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Functionalization of polypropylene, polyamide and cellulose acetate materials with pyrethrum extract as a natural repellent in supercritical carbon dioxide

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Graphical Abstract

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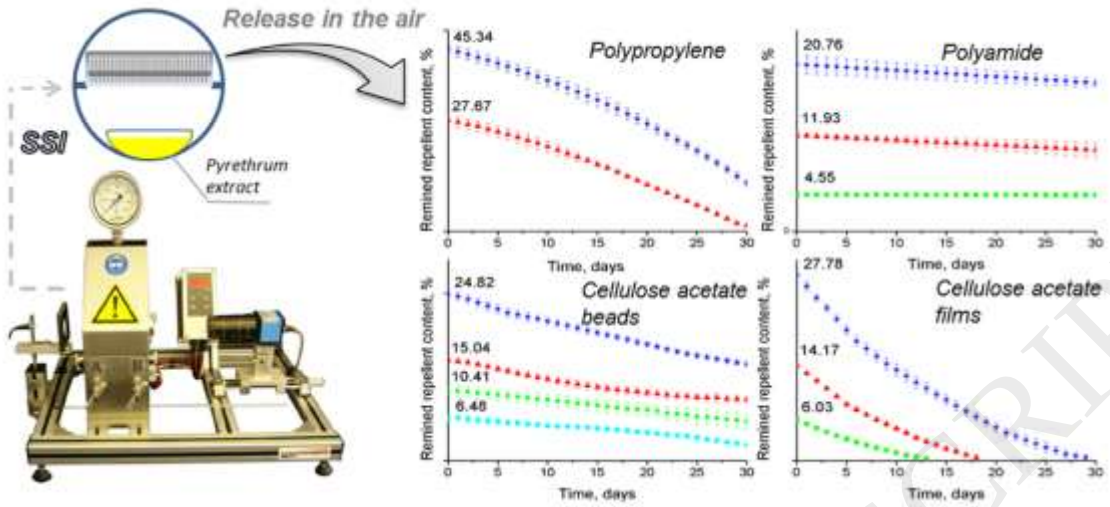

Highlights

- SSI enabled incorporation of high amounts of pyrethrum extract in tested materials
- The largest loading capacity among the tested materials had PP fabric
- Cellulose acetate is a promising carrier for controlled release of pyrethrum extract
- Physical form of cellulose acetate influenced the rates of impregnation and release
- Amount of pyrethrum extract in polyamide fabric remained stable after 30 days

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Abstract

This study discusses the possibility of supercritical solvent impregnation of polypropylene and polyamide fabrics as well as cellulose acetate in the form of beads and films with pyrethrum extract in order to fabricate functionalized materials with repellent properties. Impregnation experiments were performed at temperature of 40 ºC and pressures of 10 and 20 MPa in supercritical carbon dioxide. The time of impregnation was varied from 0.5 to 18 h. Loadings of pyrethrum extract into polypropylene fabrics and cellulose acetate films higher than 30% were attainable at 10 MPa. In the case of polyamide fabrics and cellulose acetate beads, the pressure of 20 MPa was needed for obtaining the loadings higher than 11%. Pyrethrum extract release study revealed different capabilities of the tested materials for the repellent release, implying a variety of their possible

applications. The impregnated solids were characterized by SEM, DSC, FTIR, Mercury intrusion porosimetry analyses and HPLC analyses.

Keywords: Supercritical solvent impregnation; pyrethrum extract; polypropylene; polyamide; cellulose acetate.

1. Introduction

Over the past years, new vector-borne diseases have continued to emerge in regions where they had not previously been a concern. The ever growing population in the 21st century, increased global travel and urbanization contribute to the fast spread of infectious illnesses [1]. To address these challenges, serious efforts in the protection of humans against arthropod bites and vector borne diseases have been made. In particular an interest for fabrication of repellent treated clothes, nets and tents significantly increased [2–4]. Commonly applied repellents are N,N-diethyl-meta-toluamide (DEET), picaridin, ethyl butylacetylaminopropionate (IR3535) and pyrethroids [5–8]. A wide use of these repellents alerted the researchers to the appearance of resistance in some insect species as well as to the fact that they are not eco-friendly [9,10]. This was the motivation for starting up a new research dealing with natural substances possessing repellent properties [1].

Plants and their essential oils such as mint (*Mentha*), hyptis (*Hyptis*), lavender (*Lavandula*), sage (*Salvia*), basil (*Ocimum*), thyme (*Thymus*), catnip (*Nepeta cataria)*, palmarosa (*Cymbopogon martinii*), rue (*Ruta chalepensis*), pyrethrum (*Chrysanthemum cinerariaefolium*), geranium (*Pelargonium*), rosemary (*Rosmarinus officinalis*) showed great potential as natural repellents [1,11–13]. Both monoterpenes such as limonene, α-pinene, citronellal, citronellol, camphor and thymol [11,14–18] and sesquiterpenes such as β-caryophyllene [15,18–20] were found to possess repellent properties. In addition, their combination is considered to be a promising natural repellent [15,20,21]. Insecticidal activity of pyrethrum extract originates from its six active components: pyrethrin I and II, cinerin I and II and jasmolin I and II (Fig. 1) [22]. Pyrethrins target a wide variety of pests and they have a short half-life in the environment. Furthermore, they are highly lipophilic, low toxic to mammals and they do not cause biomagnification (persistence in tissues of organisms) [12].

Major attention was focused on the formulations of different lotions for topical application as well as on the repellent treatment of various kinds of textiles aimed for clothes, tents and nets [2,5,6,23]. On the other hand, there is limited data dealing with non-topical applications and controlled repellent release products for human protection from pests, which would provide a safe stay in nature for instance. Reitizig [24] reported the invention of different shapes of disposable bottle entry barriers coated with essential oil of lemongrass by spraying technique. It was also reported that the polyhydroxyvalerate based tablets with plant essential oils were found to be effective against mosquitos [25]. Furthermore, available literature offers scarce information concerning the preservation of goods (stored in the warehouses or in the open air) and plants by utilization of natural repellent products. Recently, a method for preparation of multifunctional mulching paper for application in agriculture was introduced [26]. The multifunctional mulching paper was prepared by a coating method, whereby a mixture of dried herbal powder, mothproofing oil, clay, red algae extract, nano-clay and starch were applied to the craft paper [26].

As the simplest one, exhaustion method has been commonly used for the impregnation of textiles with a suitable repellent [4,27,28]. In addition to significant generation of waste water this method requires large amounts of repellent matter. Further, the absorption of active substance is mainly restrained on the fiber surface [29]. Spraying technique is proven to be slightly more efficient in terms of active substance consumption [30,31]. It is reported that ten to twelve uniforms were successfully treated with approximately 7.7 l of emulsion with contraction of 0.020 $l_{permethrin}/l_{water}$ [32]. In order to extend the washing fastness of the impregnated cotton fabric, the efforts have been made to introduce β-cyclodextrin molecules onto the fabrics surface prior to its impregnation with essential oil of eucalyptus [33]. Although the technique is perspective, further development is needed since repellent activity of the impregnated fabric was only detectable after the first washing cycle. Eventually, polymer-coating technique [4,29] and the microencapsulation method [3,34] were

developed for the same purpose. It was reported that the microencapsulation technique required significantly reduced amounts of repellent [34]. . The amounts that could be potentially absorbed by skin are also reduced [34].

Among the various methods for incorporation of a bioactive substance into a polymer matrix, supercritical solvent impregnation (SSI) was proven to be beneficial. The avoidance of organic solvents, the homogeneous distribution of an active component throughout the whole polymer volume, the absence of an effluent generation and lower energy demands comparing to conventional impregnation processes are the main features of this technique [35,36]. In our previous report [37], large potential of the SSI technology in the domain of repellent materials fabrication was disclosed. SSI was found to be a feasible technique for manufacturing of cotton fabrics functionalized with pyrethrum extract aimed for clothing. By adjusting the SSI process parameters it was possible to obtain pyrethrum extract content in the cotton fabric that meet the demands of regulations for repellent contents in the dressing (the United States Environmental Protection Agency, German Federal Institute for Risk Assessments [7,38,39]). However, the results [37] indicated that much higher loadings of pyrethrum extract could be obtained by the SSI than those allowed by the clothing additive regulations, thus implying a potential exploitation of the SSI in fabrication of polymers with the prolonged release of a repellent compound. This study discusses the fabrication of functionalized polypropylene (PP) non-woven and polyamide (PA) woven fabrics as well as cellulose acetate in the form of beads (CAB) and film (CAF) with pyrethrum extract in order to produce materials containing high amounts of the repellent substance suitable for applications such as disposable outdoor protective secondary clothes (not in a direct contact with skin), tent materials and different outdoor repellents. To the best of our knowledge, there is no data available in the scientific literature on impregnation of named materials with a repellent using a supercritical carbon dioxide ($scCO_2$).

2. Materials and methods

2.1. Materials

Pyrethrum extract was supplied by Sigma-Aldrich (Germany). Total pyrethrin content in the extract was determined to be 61.1 %, by a HPLC method. There were 39.4 % of pyrethrins I (3.4 % of cinerin I, 33.3 % of pyrethrin I and 2.7 % of jasmolin I) and 21.7 % of pyrethrins II (2.3 % of cinerin II, 17.8 % of pyrethrin II and 1.6 % of jasmolin II). Standard pyrethrum extract (Sigma-Aldrich, No, 33739) with defined total pyrethrins (pyrethrin I and II, cinerin I and II and jasmolin I and II) content of 49.2% was used for HPLC analyses. Cellulose acetate beads (CA-320S NF/EP) with acetyl content of 32.0% (CAB) were generous donation from Eastman (Poland). Acetone (pro analysis) was supplied by Zorka Sabac (Serbia). Acetonitrile (ACN) (for liquid chromatography) was supplied by Meck (Germany). Commercial CO_2 (purity 99%) was purchased from Messer–Tehnogas (Serbia).

