (%) to 25.4 (%). The increased mechanical properties could be attributed to the strong interaction among the each component. At higher concentration of curry leaf has shown decreased mechanical properties i.e. tensile strength 24.8 MPa, Young's modulus 1842.7 MPa and increased elongation at break

29.9 (%). This could be possible due to the increase os curry leaf extract in PVA films leading to the agglomeration of curry leaf extract.

Scanning electron microscopy (SEM)

Figure (1) reports the SEM micrographs of pure PVA and PVA/PCL blend films. SEM is used to evaluate the effect of curry leaf extract on PVA films. Initially SEM micrographs of PVA/PCL blend films showed smooth homogeneous phase morphology, indicating the complete miscibility among the PVA and curry leaf extract. The presence of single homogeneous phase morphology confirms the strong interaction among the PVA and curry leaf extract which lead to the increased mechanical properties. As the volume of curry leaf extract increased in the PVA blend films showed different phase morphology not completely heterogeneous phase morphology. The results of SEM micrographs confirm the complete miscibility and increased mechanical properties due to the strong interaction among the blend films. SEM results were in agreement with the mechanical properties and the results indicated by and AFM.

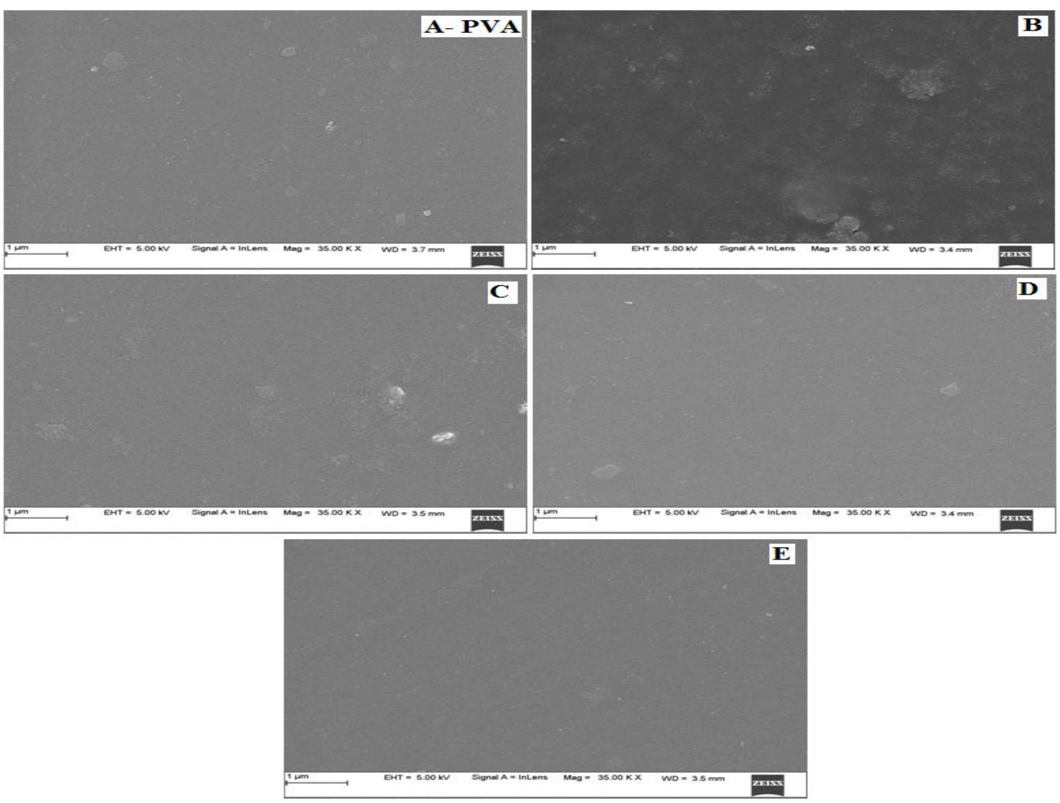


Figure 1. SEM micrographs of pure PVA and PVA/PCL blend films.

Atomic force microscopy (AFM)

In support to the SEM results, Atomic force microscopy was used to evaluate the surface morphology of the blend films. Figure (2) presents the AFM images of pure PVA and blend films. The result of AFM study confirms that, both pure PVA and blend films presented smooth uniform surface morphology. This could be attributed to the good interaction between PVA and curry leaf extract. Both area roughness and line roughness showed uniform and homogeneous surface morphology.

