Materials Technology Reports 2023; 1(1): 459.
Original Research Article

Effects of pyrolyzed Buxus sempervirens ingredient as micro and bio fillers on polystyrene: Spectroscopic characteristics

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ARTICLE INFO

Received: 20 September 2023
Accepted: 27 October 2023
Available online: 20 December 2023

doi: 10.59400/mtr.v1i1.459

ABSTRACT: In this study, *Buxus sempervirens* leaf ingredient (LP) and the carbon (LC) and the ash (LA) were obtained, which are the bio-originated materials. Carbon and ash obtained from this natural plant were prepared by heating and pyrolysis for 2 h at 250 °C and 700 °C, respectively. Then, the solution casting method was used to prepare the composites of these bio-additives with polystyrene. Next, the effects of the additives on diffuse reflectance spectroscopy (DRS) and X-ray diffraction (XRD) spectra of polystyrene were investigated. In addition, the additives led to noticeable changes in X-ray diffraction results, implying a change in the morphology of the polymer. All of these observations imply the uniform formation of the polystyrene (PS) composites with the micro and bio-fillers.

KEYWORDS: polystyrene; Buxus sempervirens ingredient; bio-composite; spectroscopy

1. Introduction

Agricultural and vegetable wastes are associated with some environmental issues that need to be solved. Using these residual materials in various composite materials is a way utilized in many research and industrial applications. For example, Nazarpour-Fard et al. used *Buxus sempervirens* ingredients for modifying the polyvinylpyrrolidone (PVP) properties[1]. Also, they utilized the rice husk ash for modifying the thermal, hydrophilicity, and spectroscopic characteristics of polyvinylpyrrolidone and polystyrene[2,3], thermal characteristics of chitosan[4], and mechanical properties of linear low-density and high-density polyethylene[5].

Polystyrene is one of the famous thermoplastics used in various fields and its composites with various micro and nano materials have been studied and practically used. It should be noted that the suspension method is one of the common and widely used methods in the synthesis of polystyrene[6,7].

Solution casting is the most common method used to prepare polymer and non-polymer composites. In this procedure, all components of the composite are dissolved in a suitable solvent, and after the evaporation of the solvent and drying of the sample, the desired composite is prepared. For example, we can refer to many research studies such as the preparation of graphene oxide/polyaniline/polystyrene composites[8]. Moreover, Yadav et al.[9] employed this procedure for preparing poly (methylmethacrylate)-$BiFeO_3$Polystyrene-2% divinyl benzene composites[9].

The preparation of polymer composites from biomaterials has attracted increasing attention due to the excessive consumption and exploitation of non-renewable resources such as coal and oil. In this context, the composite compounds obtained from plant wastes have received more attention owing to their abundance and in order to protect the environment. For instance, the leaves of various plants are widely used resources that can be utilized in many research and industrial fields[10,11]. In other studies, chitosan/pectin-rich vegetable waste composites were successfully prepared for use in the active packaging of dry foods[12]. Also, Cherkashina et al. employed *Hazelnut Shells* as a valuable additive for modifying polystyrene properties[13]. Moreover, Nazarpour-Fard used bio-additives prepared from rice husk to modify the polystyrene and polyvinylpyrrolidone characteristics and obtained valuable results[1–5].

Here, based on the above-mentioned explanations and for protecting the environment and the correct use of plant and environmental wastes, it was decided to use the waste of *Buxus sempervirens* ingredient (which is left into the environment as a waste originated from biomaterial) as an additive for polystyrene composites. Its carbon and ash derivatives obtained by thermal pyrolysis, were also used as bio-derived and valuable additives to prepare polystyrene composites. These additives showed the observable effects on the DRS and XRD spectra of the polymer, which will be discussed detailly in the next sections.

2. Experimental

2.1. Materials

Polystyrene was synthesized by suspension polymerization method based on the published article[14], as its schematic representation has been shown in **Figure 1**. Toluene (used to dissolve polystyrene) was manufactured by Merck, Germany. The carbon and ash materials were obtained by thermal pyrolysis method in a laboratory furnace as previously reported by Nazarpour-Fard et al.[1–5].