Polypropylene non-woven fabric (40 g/m^2) was immersed in ethyl alcohol (Zorka, Serbia) for 10 min at liquor-to-fabric ratio of 40:1. Afterwards it was rinsed with tap and distilled water, and dried at room temperature.

Desized and bleached polyamide fabric (PA, 150 g m^{-2}) was initially cleaned in a bath containing 0.5% nonionic washing agent Felosan RG-N (Bezema). Liquor–to-fabric ratio was 50:1. After 15 min of washing at 50 °C, the fabric was rinsed once with warm water (50 °C) for 3 min and three times (3 min) with cold water. The fabric was then dried at room temperature.

Chemical structures of PP, PA and CA monomers are presented in Fig. 2.

2,2. HPLC analysis

HPLC (Agilent Technologies 1200) was used for identification of components of the commercial pyrethrum extract. Detection was performed using a Diode Array Detector (DAD), and the

chromatograms were recorded at λ = 225 nm. HPLC separation of components was achieved using a LiChrospher 100 RP 18e (5 µm), 250 × 4 mm i.d. column, with a flow rate of 1.4 mL/min and mobile phase, A (H2O), B (MeCN), elution, combination of gradient mode: 0-60% A, 0-15 min; 60-80% A, 15-25 min; isocratic 80% A, 25-35 min).

The sample was prepared by dissolving of 2 mg of the liquid extract in 1 ml of acetonitrile (ACN). The standard solution was prepared dissolving 0.7 mg of the standard extract in 1.0 mL of ACN. The prepared sample and standard were filtered through 0.2 µm PTFE filters prior to the HPLC analysis. The injected volume was 4 µL. The identification was carried out on the basis of retention time and spectra matching. Quantification was performed by external calibration with standard.

2.3. Cellulose acetate films preparation

CAFs were prepared by the solvent casting method. The film forming solution containing CAB (1.00 g), acetone (27 ml) and water (3 ml) was stirred with a magnetic stirrer for 1.5-2 h at the room temperature. The obtained clear solution was poured into a ceramic mold and dried in the air for 3-5 days, until the mass of the dried film became constant.

2.4. Supercritical impregnation

Impregnation of PP non-woven fabric, PA fabric, CAB and CAF materials with pyrethrum extract was performed in a high-pressure view cell (Eurotechnica GmbH, 25 mL) previously described in detail [40], using the static method. Pyrethrum extract (1.00 g) was placed on the bottom of the view cell in a glass container. The samples of solid carriers were put in the porous basket and placed above the glass container containing pyrethrum extract. Polytetrafluoroethylene (PTFE) coated fiberglass fabrics were placed below and above the tested materials to prevent possible splashing of the extract onto the surface of the sample during the decompression. After the required temperature in the view cell was reached, the system was pressurized. The duration of experiments ranged from

0.5 to 18 h. Impregnation of all tested materials was performed at temperature of 40 °C and pressures of 10 and 20 MPa. At the end of each experiment CO_2 was released from the bottom of the view cell at the decompression rate of 0.5 MPa/min. In order to provide pyrethrum extract in excess, the mass ratio of PP non-woven fabric / pyrethrum extract was set to 0.043± 0.005, while the ratio of other materials (PA fabric, CAB, CAF) / pyrethrum extract was 0.067± 0.005. Mass of the impregnated pyrethrum extract (m_{ex}) was determined gravimetrically as the mass difference of each material after and before the impregnation process (quantified on analytical scale with accuracy of ±0.0001 g). Impregnation yield (I) was calculated as the mass ratio of the impregnated extract and impregnated material (m_{im}) multiplied by 100% (Eq. 1).

$$I = \frac{m_{ex}}{m_{im}} \cdot 100\% \quad (1)$$

Prior to measurements, the impregnated sample surface was gently wrapped with a cotton fabric in order to remove possible pyrethrum extract droplets attached to the surface during the decompression. All the experiments were performed in triplicate. Standard deviation (σ) was calculated according to Eq. 2.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \quad (2)$$

where x_i is the i-th value of impregnation yield from the set of experiments, $\overline{x}$ is the mean value of impregnation yields for each set of experiments, and n is the number of experiments.

2.5. Pyrethrum extract release study

Kinetic studies on the pyrethrum extract release from the selected impregnated PP non-woven fabric, PA fabric, CAB and CAF materials were carried out by evaluation of 30 days long exposure to air under controlled conditions. Selected impregnated samples were kept in a digital

incubator (J. P. Selecta; temperature stability: ±0.1 °C, up to 37 °C; temperature homogeneity: ±0.5 °C, up to 37 °C) during 30 days at the temperature of 25 ºC. The repellent release from the impregnated solids was monitored daily. Mass of the samples with retained amount of extract (m_i') was determined using an analytical scale (± 0.00001g accuracy). The remained repellent content (RRC) was calculated according to Eq. 3:

$$RRC_i = \frac{m_i' - m_0}{m_i'} \cdot 100\% \quad (3)$$

where m_0 is the initial mass of the sample before the impregnation.

All the experiments were performed in triplicate.

2.6. Characterization of the samples

2.6.1. SEM analysis

The surface morphology of the PP non-woven fabric, PA fabric, CAB and CAF samples before and after the SSI with pyrethrum extract was analyzed by field emission scanning electron microscopy (FESEM, Tescan Mira3 FEG). The samples were coated with a thin layer of gold prior to analysis.

2.6.2. DSC analysis

Differential scanning calorimetry (DSC) analysis of the PP non-woven fabric, PA fabric, CAB and CAF samples before and after the SSI with pyrethrum extract was carried out using a TA Instrument differential scanning calorimeter thermal analyzer (DSC Q10). The samples (5-10 mg) were weighed in the aluminium pan and heated starting from the room temperature up to 300 °C at a heating rate of 10 °C/min, using nitrogen purge gas at 50 mL/min.

2.6.3. Mercury intrusion porosimetry

Mercury porosimetry measurements of the CAB and CAF samples before and after the SSI with pyrethrum extract were performed in the fully automated conventional porosimeter Carlo Erba 2000 series (pressure range: 0.1–200 MPa; pore diameter range: 7.5–15000 nm) supplied with the Macropore 120 Unit and data processing acquisition software package Milestone 200.

2.6.4. Fourier-transform infrared analysis

Fourier-transform infrared (FT-IR) spectra of the impregnated and control PP non-woven fabric, PA fabric, CAB and CAF samples were recorded in the ATR mode using a Nicolet™ iS™ 10 Spectrometer (Thermo Fisher SCIENTIFIC) with a resolution of 4 cm^{-1} at wavenumbers in the range of 500-4000 cm^{-1}.

2.6.5. Re-extraction of the pyrethrum extract from impregnated materials and its HPLC analysis

The pyrethrum extract was re-extracted from the impregnated materials before and after the release study employing an ultrasound extraction with ACN. The samples were cut into small pieces (~3x3 mm) and rinsed in an appropriate volume of ACN to obtain the final extract concentration of approximately 2 mg/mL. The samples were sonicated using an ultrasonic bath in three cycles, each lasting for 20 min. The standard solution was prepared by dissolving a 0.7 mg of the standard extract (Sigma, No, 33739) in 1.0 mL of ACN.

HPLC fingerprint of the samples and quantification of identified compounds was achieved by HPLC (Agilent Technologies 1200) in a manner described in section 2.2. The prepared samples and standard were filtered through 0.2 μm PTFE filters prior to HPLC analysis. The injected volume was 4 μL. The identification was carried out on the basis of retention time and spectra matching. Quantification was performed by external calibration with standard.

3. Results and discussion

3.1. Impregnation in $scCO_2$ and characterization of the samples

Operating pressure and temperature are the key factors in the SSI processes as they directly affect the dissolution of an active compound in the $scCO_2$ and diffusion of the supercritical fluid mixture into a solid carrier. Since the objective of the conducted experiments was fabrication of materials with high contents of pyrethrum extract, the temperature of 40 ºC and the pressures of 10 and 20 MPa were selected as these conditions had been previously identified as suitable to provide high solubility of pyrethrum extract in the $scCO_2$, as well as high loadings of the extract into cotton gauze [37]. The impregnation kinetics for tested materials is presented in Fig. 3. The impregnation yield increased with an increase of pressure ($scCO_2$ density) as well as with the prolongation of impregnation time until the maximal loadings of the active component in each material were achieved. Due to the fast impregnation process and considerably high impregnation yields obtained under the selected operating settings, other temperature and pressure conditions for the SSI were not taken into consideration.