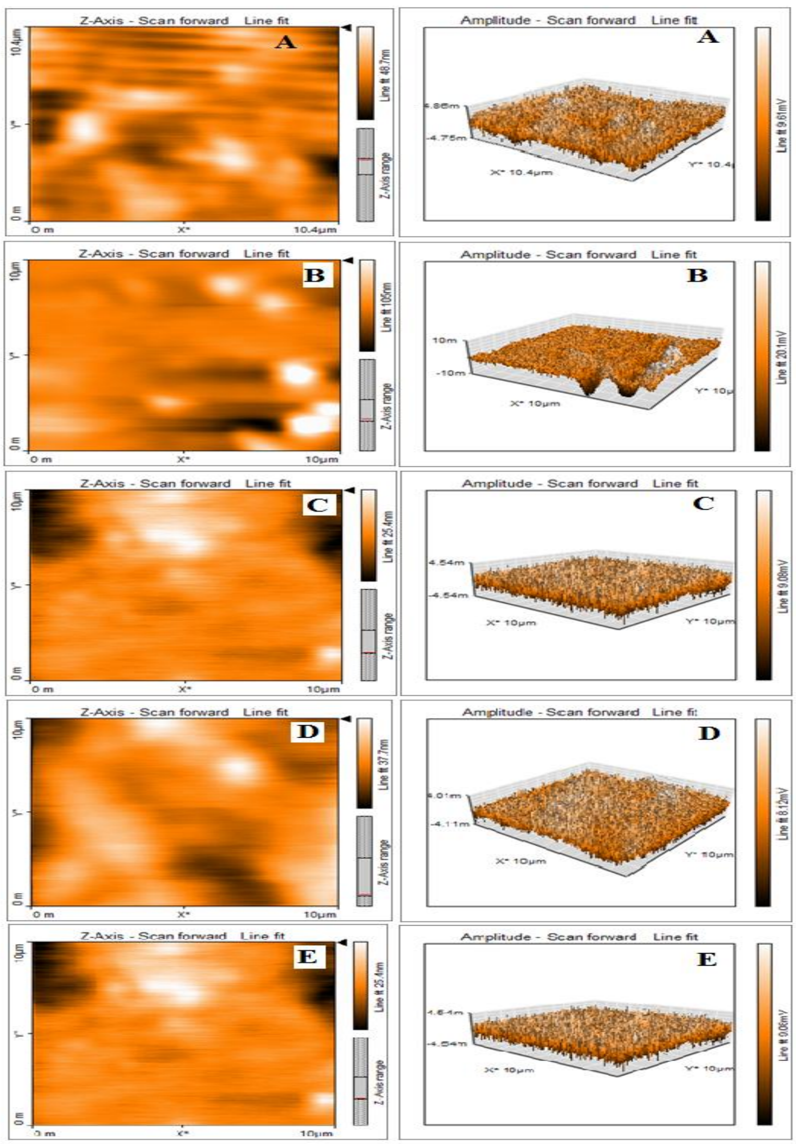


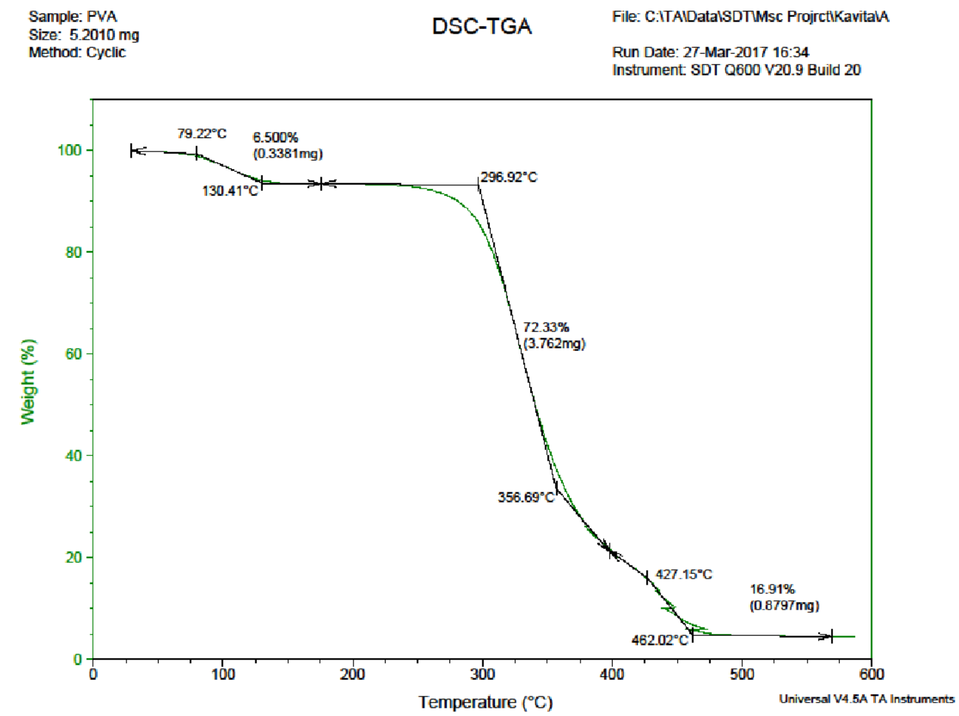
Figure 2. AFM images of pure A)PVA, B) PCL-1, C) PCL-2, D) PCL-3, E) PCL-4 blend films.

Thermogravimetric analysis

Figure (3) reports the TGA thermogram of pure PVA and PVA/PCL blend films. Thermogravimetric analysis was performed to evaluate the mass change as a function of temperature. The thermal decomposition of pure PVA and blend films exhibited three step degradation patterns. The pure PVA showed first degradation step at 0°C to 130°C, which attributed to the removal of water molecules. The second major degradation occurred at 130°C to 296.92°C (percent of weigh loss observed was 72.33%), this is due to the destroying of PVA film. The third degradation pattern observed from 356.69°C to 462.02°C (weight loss of 19.91%), due to the complete degradation of PVA molecule. Meanwhile same three step degradation pattern was observed in all PVA/PCL blend films. The first degradation was observed from 0°C to 150°C due to the evaporation of water molecules from the film. The second major degradation occurred at 134°C to 300.82°C, corresponds to the rapid mass due to the breaking PVA and curry leaf extract into different by products. The third step observed at 356°C to 471.33°C, is attributed to the complete destruction of PVA and curry leaf extract. The TGA results of blend films revealed that, pure PVA blend films showed complete degradation at 471.33°C and PVA/PCL showed complete degradation at high temperature range near to 471.33°C. The results of TGA also confirm the stability of the blend films increased slightly compared to that of pure PVA. Table (3) summarizes the degradation and percent of weight loss (% yield).

Table 3. Degradation and percent of weight loss (% yield).