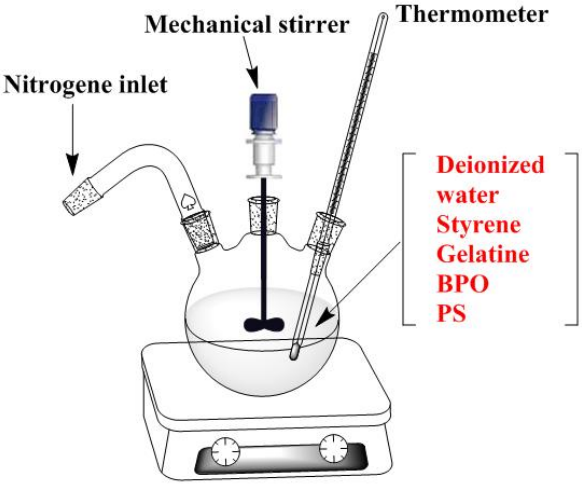

Figure 1. Schematic of the system for polystyrene synthesis.

2.2. Instrumentation

The sonication of the solutions was carried out by using an ultrasonic bath (Sono Swiss, Sw3H, Switzerland). Knauer Instrument (Germany) was used as gel permeation chromatography (GPC) for determining the average molecular weight and polydispersity index of the prepared polystyrene. X-ray diffraction (XRD) analysis was performed on a Philips diffractometer (PW1840 made in Holland Netherlands) with Cu-Kα radiation. burning the plant waste to provide the favorite carbon and ash was done by using a Nabertherm furnace (made in Germany) adjustable up to the temperature of 3000 °C. Visible Reflection Transmission Spectra (DRS) was taken using a Shimadzu UV-2100 spectrometer.

2.3. Polystyrene synthesis

The process of polymer synthesis was carried out as radical suspension polymerization. Here, deionized water (250 cm^3) and gelatine (1.25 g) were poured into a 500 cm^3 three-neck glass reactor fitted with a nitrogen inlet, a stirrer, and a condenser. 20 $cm^3$of styrene was mixed with 0.5 g of benzoyl peroxide (BPO) and then added into the reactor. The reaction medium was mechanically agitated to prepare the uniform condition for polymerization. The temperature inside the reactor was continuously computed by a thermometer fixed to the reactor system. The temperature of the suspension reaction was gradually enhanced to 95 °C, where the polymerization was done for 3.5 h under nitrogen atmosphere. Then, the synthesized PS particles as uniform granules were filtered and separated, washed with deionized water, and dried in an oven at 60 °C. The example of synthesized PS granules has been reported by Slobodian et al.[14].

2.4. Preparation of carbon and ash from the plant waste

In order to prepare carbon and ash from the waste of plant leaves, the dried waste was first powdered with the size of fine particles by using a ball mill (**Figure 2(a)**). Then it was heated in a laboratory furnace at the temperature of 250 °C for 2 h to turn into a carbon material (**Figure 2(b)**). Additionally, it was passed through a sieve with 200 mesh to be used in the preparation of polymer composites as a bio-additive. The process of ash preparation (**Figure 2(c)**) was also done in the same way but at the temperature of 700 °C.

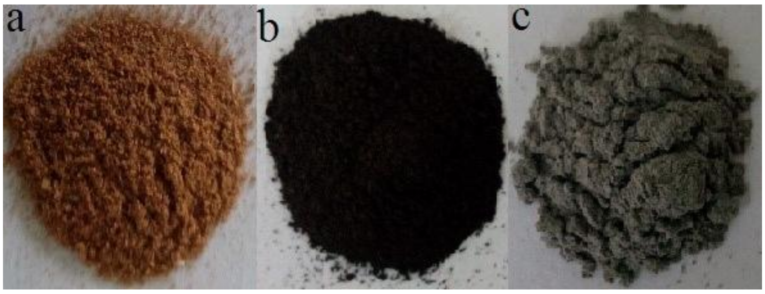

Figure 2. Image of **(a)** *Buxus sempervirens* leaf ingredient, and **(b)** carbon and **(c)** ash obtained from this type of plant waste.

2.5. Preparation of polystyrene composites with the additives

To prepare a polystyrene composite, a polystyrene solution was obtained in toluene solvent at ambient temperature. Then, using mechanical and ultrasonic stirring methods, the additives were well distributed in the polystyrene solution. The polystyrene composites with *Buxus sempervirens* leaf ingredient (PS-L), carbon (PS-C), and ash (PS-A) were prepared through the evaporation of toluene by drying process at a suitable temperature. The composition of the additives in all the composites was 2 wt%.

3. Results and discussion

3.1. Identification of polystyrene by gel permeation chromatography (GPC)

The molecular weight and molecular weight distribution (PDI) of the synthesized polystyrene were determined through gel permeation chromatography analysis. The results of these investigations are shown in **Figure 3** and **Table 1**. As it is clear that, the weight and number average molecular weights are 33,949 and 19,905 g mol^{-1}, respectively. It was found that the polydispersity index (molecular weight distribution) value of the synthesized polystyrene (1.705) was in accordance with that of commercial PS as formerly reported by Chen et al.[15].