The largest loading capacity among the tested materials showed PP non-woven fabric (78.01%). High impregnation yields were obtained even after short impregnation time (30 min) at both pressures. Namely, impregnation yields for PP non-woven fabric were 27.67% and 45.34% at 10 and 20 MPa, respectively. A slight fiber damage induced by the high amount of pyrethrum extract was visually noticeable in the PP fabric with the highest impregnation yield. The PP samples with pyrethrum extract content higher than 50% were in a soaked-like state. Therefore, the samples with the extract content lower than 50% were selected for the consecutive release study. The SEM image of the untreated PP fibers and impregnated fibers (impregnation yield around 45%) are shown in Fig. 4a and 4b, respectively. Smooth surface of the control fibers has been changed during the

impregnation and the fibers became wrinkled. Such morphological changes resulted from partial melting of the polymer. SEM image of the impregnated PP fiber is in line with the results of DSC analysis. Fig. 5 shows that DSC curves of the control and impregnated PP samples considerably differ. A decrease of melting temperature (T_m) from 162 °C to 154 °C suggested that the impregnated pyrethrum extract acted as a plasticizer. In addition, evident drop in the enthalpy change of melting (ΔH_m) from 79.5 J/g to 48.6 J/g indicated that the decrease of crystallinity in the impregnated polymer occurred.

In the case of PA fabric, pyrethrum extract loadings of 11.93% and 30.84% (an average of three experiments) were obtained after 18 h at 10 MPa and 20 MPa, respectively. The rate of impregnation was considerably faster under the higher pressure. PA fibers underwent neither significant morphological changes during the SSI (Fig. 4c and 4d) nor the changes in crystallinity. Namely, DSC analysis of the control PA fabric revealed the presence of moisture in the temperature range from 50-125 ºC (Fig. 5). In addition, the appearance of two melting peaks suggested the existence of two crystalline forms in the polymer [41,42]. The endothermic peak at 222.7 ºC is related to the melting of α-crystalline form, while the second melting peak at 210.0 ºC is assigned to the melting of the thermodynamically unstable γ-crystalline form [41,42]. A negligible difference in the ΔH_m between the control and impregnated PA samples (68.4 J/g vs. 62.9 J/g) implied that the crystallinity of the system remained unaltered.

Higher impregnation yields in the case of PP non-woven fabric are likely due to the chemical structure of these fibers. Larger hydrophobicity of PP fibers contributes to stronger hydrophobic-hydrophobic interactions with repellent molecules. In addition, PA fabric has a compact structure that makes the initial penetration of repellent molecules within yarns more difficult. In contrast, PP non-

woven fabric has a web structure which is more opened. Thus, the fibers are more accessible to various molecules.

Even though the same polymer (cellulose acetate) was used for the SSI, impregnation kinetics profiles for the CAB and the CAF differed considerably, implying the significance of the polymer physical form. The rate of SSI was much faster in the case of CAF compared to CAB due to larger outer surface exposed directly to $scCO_2$ and shorter pathways of sorbed molecules which led to higher values of mass transfer coefficients in CAF. Additionally, solvent evaporation performed in the solvent casting method for the fabrication of films, induced a larger void fraction in the CAF compared to the CAB which eventually brought about easier diffusion of the supercritical fluid in films than in beads. The existence of large voids in the structure of the CAF was confirmed by SEM analysis (Fig.6). Consequently, obtained yields for the CAF at 10 MPa (max. value 30.51%) were approximately three times higher during the whole impregnation period compared to the CAB (max. value 10.41%). SEM analysis of the control CAB cross section (Fig. 7) revealed highly porous structure [43]. Such structure was preserved after the SSI (Fig. 7). The SSI was considerably faster at 20 MPa for both materials. Higher pressure provided much higher loadings in the CAB (up to 24.82%) compared to those obtained at 10 MPa (up to 10.41%). In the case of CAF, the maximum material loading (around 30%) which was obtained after 18 h of the SSI at 10 MPa, was reached after only 3 h of the impregnation at 20 MPa. With the prolongation of impregnation time at 20 MPa, melting of films started.

The SSI brought about the changes in the crystallinity in both CAB and CAF. The thermograms of the control and pyrethrum extract impregnated CAB and CAF samples are presented in Fig. 8. Two characteristic endothermic peaks are noticeable on the DSC curves of both control samples. These peaks are likely due to various pyrethrum contents and different preparation methods of the CA samples. The first broad endothermic peaks located at ~120 ºC and ~100 ºC are attributed to the

evaporation of remained water [44,45] and to evaporation of the plasticizer used for the fabrication of CAB [45,46] from the control and impregnated CAB and CAF samples, respectively. The T_m of both control samples are almost identical (246.3 ºC for CAB and 246.9 ºC for CAF). The ΔH_m of the CAB and the CAF are 6.6 J/g and 4.2 J/g, respectively. Glass transition temperature (T_g) of the control CAB and CAF is detected at 218.5 ºC and 221.7 ºC, respectively.

The ΔH_m cannot be determined in the case of impregnated CAB and CAF due to the loss of crystalline arrangement. DSC analysis of these samples also implied that impregnated extract exhibited a plasticizing effect during the impregnation of CA samples. This was concluded on the basis of the T_m changes. Namely, the T_m of both impregnated CAB and CAF was shifted towards lower values (222.5 ºC and 137.5 ºC, respectively). The endothermic peak corresponding to pyrethrum extract persisted in the impregnated CAF perhaps due to higher concentrations. The decomposition of the impregnated CAB and CAF materials started at temperatures above 250 ºC and 200 ºC, respectively.

In order to define the textural properties of the CAB and CAF materials, mercury intrusion porosimetry analysis was applied. The experimental pore size distributions data are presented in the form of cumulative pore diameters distribution curves in Fig. 9a, while the derivate distribution function (dV/dlogD) is represented in Fig. 9b. The data are cumulated from larger pore diameters measured to the smallest diameter limit set by the pressuring capacity of the instrument. The samples' pore diameter was calculated from the mercury penetration curve. It should be noted that the pressurization data from mercury intrusion yields information about the size of the opening of pores and/or voids. The control sample of the CAB had the highest pore volume, the highest surface area and the smallest pores (Table 1). On the other hand, the impregnated CAB sample showed an overall reduction in total intrusion volume and a significant reduction in the specific surface area (from 34.6

to16.6 m^2/g). This result is consistent with the shift of an average pore diameter towards higher values in the case of impregnated CAB (Fig. 9b).

The samples of the control and impregnated CAF exhibited significant difference in morphology compared to CAB. Each of these average pore diameters (neat and impregnated sample) was approximately 15 times larger than the ones of CAB. Although the SEM images revealed that the slight plasticization of the polymer (CAF) occurred after the impregnation process, mercury intrusion porosimetry showed no significant change between the control and impregnated CAF sample probably due to the presence of large pores (average pore diameter >5000 nm) and voids.

The kinetics of cotton fabric SSI with pyrethrum extract at 10 MPa reported in our previous work [37] was similar to the PA fabric and the CAB SSI kinetics attained in this study, i.e. impregnation yields of 9.60%, 11.93% and 10.41% were achieved after 18 h for cotton fabric, PA fabric and CAB, respectively. The other materials tested in this study (PP non-woven fabric and CAF) showed significantly higher loading capacities compared to cotton fabric.

3.2. Fourier transform infrared analysis of samples

In order to identify the presence of pyrethrins on the surface of impregnated 210 materials, FT-IR spectroscopy of both control and impregnated samples was performed. 211 Impregnated samples with minimum impregnation yields were selected for the analysis (Fig. 10).

FT-IR analysis of the control PP sample confirmed the spectrum characteristic for polypropylene: the bands at 2950 cm^{-1} and 2877 cm^{-1} (CH_3 asymmetric and symmetric stretching vibrations, respectively) [48,49], the band at 2917 cm^{-1} (CH_2 asymmetric stretching vibrations) [48,49], the bands at 2867 and 2838 (CH_2 symmetric stretching vibrations) [48–50], the band at 1454 cm^{-1} (CH_3 asymmetric deformation vibrations or CH_2 scissor vibrations) the strong band at 1376 cm^{-1} (CH_3 symmetric deformation vibrations) [48,49,51], the band at 1167 cm^{-1} (CH_3 asymmetric rocking, C-C

asymmetric stretching, and C-H bending vibrations) the band at 997 $^{-1}$ (CH_3 symmetric rocking, C-H bending and CH_2 wagging vibrations) [48,50,52], the band at 972 cm $^{-1}$ (CH_3 rocking and C-C asymmetric stretching vibrations [50]. The band at 898 cm $^{-1}$ appears due to CH_3 and CH_2 rocking and C-H bending vibrations) [50] and the bands at 840 and 809 cm $^{-1}$ (CH_2 rocking vibrations) [48].

FT-IR spectrum of the control PA sample revealed characteristic bands, which fit well the literature data: the band at 3289 cm^{-1} (N-H stretching vibrations) [53], the band at 3087 cm^{-1} (N-H bending vibrations of secondary amide) [54], the bands at 2926 and 2855 cm^{-1} (asymmetric and symmetric stretching vibrations of CH_2 group, respectively) [54,55], the band at 1632 cm^{-1} (C =O stretching of amide I group) [56], the band at 1538 cm^{-1} (N-H bending of amide II group) [57], and the band at 687 cm^{-1} (bending of O=C-N group) [57].

Both cellulose acetate control samples (CAB and CAF) showed characteristic bands that also fit well the literature data. The broad bands between 3500 $cm^{-1}$and 3200 cm^{-1} in the spectra of CAB and CAF are attributed to OH stretching of hydroxyl group [58–61]. A broad band approximately centered at 2900 cm^{-1} originate from C-H stretching vibrations [58–60,62]. The bands at 1730 cm^{-1} in both spectra correspond to stretching vibrations of C=O group [58,59,61–63]. The band at 1430 (CAB) and 1434 (CAF), 1368, and 1221 cm^{-1}(CAB) and 1225 cm^{-1} (CAF) are assigned to C-H in plane bending, C-H bending (deformation stretch) vibrations and wagging vibrations, respectively [58,59]. The band at 1160 cm^{-1} is attributed to asymmetric bridge C-O-C [64]. The bands at 1027 cm^{-1} (CAB) and 1029 cm^{-1} (CAF) are related to C-O stretching [64]. The peak corresponding to asymmetric out-of-phase ring stretching at C_1-O-C_4 β glucosidic bond appears at 901 cm^{-1} (CAB) and 903 cm^{-1} (CAF) [58,60,61].