Sample code	I-Degradation	II-Degradation	III-Degradation
PVA	0°C to 130°C	130°C to 296.92°C	356.69°C to 462.02°C
B	0°C to 150°C	150°C to 300.82°C	367.20°C to 470.12°C
C	0°C to 135C	135°C to 299.73°C	360.99°C to 471.33°C
D	0°C to 142°C	142°C to 299.95°C	356.85°C to 471.55°C
E	0°C to 137°C	137°C to 297.70°C	359.63°C to 468.38°C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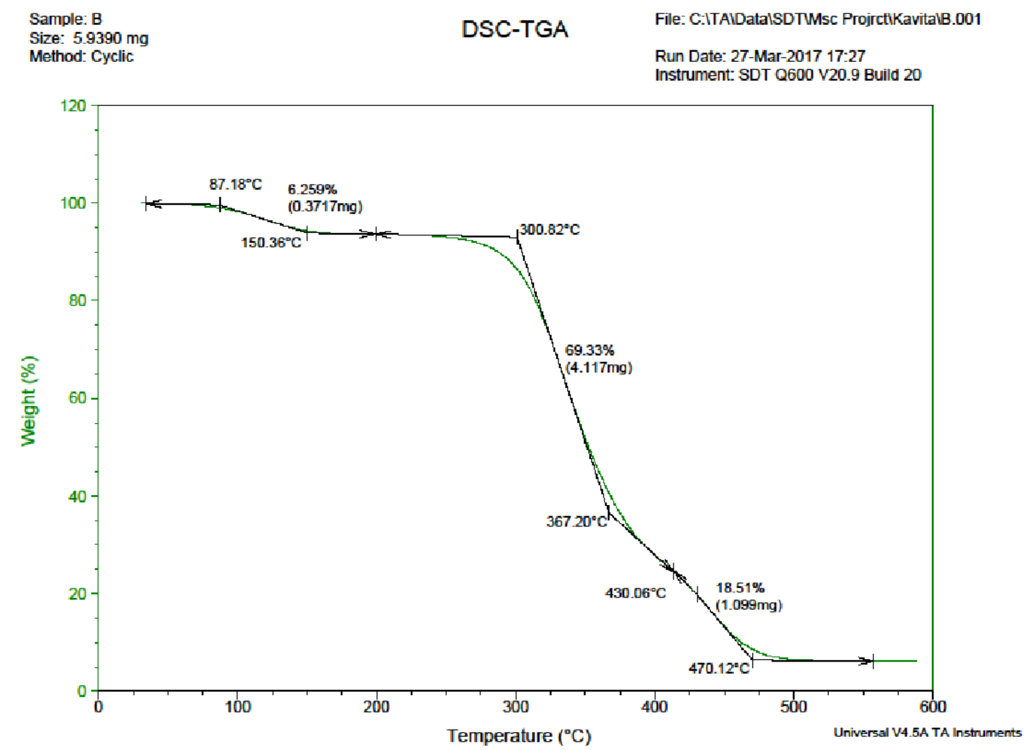
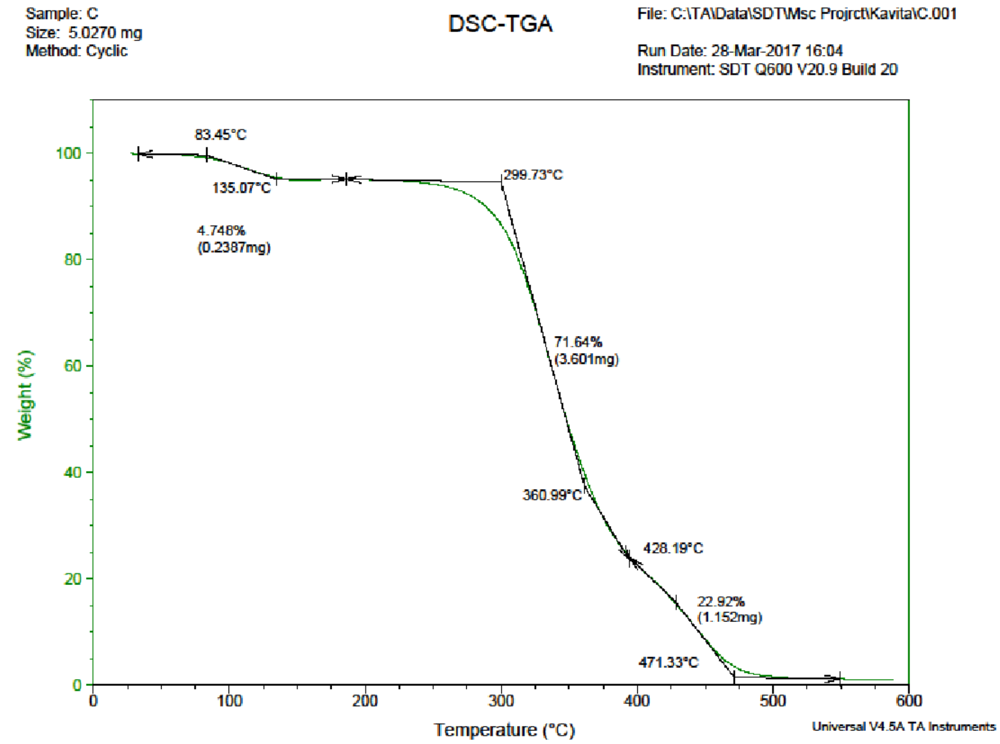
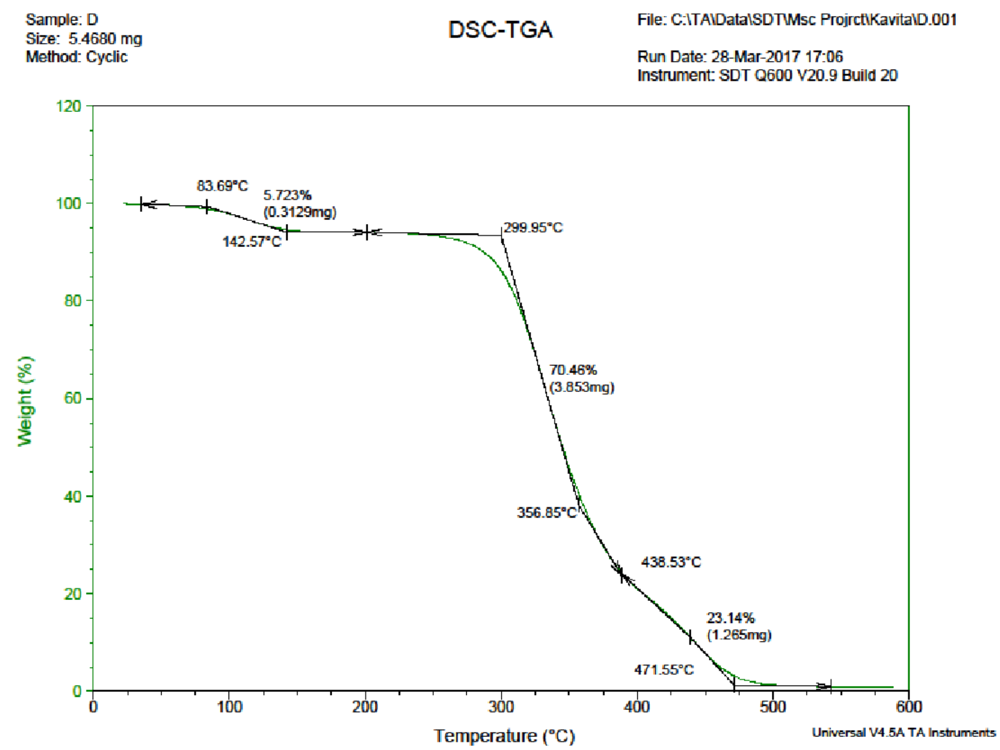
Size: 5.2010 mg
Method: Cyclic
DSC-TGA
File: C:\TA\Data\SDT\Msc Projrct\Kavita\A
Run Date: 27-Mar-2017 16:34
Instrument: SDT Q600 V20.9 Build 20
79.22°C
6.500%
(0.3381mg)
130.41°C
296.92°C
72.33%
(3.762mg)
356.69°C
427.15°C
16.91%
(0.8797mg)
462.02°C
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments


Sample: B
Size: 5.9390 mg
Method: Cyclic
DSC-TGA
File: C:\TA\Data\SDT\Msc Projrct\Kavita\B.001
Run Date: 27-Mar-2017 17:27
Instrument: SDT Q600 V20.9 Build 20
87.18°C
6.259%
(0.3717mg)
150.36°C
300.82°C
69.33%
(4.117mg)
367.20°C
430.06°C
18.51%
(1.099mg)
470.12°C
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments


Sample: C
Size: 5.0270 mg
Method: Cyclic
DSC-TGA
File: C:\TA\Data\SDT\Msc Projrct\Kavita\C.001
Run Date: 28-Mar-2017 16:04
Instrument: SDT Q600 V20.9 Build 20
83.45°C
135.07°C
4.748%
(0.2387mg)
299.73°C
71.64%
(3.601mg)
360.99°C
428.19°C
22.92%
(1.152mg)
471.33°C
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments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Size: 5.4680 mg
Method: Cyclic
DSC-TGA
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Instrument: SDT Q600 V20.9 Build 20
83.69°C
5.723%
(0.3129mg)
142.57°C
299.95°C
70.46%
(3.853mg)
356.85°C
438.53°C
23.14%
(1.265mg)
471.55°C
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments

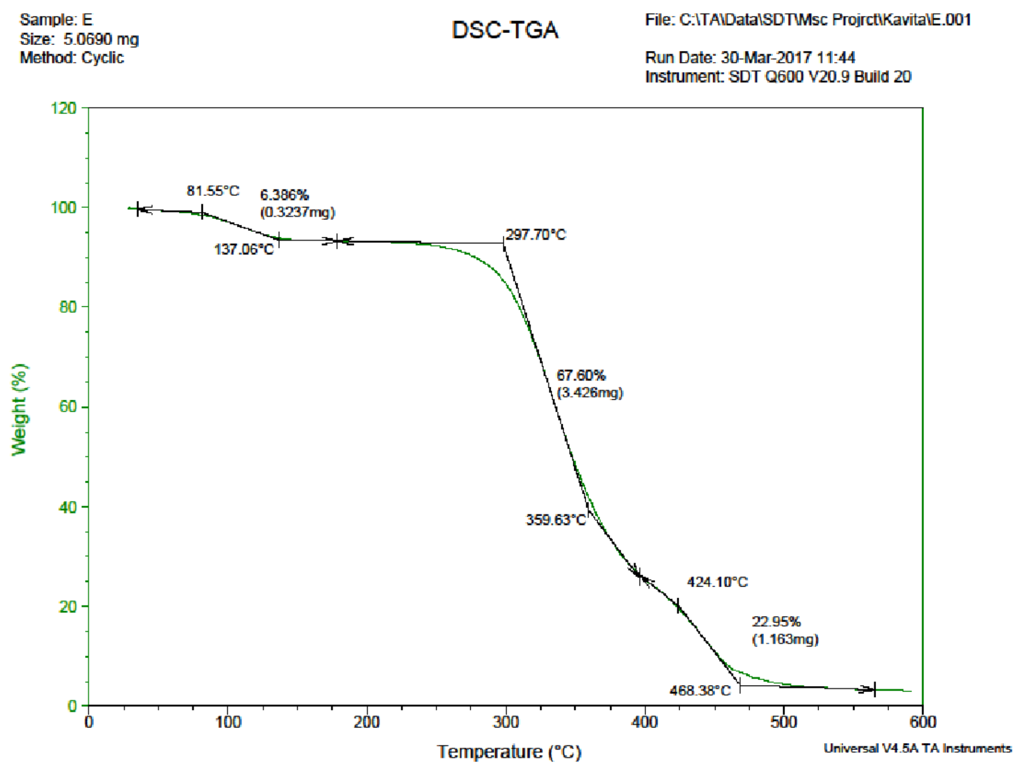


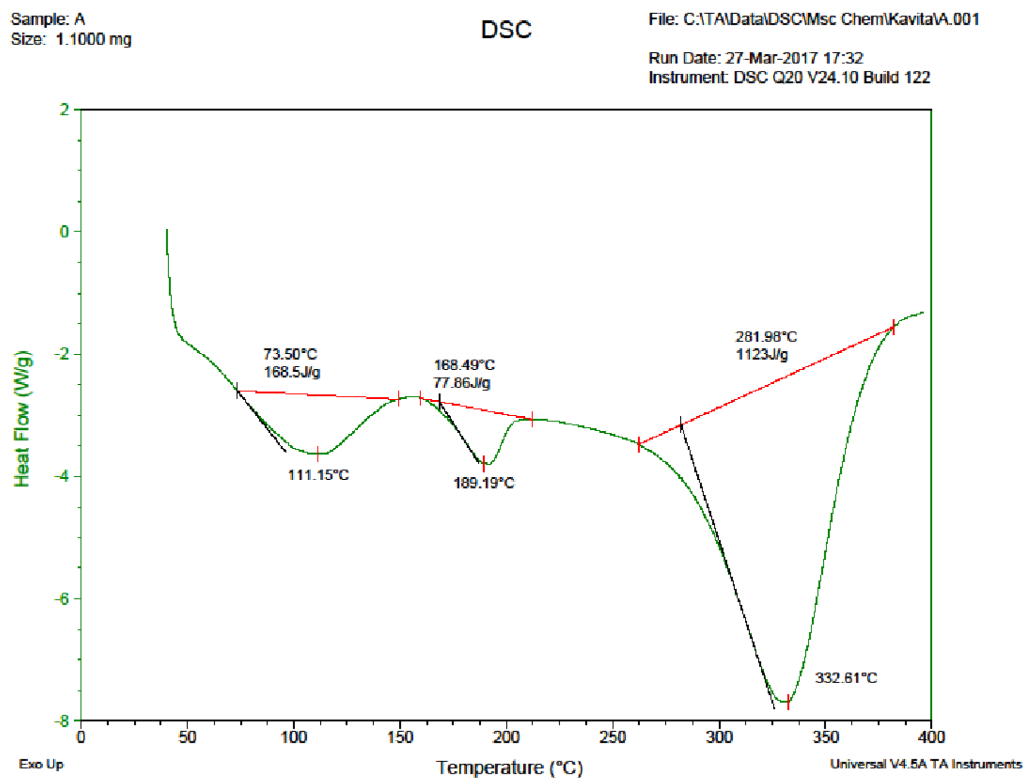
Figure 3. TGA thermogram of pure A-PVA, B- PCL-1, C-PCL-2, D-PCL-3, and E-PCL-4 blend films.