FT-IR spectra of impregnated PP non-woven fabric, PA fabric, CAB and CAF samples clearly indicated the presence of pyrethrins. Higher intensity of the bands at ~2900 cm^{-1} is likely due to the overlap of the characteristic bands of control samples with C–H asymmetric and symmetric vibrations

of jasmolins and cinerins, respectively [65]. The appearance of the peak at ~1715 cm^{-1} is ascribed to C=O group, while the band at 1650 cm^{-1} originates from C=C group of pyrethrins [65]. The bands at ~1257, 1150 and 1112 cm^{-1} correspond to stretching vibrations of C-O groups of pyrethrins [65].

3.3. Pyrethrum extract release study

Results of in *vivo* experiments performed with ticks in our previous study [37] showed that cotton fabric with 0.5% of pyrethrum extract successfully repelled the ticks and this data should be kept in mind when discussing the possible applications of impregnated materials obtained in this study. The kinetics of the pyrethrum extract release from the selected impregnated PP, PA, CAB and CAF samples exposed to air under controlled conditions within 30 days is presented in Fig. 11. As can be observed (Fig. 11), different materials exhibited different patterns of the repellent release.

PP non-woven fabric showed the potential to release large quantities of impregnated pyrethrum extract. The sample with 27.67% of pyrethrum extract released almost the whole repellent amount within 30 days in a nearly linear manner. The sample containing 45.34% of pyrethrum extract released around 73.5% of the repellent during 30 days. Demonstrated ability of PP fiber to release large amounts of repellent in a controlled (almost linear) manner might be of interest for fabrication of multiple use protective ankle strips for outdoor usage, as well as for fabrics with repellent properties durable for at least30 days period.

In contrast to PP non-woven fabric, PA fabric showed potential for slow release of pyrethrum extract thus preserving high repellent contents in the polymer after 30 days of exposure to air. PA sample with 4.55% of impregnated pyrethrum extract exhibited minor loss of the repellent (0.05%), while the samples with concentrations of 11.93% and 20.76% demonstrated slightly higher repellent evaporation of 1.83% and 2.36%, respectively. Reason for such different release kinetics of PP and PA samples might be stronger electrostatic interactions between functional groups of PA and pyrethrins

than between PP chains and pyrethrins. Namely, strong electrostatic interactions between nitrogen and oxygen atoms of PA (Fig. 2) and hydrogen atoms of pyrethrins (Fig. 1) are attainable. Accordingly, PA fabrics could be successfully utilized as net or tent materials, since the repellent content in textile remained stable after 30 day period.

The CAB samples with 24.82%, 15.04% and 10.41% of pyrethrum extract expressed similar behavior when exposed to air under the controlled conditions, releasing around 42% of the impregnated substance during 30 days. The sample with the lowest pyrethrum extract content (6.48%) released around 62% of the active component. This was probably because of the pyrethrum extract distribution near the bead surface due to the short impregnation time (2 h). Based on the results obtained, biodegradable polymer as CAB impregnated with pyrethrum extract would be suitable as an outdoor repellent in gardens, playgrounds, campsites etc.

As expected CAFs released pyrethrum extract faster than CABs due to the larger polymer void fraction, which was confirmed by the SEM analysis (Figs.6 and 7) and the mercury intrusion porosimetry (Table 1), larger surface exposed directly to air and shorter diffusion pathways in the solid phase. CAF with 27.78% of pyrethrum extract contained 0.47% of the repellent at the end of the experiment, while the samples with the pyrethrum extract contents of 14.17% and 6.03% released almost the whole repellent quantities in 18 and 13 days, respectively. According to obtained results, impregnated CAFs may have potential application as repellents for outdoor storage of goods in short periods.

3.4. HPLC analysis of the re-extracted matter

Chemical profile of re-extracted components from impregnated samples before and after the release study was followed by HPLC analyses. The samples with the highest impregnation yields investigated in the release study were selected for the analysis. Chemical profiles of the pyrethrum

extract used for the SSI and extracts obtained by the re-extraction from the impregnated samples before and after the release study (denoted by subscripts $_I$ and $_{RRC}$, respectively) are presented in Table 2. Percentages of the pyrethrum extract in each sample before the re-extraction are given in brackets (Table 2.). The results presented indicate that chemical profiles of the impregnated substances were consistent with the chemical profile of the extract. The analysis of total content of all pyrethrines revealed that the release of the auxiliary substances was faster compared to the release in pyrethrines in the case of PA.

CAB showed a slightly higher affinity towards auxiliary components present in the commercial pyrethrum extract compared to pyrethrins, resulted in a decrease in total pyrethrin content (53.2%) in the extract from the impregnated sample. Analyzing the contents of the active components in the extracts obtained from the samples after the release study and taking into account their ratios in the samples before and after release, it can be concluded that the extract release of all the active components was fairly uniform for all materials. CAF showed high potential for the release of the pyrethrum extract (0.57% of the extract remained after the release study). Concentration of pyrethrins in the extract obtained from the sample after the release, was considerably lower (34.1%) compared to the starting material (57.9%).

4. Conclusion

Impregnation of PP, PA, CAB and CAF materials with a natural repellent agent, pyrethrum extract, can be successfully performed in supercritical carbon dioxide. Selected temperature (40 ºC) and pressures (10 and 20 MPa) provided loading of large amounts of pyrethrum extract into tested materials. In PP non-woven fabric and CAF contents of pyrethrum extract higher than 30% were obtainable under the pressure of 10 MPa. On the other hand, to reach high pyrethrum loadings in the PA fabric and the CAB, pressure of 20 MPa was needed. A time required for obtaining high

impregnation yields varied among materials significantly. Only after 0.5 h of the process at 10 MPa impregnation yield of PP non-woven fabric reached 27.67%, while the PA fabric and the CAF needed 10 hours at 20 MPa and 10 MPa to attain similar loadings, respectively. On the other hand, the pressure increase up to 20 MPa shortened the process time to ~2.5 h for the CAF. In the case of CAB the highest yield (24.82%) was obtained after 18 h of the experiment at 20 MPa. The characteristic groups of pyrethrins in all tested materials were confirmed by the FT-IR. Pyrethrum extract release study showed different potentials of tested materials for the repellent release when exposed to air. Both tested PP non-woven fabrics (27.67 and 45.34%) showed almost linear release with time of large amounts of the repellent. On the other hand, the repellent content in PA fabrics remained stable during the 30 days of exposure to air. Biodegradable polymer such as CA loaded with pyrethrum extract was also found to be a promising repellent. It can be concluded that PP, PA and CA materials functionalized by the proposed SSI process with pyrethrum extract present novel solvent-free materials with repellent properties. Further research concerning utilization of these materials under different conditions (e.g. temperature, humidity) is needed.

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References

[1] N. Tabanca, U.R. Bernier, N.M. Agramonte, M. Tsikolia, J.R. Bloomquist, Discovery of Repellents from Natural Products, Curr. Org. Chem. 20 (2016) 2690–2702. doi:10.2174/1385272820666160421151.

[2] T. American, S. Carolina, N. Carolina, C. Hill, C. Mores, U.S.N. Medical, Long-Lasting Permethrin-Impregnated Clothing Protects Against Mosquito Bites in Outdoor Workers, Am. J. Trop. Med. Hyg. (2016). doi:10.4269/ajtmh.15-0130.

[3] R. N'Guessan, B.G.J. Knols, C. Pennetier, M. Rowland, DEET microencapsulation: a slow-release formulation enhancing the residual efficacy of bed nets against malaria vectors, Trans. R. Soc. Trop. Med. Hyg. 102 (2008) 259–262. doi:10.1016/j.trstmh.2007.10.012.

[4] M.K. Faulde, W.M. Uedelhoven, R.G. Robbins, Contact toxicity and residual activity of different permethrin-based fabric impregnation methods for Aedes aegypti (Diptera: Culicidae), Ixodes ricinus (Acari: Ixodidae), and Lepisma saccharina (Thysanura: Lepismatidae)., J. Med. Entomol. 40 (2003) 935–941. doi:10.1603/0022-2585-40.6.935.

[5] M.K. Faulde, G. Albiez, O. Nehring, Insecticidal , acaricidal and repellent effects of DEET- and IR3535-impregnated bed nets using a novel long-lasting polymer-coating technique, Parasitol Res. 106 (2010) 957–965. doi:10.1007/s00436-010-1749-6.

[6] X. Deparis, B. Frere, M. Lamizana, R.N.J. Guessan, F. Leroux, P. Lefevre, L. Finot, J. Hougard, P. Carnevale, P. Gillet, D. Baudon, Efficacy of Permethrin-Treated Uniforms in Combination with DEET Topical Repellent for Protection of French Military Troops in Cote d'Ivoire, J. Med. Entomol. 41 (2004) 914–921.

[7] M.K. Faulde, F. Pages, W. Uedelhoven, Bioactivity and laundering resistance of five commercially available, factory-treated permethrin-impregnated fabrics for the prevention of mosquito-borne diseases: the need for a standardized testing and licensing procedure, Parasitol. Res. 115 (2016) 1573–1582. doi:10.1007/s00436-015-4892-2.