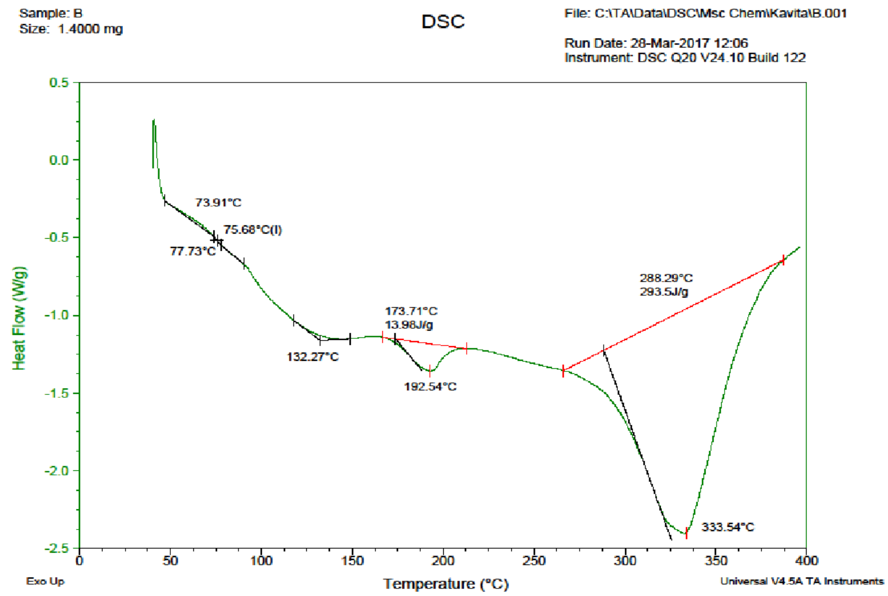
Differential scanning calorimetry (DSC)

The Figure (4) shows the DSC thermograms of pure PVA and blend films. The DSC thermogram of PVA showed glass transition temperature at 111.15^{o}C, melting temperature occurred at 189.19^{o}C and degradation temperature occurred at 332.61^{o}C. Meanwhile, DSC thermogram of blend films showed single glass transition temperature which confirms the complete miscibility of the blend components. The addition of curry leaf extract to the PVA films leads to the complete miscibility indicated by the presence single glass transition temperature. The addition of curry leaf extract slightly increased the glass transition temperature of the blend films compared to the pure PVA (PCL-1-132.54^{o}C, PCL-2- 116.62^{o}C, PCL-3- 121.36^{o}C and PCL-4- 177.43 (Table 4). This could be due to the dispersion of curry leaf extract in the PVA film leading to the amorphous structure. The shift of Tg to higher value could be attributed to the formation of strong interaction between the PVA and curry leaf extract. The melting temperature of blend films also slightly increased compared to the pure PVA. Table (4) lists the T_g, T_m and T_d of PVA and blend films.

Table 4. T_g, T_m and T_d of PVA and blend films.

Sample code	Glass Transition Temperature (T_g)	Melting Temperature (T_m)	Degradation Temperature (T_d)
PVA	111.15°C	189.19°C	332.61°C
B	132.27°C	192.54°C	333.54°C
C	116.65°C	191.62°C	333.09°C
D	121.66°C	188.47°C	333..88°C
E	177.43°C	190.36°C	331.40°C

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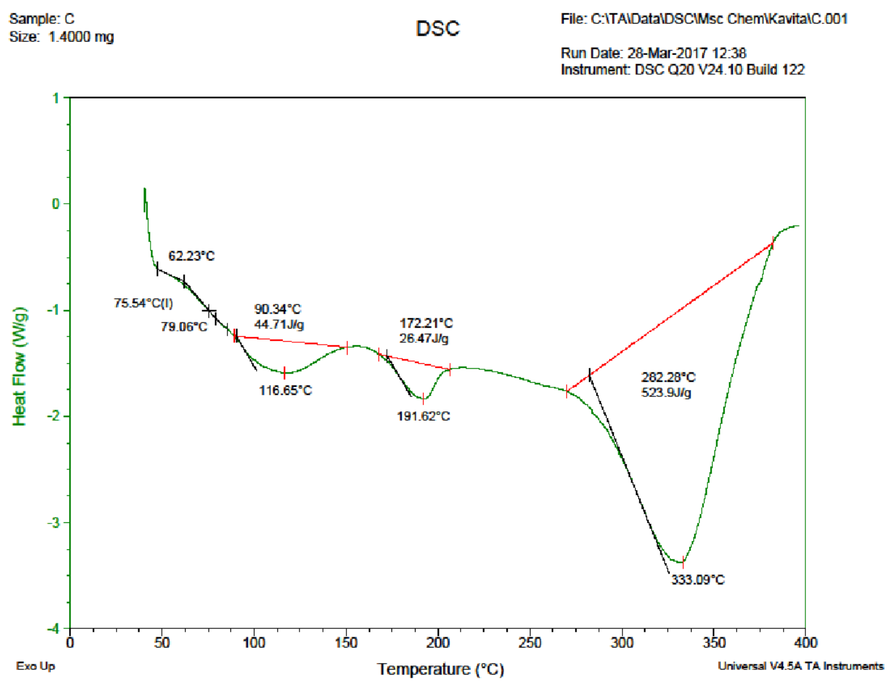
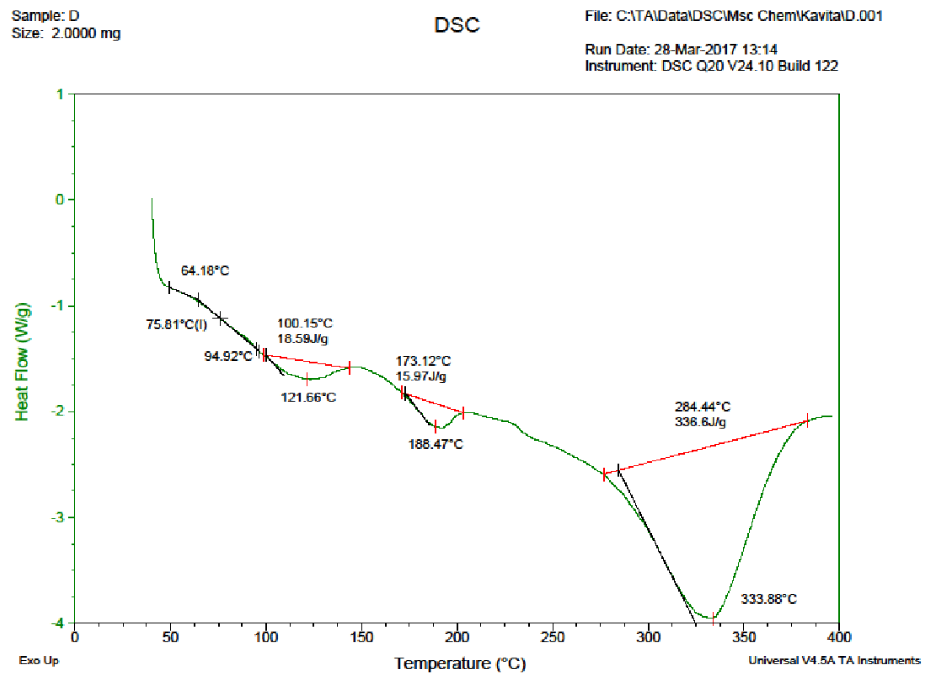
Size: 1.4000 mg
DSC
File: C:\TA\Data\DSC\Msc Chem\Kavita\B.001
Run Date: 28-Mar-2017 12:06
Instrument: DSC Q20 V24.10 Build 122
73.91°C
75.68°C(I)
77.73°C
132.27°C
173.71°C
13.98J/g
192.54°C
288.29°C
293.5J/g
333.54°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments


Sample: C
Size: 1.4000 mg
DSC
File: C:\TA\Data\DSC\Msc Chem\Kavita\C.001
Run Date: 28-Mar-2017 12:38
Instrument: DSC Q20 V24.10 Build 122
62.23°C
75.54°C(I)
79.06°C
90.34°C
44.71J/g
116.65°C
172.21°C
26.47J/g
191.62°C
282.28°C
523.9J/g
333.09°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments



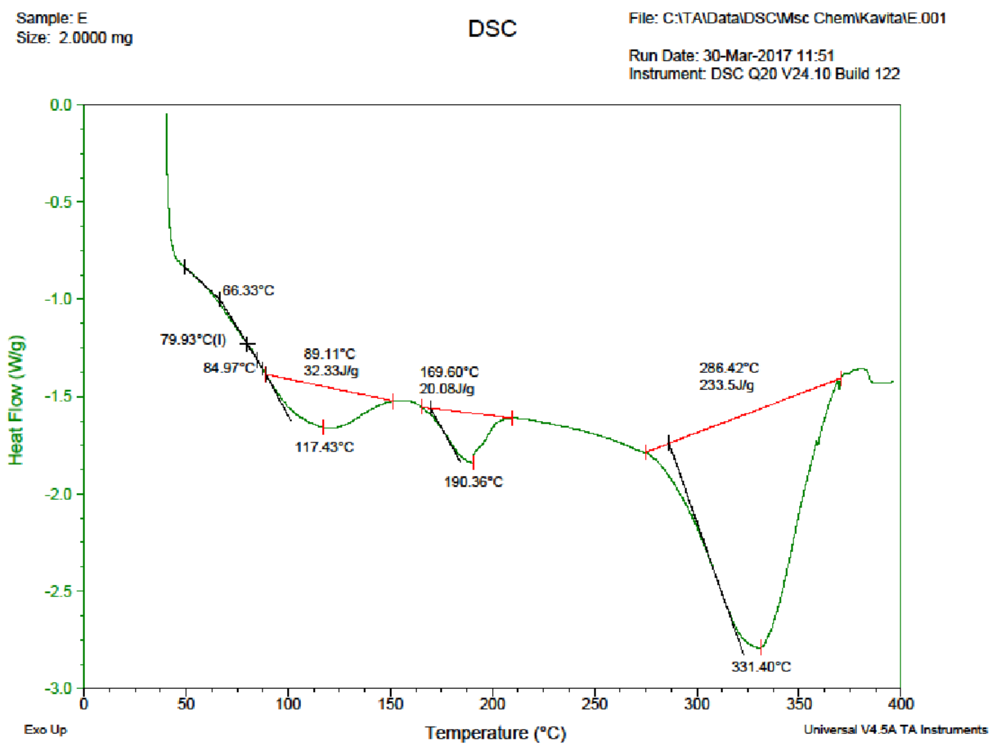
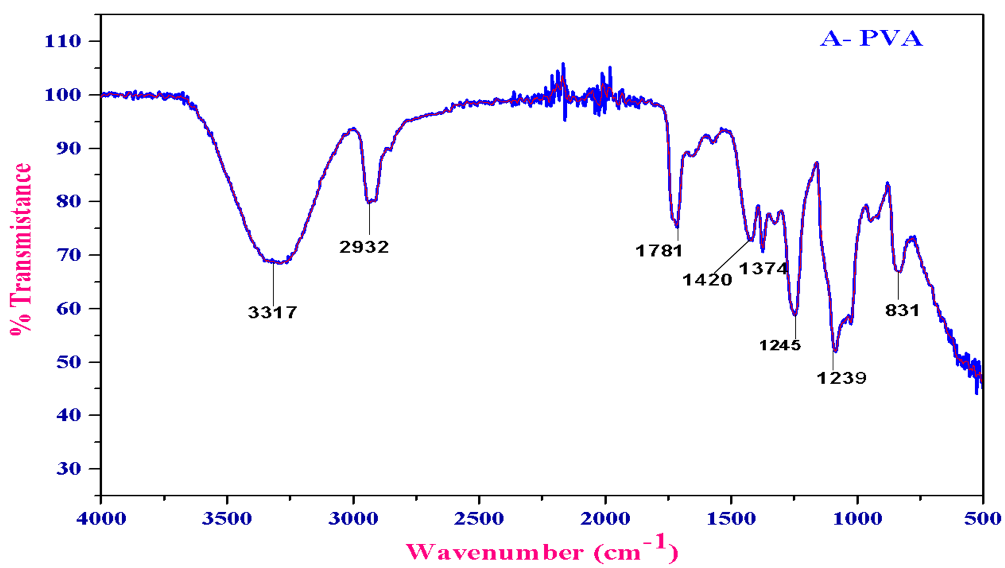