[8] K. Van Roey, M. Sokny, L. Denis, N. Van Den Broeck, S. Heng, S. Siv, V. Sluydts, T. Sochantha,

M. Coosemans, L. Durnez, Field Evaluation of Picaridin Repellents Reveals Differences in Repellent Sensitivity between Southeast Asian Vectors of Malaria and Arboviruses, PLoS Negl. Trop. Dis. 8 (2014) e3326. doi:10.1371/journal.pntd.0003326.

[9] F. Chandre, F. Darrier, L. Manga, M. Akogbeto, O. Faye, J. Mouchet, P. Guillet, Status of pyrethroid resistance in Anopheles gambiae sensu lato, Bull. World Health Organ. 77 (1999) 230–234. doi:10.1016/j.revmed.2010.08.002.

[10] H. Ranson, B. Jensen, J.M. Vulule, X. Wang, J. Hemingway, F.H. Collins, Identification of a point mutation in the voltage-gated sodium channel gene of Kenyan Anopheles gambiae associated with resistance to DDT and pyrethroids, Insect Mol Biol. 9 (2000) 491–497. doi:10.1046/j.1365-2583.2000.00209.x.

[11] B.-S. Park, W.-S. Choi, J.-H. Kim, K.-H. Kim, S.-E. Lee, Monoterpenes from thyme (Thymus vulgaris) as potential mosquito repellents, J. Am. Mosq. Control Assoc. 21 (2005) 80–83. doi:https://doi.org/10.2987/8756-971X(2005)21[80:MFTTVA]2.0.CO;2.

[12] Glynne-Jones, Antonia, Pyrethrum, Pestic. Outlook, Biopestic. 12 (2001) 195–198. doi:10.1039/b108601b.

[13] J.J. Schleier III, R.K.D. Peterson, Pyrethrins and Pyrethroid Insecticides, in: O. Lopez, F.-B. Jose G. (Eds.), Green Trends Insect Control, RSC Publishing, 2011: pp. 94–131. doi:10.1039/9781849732901-00094.

[14] Y.-C. Yang, E.-H. Lee, H.-S. Lee, D.-K. Lee, Y.-J. Ahn, Repellency of aromatic medicinal plant extracts and a steam distillate to Aedes aegypti., J. Am. Mosq. Control Assoc. 20 (2004) 146–149. http://www.ncbi.nlm.nih.gov/pubmed/15264623.

[15] T.G.T. Jaenson, K. Pålsson, A.-K. Borg-Karlson, Evaluation of extracts and oils of mosquito

(Diptera: Culicidae) repellent plants from Sweden and Guinea-Bissau., J. Med. Entomol. 43 (2006) 113–119. doi:10.1603/0022-2585(2006)043[0113:EOEAOO]2.0.CO;2.

[16] I. Jantan, Z.M. Zaki, Development of Environment-Friendly Insect Repellents From the Leaf Oils of Selected Malaysian Plants, ASEAN Rev. Biodivers. Environ. Conserv. 5 (1998) 1–7.

[17] M.O. Omolo, D. Okinyo, I.O. Ndiege, W. Lwande, A. Hassanali, Repellency of essential oils of some Kenyan plants against Anopheles gambiae, Phytochemistry. 65 (2004) 2797–2802. doi:10.1016/j.phytochem.2004.08.035.

[18] Y.G. Gillij, R.M. Gleiser, J.A. Zygadlo, Mosquito repellent activity of essential oils of aromatic plants growing in Argentina, Bioresour. Technol. 99 (2008) 2507–2515. doi:10.1016/j.biortech.2007.04.066.

[19] Y. Trongtokit, C.F. Curtis, Y. Rongsriyam, Efficacy of repellent products against caged and free flying Anopheles stephensi mosquitoes, Southeast Asian J. Trop. Med. Public Health. 36 (2005) 1423–1431. doi:10.1002/ptr.1637.

[20] J.U. Rehman, A. Ali, I.A. Khan, Fitoterapia Plant based products : Use and development as repellents against mosquitoes : A review, Fitoterapia. 95 (2014) 65–74. doi:10.1016/j.fitote.2014.03.002.

[21] S.R. Kiran, P.S. Devi, Evaluation of mosquitocidal activity of essential oil and sesquiterpenes from leaves of Chloroxylon swietenia DC, Parasitol. Res. 101 (2007) 413–418. doi:10.1007/s00436-007-0485-z.

[22] T.G.E. Davies, L.M. Field, P.N.R. Usherwood, M.S. Williamson, DDT, pyrethrins, pyrethroids and insect sodium channels., IUBMB Life. 59 (2007) 151–162. doi:10.1080/15216540701352042.

[23] J. Cai, Clothing composite fabrics, CN 102756524, 2012.

[24] W.G. Reitzig, Disposable pest entry cover for open bottles, US 20130153590 A1, 2012.

[25] Z. Zhengping, Z. Zheping, Environment-friendly polyhydroxyvalerate mosquito-repellent tablet and preparation method thereof, CN 104782682 A, 2015.

[26] H.S. Woon, Multifuctional mulching paper for agriculture and the method thereof, KR20170001311 (A), 2017.

[27] M. Khoobdel, M. Shayeghi, H. Vatandoost, Y. Rassi, M.R. Abaei, H. Ladonni, A. Mehrabi Tavana, S.H. Bahrami, M.E. Najafi, S.H. Mosakazemi, K. Khamisabadi, S. Azari Hamidian, M.R. Akhoond, Field evaluation of permethrin-treated military uniforms against Anopheles stephensi and 4 species of Culex (Diptera:Culicidae) in Iran, J. Entomol. 3 (2006) 108–118. doi:10.3923/je.2006.108.118.

[28] K.S. Sum, J.M. Vulule, N. Mulaya, C. Ouma, W.G.Z.O. Jura, Effect of Netting Fabrics Impregnated with Different Doses of Natural Pyrethrins-Formulation against Anopheles gambiae, J. Basic Appl. Sci. Res. 1 (2011) 500–508.

[29] M. Faulde, W. Uedelhoven, A new clothing impregnation method for personal protection against ticks and biting insects, Int. J. Med. Microbiol. 296 (2006) 225–229. doi:10.1016/j.ijmm.2006.01.008.

[30] S.R. Evans, G.W.K. Jr., M.A. Lawson, Comparative Field Evaluation of Permethrin and Deet-Treated Military Uniforms for Personal Protection Against Ticks (Acari), J. Med. Entomol. 27 (1990) 829–834. doi:10.1093/jmedent/27.5.829.

[31] G.A. Mount, E.L. Snoddy, Pressurized Sprays of Permethrin and deet on Clothing for Personal Protection Against the Lone Star Tick and the American Dog Tick (Acari: Ixodidae), J. Econ.

Entomol. 76 (1983) 529–531. doi:10.1093/jee/76.3.529.

[32] C. Eamsila, S. Franceses, D. Strickam, Evaluation of permethrin treated military uniforms for personal protection against malaria in northeastern Thailand, J. Am. Mosq. Control Assoc. 10 (1994) 515–521.

[33] T. Inceboz, G. Erkan, G.C. Turkoglu, A.M. Sariisik, S. Bakirci, S. Uner, A. Uner, In-vivo and in-vitro tick repellent properties of cotton fabric, Text. Res. J. 85 (2015) 2071–2082. doi:10.1177/0040517515578326.

[34] T.T. Yao, L.K. Wang, J.L. Cheng, Y.Z. Hu, J.H. Zhao, G.N. Zhu, Optimization of pyrethroid and repellent on fabrics against Stegomyia albopicta (=Aedes albopictus) using a microencapsulation technique, Med. Vet. Entomol. 29 (2015) 37–43. doi:10.1111/mve.12088.

[35] A.M.A. Dias, M.E.M. Braga, I.J. Seabra, P. Ferreira, M.H. Gil, H.C. De Sousa, Development of natural-based wound dressings impregnated with bioactive compounds and using supercritical carbon dioxide, Int. J. Pharm. 408 (2011) 9–19. doi:10.1016/j.ijpharm.2011.01.063.

[36] I. Zizovic, J. Ivanovic, S. Milovanovic, M. Stamenic, Impregnations using supercritical carbon dioxide, in: E. Rój (Ed.), Supercrit. CO2 Extr. Its Appl., OIC Poland, Lublin, Poland, 2014: pp. 23–34.

[37] J. Pajnik, M. Stamenić, M. Radetić, S. Tomanović, R. Sukara, D. Mihaljica, I. Zizovic, Impregnation of cotton fabric with pyrethrum extract in supercritical carbon dioxide, J. Supercrit. Fluids. 128 (2017) 66–72. doi:10.1016/j.supflu.2017.05.006.

[38] K.E. Appel, U. Gundert-Remy, H. Fischer, M. Faulde, K.G. Mross, S. Letzel, B. Rossbach, Risk

assessment of Bundeswehr (German Federal Armed Forces) permethrin-impregnated battle dress uniforms (BDU), Int J Hyg Env. Heal. 211 (2008) 88–104. doi:10.1016/j.ijheh.2007.10.005.

[39] D. Young, S. Evans, Safety and efficacy of DEET and permethrin in the prevention of arthropod attack, Mil. Med. 163 (1998) 1–7.

[40] S. Milovanovic, M. Stamenic, D. Markovic, M. Radetic, I. Zizovic, Solubility of thymol in supercritical carbon dioxide and its impregnation on cotton gauze, J. Supercrit. Fluids. 84 (2013) 173–181. doi:10.1016/j.supflu.2013.10.003.