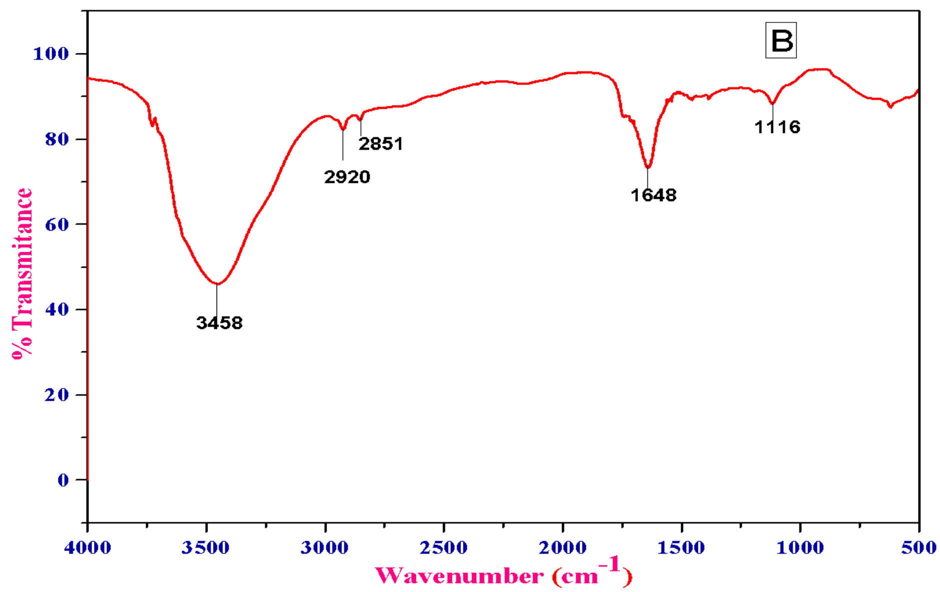
Figure 4. DSC thermogram of pure A-PVA, B- PCL-1, C-PCL-2, D-PCL-3, and E-PCL-4 blend films.

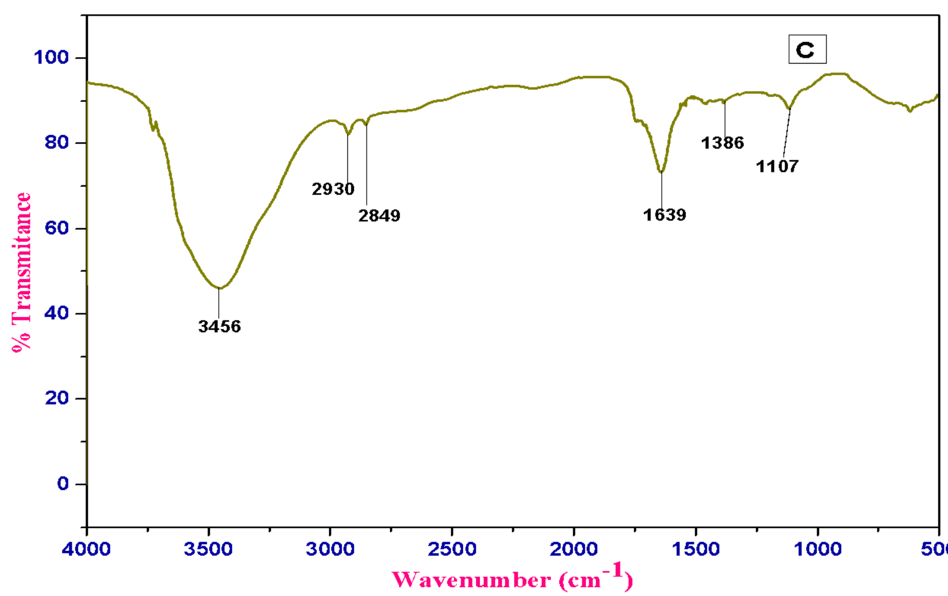
Fourier transforms Infrared spectroscopy (FTIR)

The pure spectra PVA (Figure 5), showed peak at 3317 cm^{-1}, due to –OH stretching and peak occurred at 1781cm^{-1} bending vibration of hydroxyl group, respectively. The asymmetric stretching vibration observed at 2932cm^{-1} (methylene group CH_2). Weak stretching vibration observed at 1374cm^{-1}, due to C-O-H bending and 1245cm^{-1}, 831cm^{-1} are assigned to the C-C stretching and C-H rocking of PVA. The peak occurred at 1093cm^{-1} was corresponds to the C-O stretching of acetyl group in the PVA backbone.

The successful blending of PVA and curry leaf extract was confirmed by the characteristic peak observed in the FTIR spectra. The increase of 3458 cm^{-1} –OH stretching peak of PVA/curry leaf extract confirms the strong interaction among the components. The shift of 2932cm^{-1} to lower values suggests the compatibility among the components. And disappearance of 1374cm^{-1} and 1245cm^{-1} of C-O-H and C-C stretching attests the there is interaction among the blend components. The FTIR spectra of binary blend films (PVA/PCL) indicate that there successful increase in peak value and by formation of new bonds lead to the improved mechanical properties due to the strong interaction.