[41] E. Klata, K. Van de Velde, I. Krucińska, DSC investigations of polyamide 6 in hybrid GF/PA 6 yarns and composites, Polym. Test. 22 (2003) 929–937. doi:10.1016/S0142-9418(03)00043-6.

[42] R.A. da Paz, A.M.D. Leite, E.M. Araújo, V. da N. Medeiros, T.J.A. de Melo, L.A. Pessan, Mechanical and thermomechanical properties of polyamide 6/Brazilian organoclay nanocomposites, Polímeros. 26 (2016) 52–60. doi:10.1590/0104-1428.1748.

[43] S. Milovanovic, M. Stamenic, D. Markovic, J. Ivanovic, I. Zizovic, Supercritical impregnation of cellulose acetate with thymol, J. Supercrit. Fluids. 97 (2015) 107–115. doi:10.1016/j.supflu.2014.11.011.

[44] M. Sousa, A.R. Brás, H.I.M. Veiga, F.C. Ferreira, M.N. De Pinho, N.T. Correia, M. Dionísio, Dynamical characterization of a cellulose acetate polysaccharide, J. Phys. Chem. B. 114 (2010) 10939–10953. doi:10.1021/jp101665h.

[45] S. Milovanovic, D. Markovic, K. Aksentijevic, D.B. Stojanovic, J. Ivanovic, I. Zizovic, Application of cellulose acetate for controlled release of thymol, Carbohydr. Polym. 147 (2016) 344–353. doi:10.1016/j.carbpol.2016.03.093.

[46] M. Schilling, M. Bouchard, H. Khanjian, T. Learner, A. Phenix, R. Rivenc, Application of chemical and thermal analysis methods for studying cellulose ester plastics., Acc. Chem. Res. 43 (2010) 888–96. doi:10.1021/ar1000132.

[47] M. Fernández-Pérez, F. Flores-Céspedes, I. Daza-Fernández, F. Vidal-Peña, M. Villafranca-Sánchez, Lignin and lignosulfonate-based formulations to protect pyrethrins against photodegradation and volatilization, Ind. Eng. Chem. Res. 53 (2014) 13557–13564. doi:10.1021/ie500186e.

[48] R. Morent, N. De Geyter, C. Leys, L. Gengembre, E. Payen, Comparison between XPS- And FTIR-analysis of plasma-treated polypropylene film surfaces, Surf. Interface Anal. 40 (2008) 597–600. doi:10.1002/sia.2619.

[49] K.G. Kostov, T.M.C. Nishime, L.R.O. Hein, A. Toth, Study of polypropylene surface modification by air dielectric barrier discharge operated at two different frequencies, Surf. Coatings Technol. 234 (2013) 60–66. doi:10.1016/j.surfcoat.2012.09.041.

[50] E. Andreassen, Infrared and Raman spectroscopy of polypropylene, in: J. Karger-Kocsis (Ed.), Polypropylene, Springer, Dordrecht, 1999.

[51] N. Radić, B.M. Obradović, M. Kostić, B. Dojčinović, M.M. Kuraica, M. Černák, Deposition of silver ions onto DBD and DCSBD plasma treated nonwoven polypropylene, Surf. Coatings Technol. 206 (2012) 5006–5011. doi:10.1016/j.surfcoat.2012.06.020.

[52] V. Sciarratta, D. Vohrer, D. Hegemann, M. Muller, C. Oehr, Plasma functionalization of polypropylene with acrylic acid, Surf. Coatings Technol. 174–175 (2003) 805–810. doi:10.1016/S0257-8972.

[53] C. Chang, G. Liou, S. Hsiao, Highly stable anodic green electrochromic aromatic polyamides :

synthesis and electrochromic properties, J. Mater. Chem. 17 (2007) 1007–1015. doi:10.1039/b613140a.

[54] L.A. Díaz-Alejo, E.C. Menchaca-Campos, J. Uruchurtu Chavarín, R. Sosa-Fonseca, M.A. García-Sánchez, Effects of the addition of ortho - And para NH2 substituted tetraphenylporphyrins on the structure of nylon 66, Int. J. Polym. Sci. 2013 (2013) 14. doi:10.1155/2013/323854.

[55] K. Zarshenas, A. Aroujalian, RSC Advances Surface modi fi cation of polyamide composite membranes by corona air plasma for gas separation, RSC Adv. 5 (2015) 19760–19772. doi:10.1039/C4RA15547E.

[56] D. Pavliňák, J. Hnilica, A. Quade, J. Schäfer, M. Alberti, V. Kudrle, Functionalisation and pore size control of electrospun PA6 nanofibres using a microwave jet plasma, Polym. Degrad. Stab. 108 (2014) 48–55. doi:10.1016/j.polymdegradstab.2014.05.027.

[57] M. Sadeghi-Kiakhani, S. Safapour, Improvement of dyeing and antimicrobial properties of nylon fabrics modified using chitosan-poly(propylene imine) dendreimer hybrid, J. Ind. Eng. Chem. 33 (2015) 170–177. doi:10.1016/j.jiec.2015.09.034.

[58] S. Waheed, A. Ahmad, S.M. Khan, S. e. Gul, T. Jamil, A. Islam, T. Hussain, Synthesis, characterization, permeation and antibacterial properties of cellulose acetate/polyethylene glycol membranes modified with chitosan, Desalination. 351 (2014) 59–69. doi:10.1016/j.desal.2014.07.019.

[59] A. Khalf, K. Singarapu, S. V. Madihally, Cellulose acetate core–shell structured electrospun fiber: fabrication and characterization, Cellulose. 22 (2015) 1389–1400. doi:10.1007/s10570-015-0555-9.

[60] H. Kamal, F.M. Abd-Elrahim, S. Lotfy, Characterization and some properties of cellulose

acetate-co-polyethylene oxide blends prepared by the use of gamma irradiation, J. Radiat. Res. Appl. Sci. 7 (2014) 146–153. doi:10.1016/j.jrras.2014.01.003.

[61] C. Liu, R. Bai, Preparation of chitosan/cellulose acetate blend hollow fibers for adsorptive performance, J. Memb. Sci. 267 (2005) 68–77. doi:10.1016/j.memsci.2005.06.001.

[62] S.F. Dehkordi, M. Pakizeh, M. Namvar-Mahboub, Properties and ultrafiltration efficiency of cellulose acetate/organically modified Mt (CA/OMMt) nanocomposite membrane for humic acid removal, Appl. Clay Sci. 105–106 (2015) 178–185. doi:10.1016/j.clay.2014.11.042.

[63] M. Zafar, M. Ali, S.M. Khan, T. Jamil, M.T.Z. Butt, Effect of additives on the properties and performance of cellulose acetate derivative membranes in the separation of isopropanol/water mixtures, Desalination. 285 (2012) 359–365. doi:10.1016/j.desal.2011.10.027.

[64] C. Chung, M. Lee, E. Kyung, Characterization of cotton fabric scouring by FT-IR ATR spectroscopy, Carbohydr. Polym. 58 (2004) 417–420. doi:10.1016/j.carbpol.2004.08.005.

[65] K. Essig, Z.J. Zhao, Preparation and Characterization of a Pyrethrum Extract Standard, LCGC North Am. 19 (2001) 4–8.

Figure captions

Fig. 1. Structural formulas of pyrethrins.

Fig. 2. Structural formulas of tested polymer materials.

Fig. 3. SSI kinetics of the PP non-woven fabric, PA fabric, CAB and CAF at 40 ºC.

Fig. 4. SEM images of the (a) control PP fibers, (b) impregnated PP fibers (45.22%), (c) control PA fibers and impregnated PA fibers (20.65%).

Fig 5. DSC curves of the control and impregnated PP (45.22%) and PA (20.65%) fibers.

Fig. 6. SEM images of the (a) control CAF (b) impregnated CAF (28.66%).

Fig. 7. SEM images of the cross sections of the (a) control CAB and (b) impregnated CAB (24.76%).

Fig. 8. DSC curves of the control and impregnated CAB (24.76%) and CAF (28.66%).

Fig. 9. Cumulative intrusion volume and log differential intrusion curves of the CAB and CAF samples before and after the SSI vs. pore diameter

Fig. 10. FT-IR spectra of control (PP non-woven fabric, PA fabric, CAB and CAF) and pyrethrum extract (Pyr) impregnated materials (PP + Pyr 26.40%, PA + Pyr 4.35%, CAB + Pyr 0.66% and CAF + Pyr 5.78%).

Fig. 11. Remained repellent content in the samples versus time at 25 ºC: (a) PP non-woven fabric, (b) PA fabric, (c) CAB and (d) CAF.

Table 1. Textural characteristics of the CAF and CAB before and after the SSI.

Type of material	V_p (mm^3/g)	S_s (m^2/g)	$D_{p,average}$ (nm)	P (vol%)
CAB	961	34.6	340	21
CAB+Pyr 24.76%	715	16.6	420	17

CAF	720	14.2	5800	16
CAF+Pyr 28.66%	738	14.4	5050	16

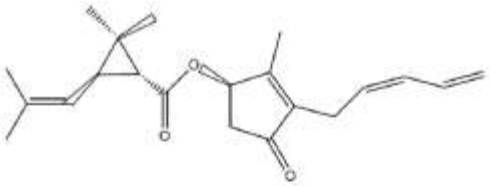
V_p, pore volume; S_s, specific surfacce area; $D_{p,\ average,}$ pore diameter average; P, Porosity.