B
100
80
60
40
20
0
% Transmitance
3458
2920
2851
1648
1116
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


C
100
80
60
40
20
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% Transmitance
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2000
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1000
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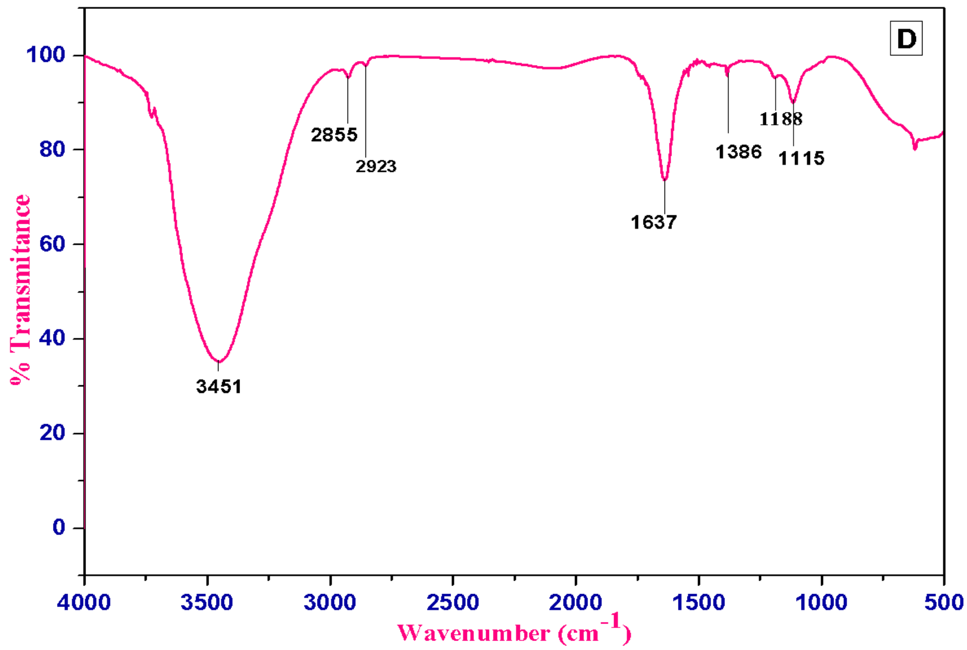
Wavenumber (cm-1)



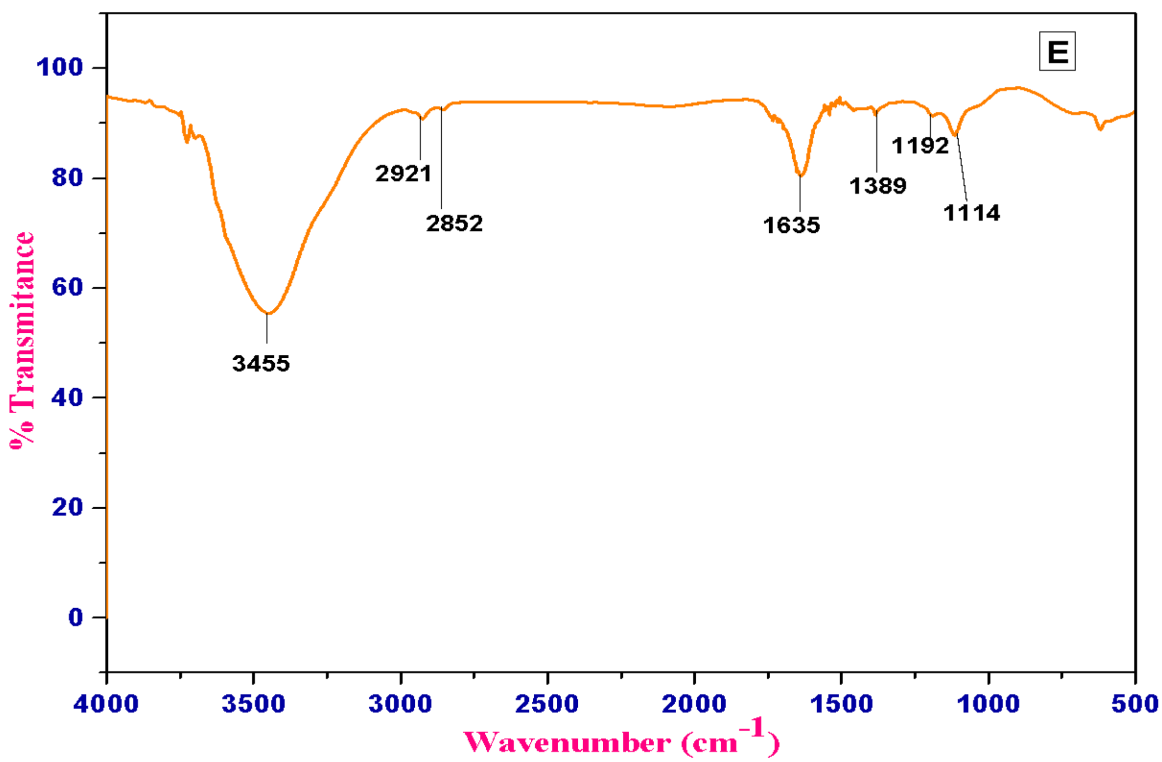


Figure 5. FT-IR Spectra of A) PVA, B) PCL-1, C) PCL-2, D) PCL-3 and E) PCL-4 blend films.

Conclusion

In summary, the study provides an insight of preparation of curry leaf extract doped PVA blend films. The mechanical properties of the blend films and its influencing factors including morphology, thermal behavior and glass transition temperature have been investigated systematically. By adjusting the blend ration with different volume of curry leaf extract has presented interestingly increased mechanical properties. Addition of curry leaf extract lower to higher volume yielded improved physicochemical properties. The smooth homogeneous morphology observed in the SEM micrographs and presence of single glass transition temperature confirmed the miscibility among the components. This also supported by the AFM study exhibiting the uniform surface morphology. The degradation pattern of blend films presented three step degradation patterns in pure PVA and blend films and thermal stability of the blend films increased slightly compared to the pure PVA. The result of FTIR study confirms the formation of intermolecular interaction between PVA and curry leaf extraction. The prepared blend films can find potential application as food packaging in future.

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