	Pyrethrum extract components content, %								
	Pyr. extract	PP_I (45.22%)	PP_{RRC} (11.69%)	PA_I (20.65%)	PA_{RRC} (18.06%)	CAB_I (24.76%)	CAB_{RRC} (14.66%)	CAF_I (28.86%)	CAF_{RRC} (0.57%)
Cinerin I	3.4	3.2	3.8	3.4	4.2	3.0	2.8	3.3	1.8
Pyrethrin I	33.3	31.2	36.3	32.5	40.1	28.9	27.6	31.4	18.6
Jasmolin I	2.7	2.4	2.8	2.5	3.1	2.2	2.2	2.5	1.4
Cinerin II	2.3	2.3	2.7	2.4	3.0	2.1	2.0	2.3	1.3
Pyrethrin II	17.8	16.7	19.4	17.4	21.5	15.5	14.8	16.8	10
Jasmolin II	1.6	1.6	1.8	1.7	2.1	1.5	1.4	1.6	1.0
∑	61.1	57.4	66.8	59.9	74	53.2	50.8	57.9	34.1

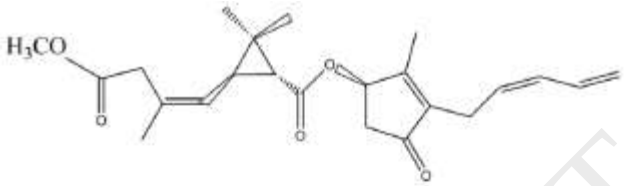
*$_I$, impregnated; $_{RRC}$, remained repellent content.

Table 2. Chemical profiles of the pyrethrum extract (Pyr. extract) and extracts obtained by the re-extracteion (pyrethrum contents in the re-extracted materials are given in the brackets)

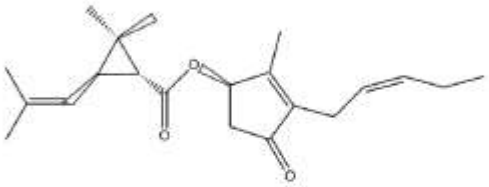
Figr-1



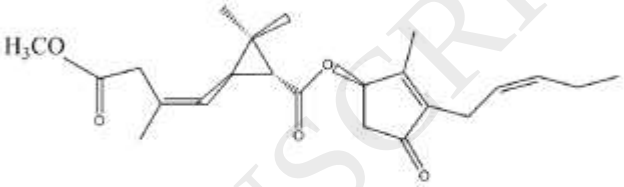
Pyrethrin I



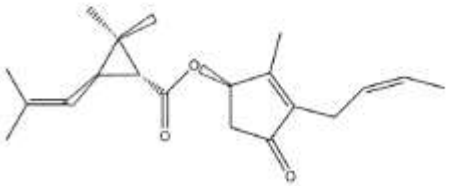
Pyrethrin II



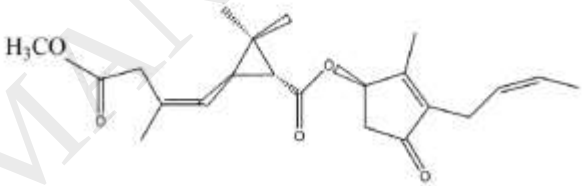
Jasmolin I



Jasmolin II

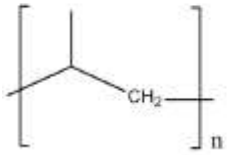


Cinerin I

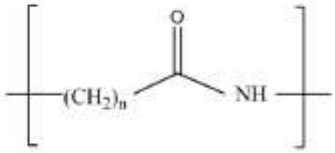


Cinerin II

Figr-2



PP



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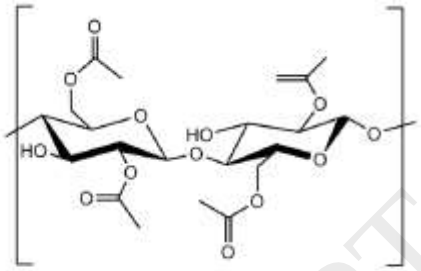
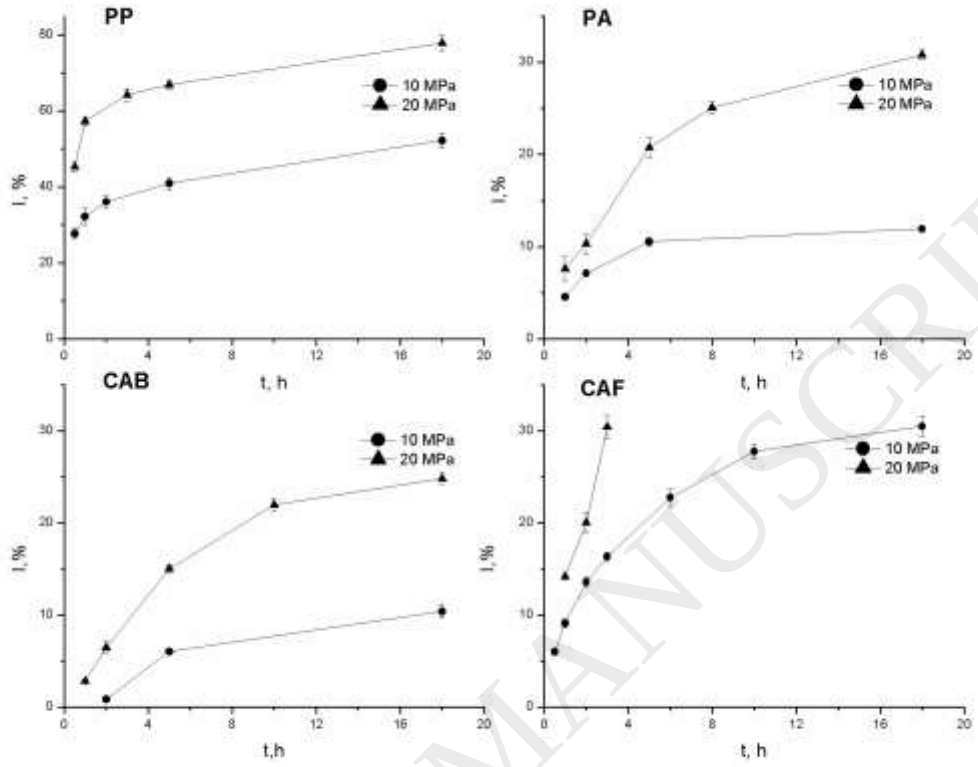
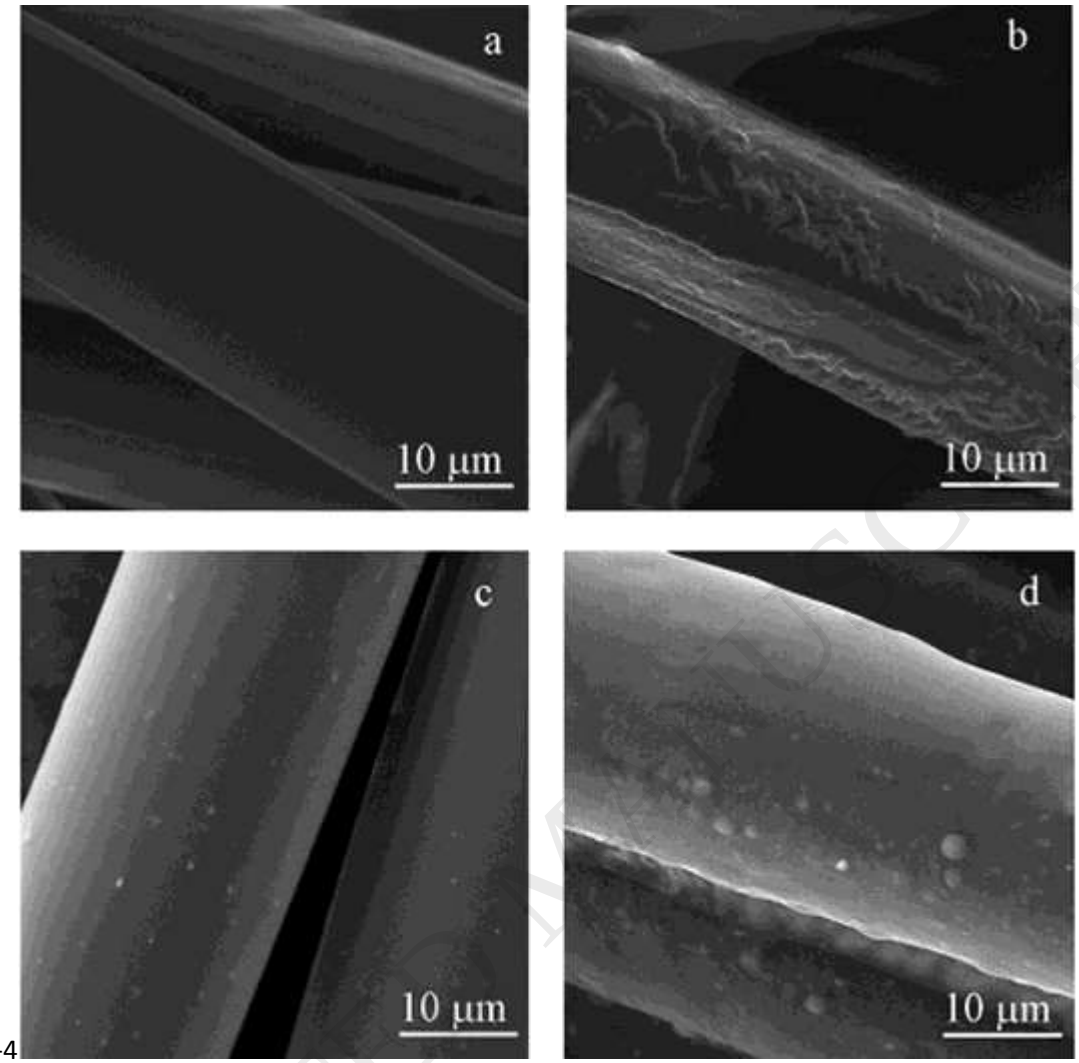


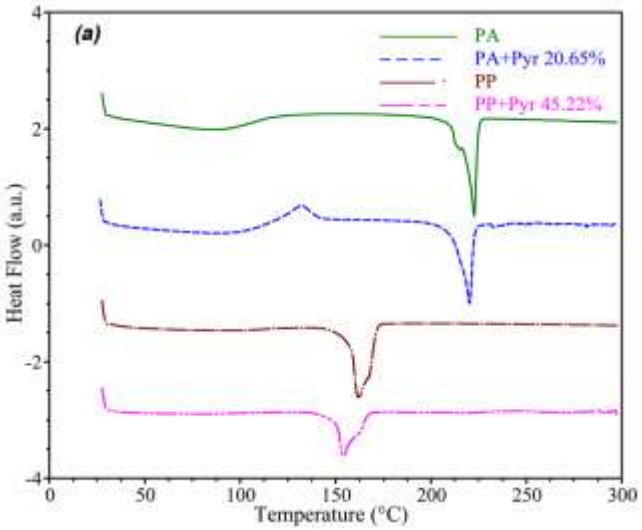
CA

Figr-3

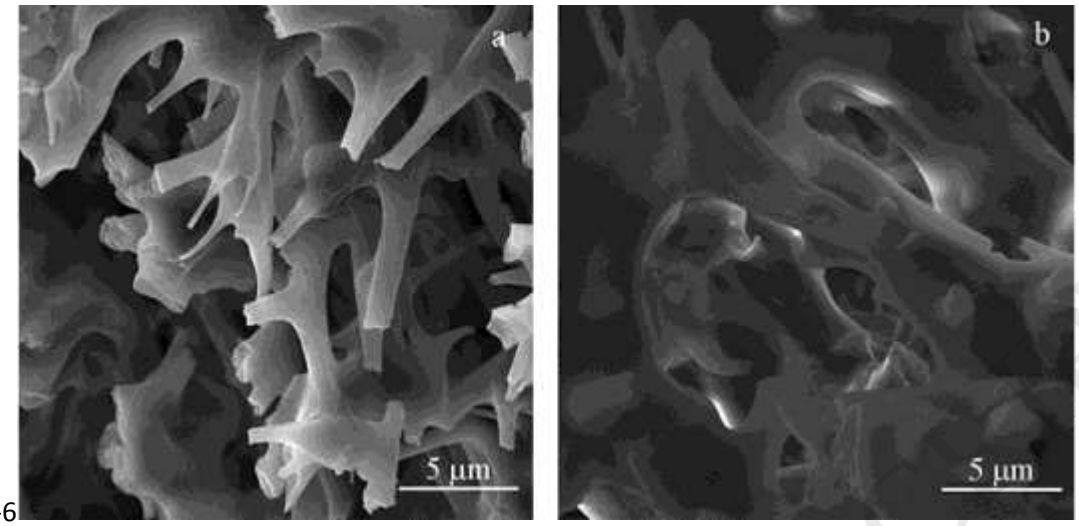




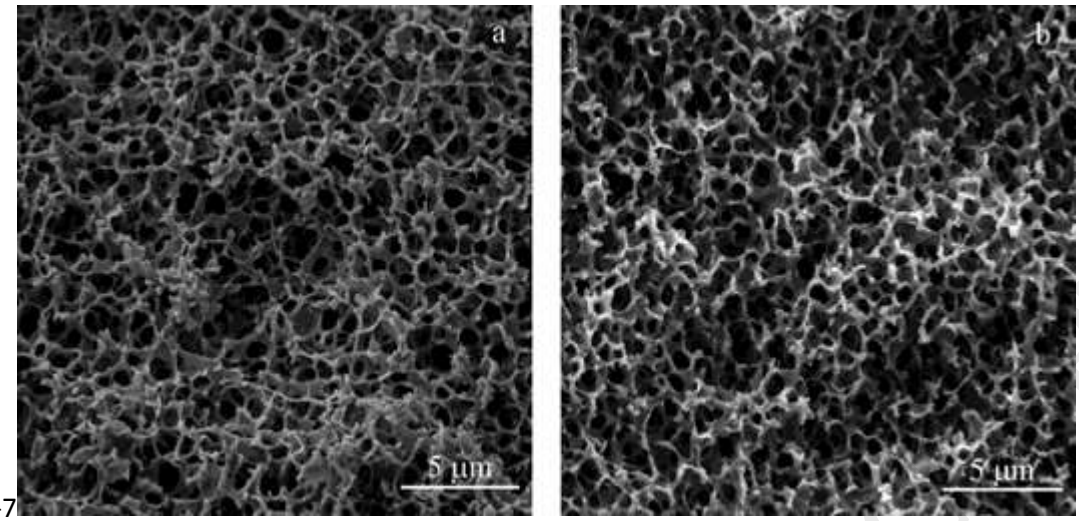
Figr-4



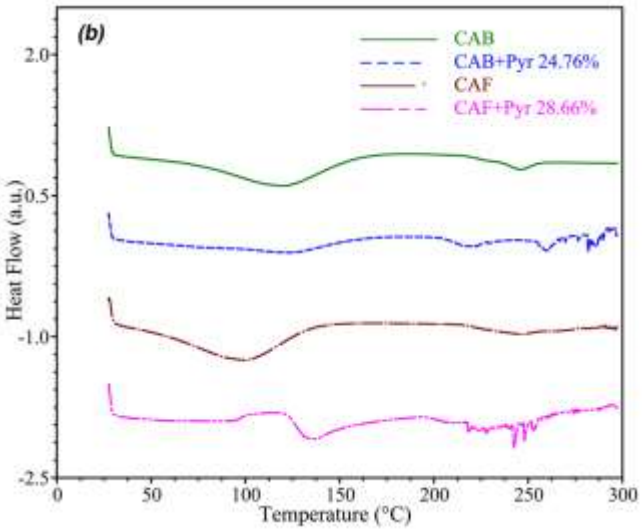
Figr-5



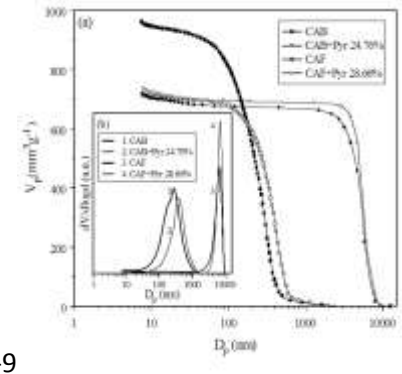
Figr-6



Figr-7

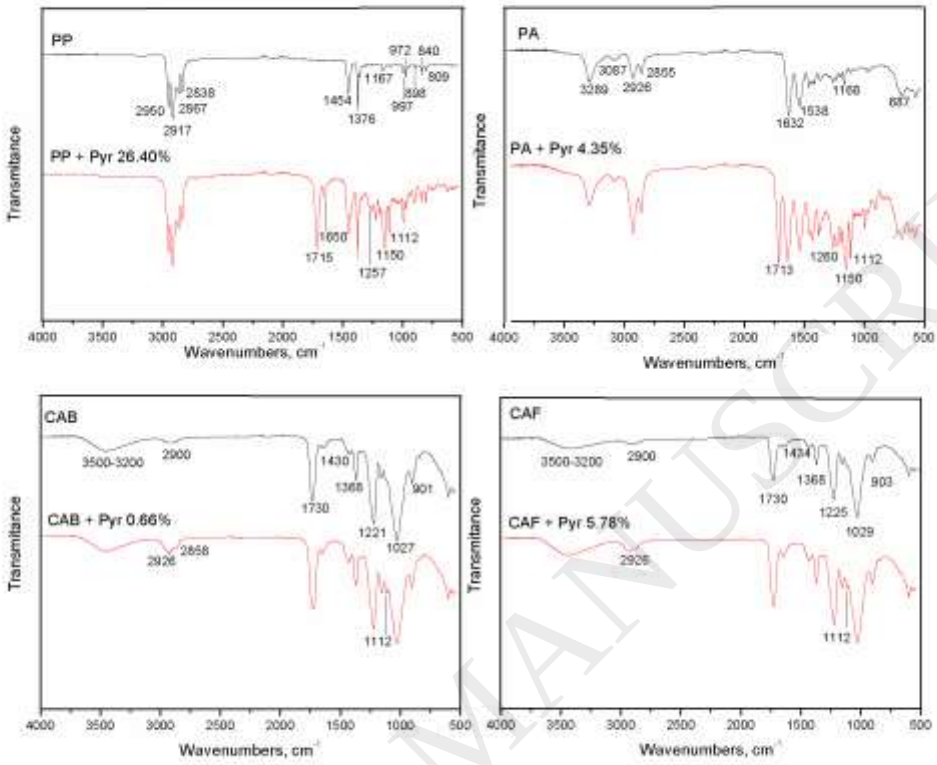


Figr-8



Figr-9

Figr-10



Figr-11