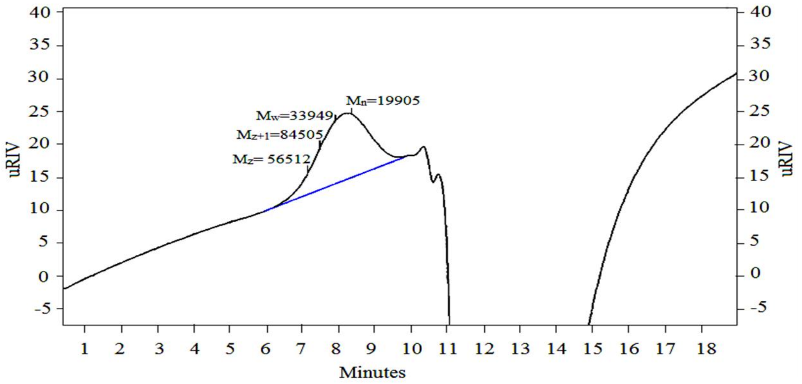

Figure 3. GPC chromatogram for the synthesized polystyrene.

Table 1. Average molecular weight and molecular weight distribution of synthesized polystyrene.

Characteristic	Amplitude
Weight average molecular weight ($\bar{M}_w$)	33,949 g mol^{-1}
Number average molecular weight ($\bar{M}_n$)	19,905 g mol^{-1}
Z average molecular weight	56,512 g mol^{-1}
Z + 1 average molecular weight	84,505 g mol^{-1}
Peak molecular weight	22,409 g mol^{-1}
Polydispersity index	1.705

3.2. The effect of additives on absorption of visible light by polyvinylpyrrolidone and polystyrene

Investigation of the additive effect on the absorption of visible waves by polystyrene composites showed that these additives have an increasing effect on the absorption of visible light by the polymer (**Figure 4**). However, it is clear that after the addition of additives to the polymer matrix, the absorption values of all the composites have increased as compared to the pure polymer. The increasing trend is also proof of the formation of composites with a uniform distribution of particles in the polymer matrix. It is obvious that in the case of composite containing carbon and ash, two peaks have been observed in the range of 400 to 450 nm, which can be due to the presence of functional groups in these additives and/or due to their different interactions with polystyrene, in comparison to PS-LP sample. The similar observations were reported for polyvinylpyrrolidone composites with *Buxus sempervirens* ingredients[1], as well as for chitosan after adding rice husk ash[4].

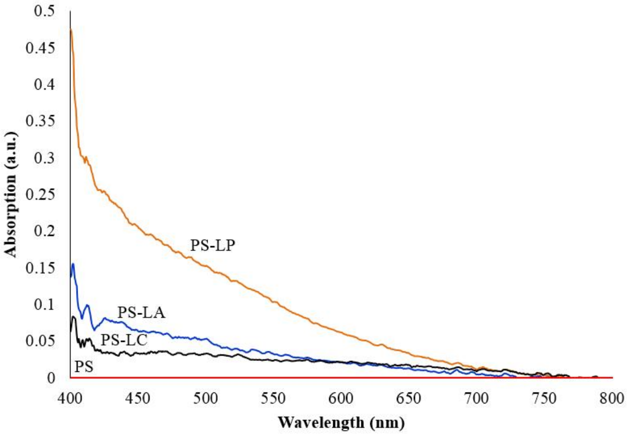

Figure 4. DRS visible spectra for polystyrene and their composites.

3.3. The effect of additives on the XRD pattern of polyvinylpyrrolidone and polystyrene

Examining the XRD results for polystyrene in **Figure 5**, shows that the additives have had significant effects on the XRD pattern of polystyrene. In other words, the addition of carbon and ash to this polymer not only caused the shift of the peak located at around 19.5° to higher degrees but also led to an increase of the full width at half maximum (*FWHM*) of the peak. In the case of PS-LP, we can see no drastic changes. All of these observations show that these additives affect the morphology and crystal structure of polystyrene. But the effects in PS-LC and PS-LA were greater compared to PS-LP, which could be due to stronger interactions and bonds between these bio-additives and the PS matrix. It is worth mentioning that the values of *d*-spacing parameter in all the composites were higher as compared to pure PSS indicating an increase in the size of crystalline particles in the semi-structured samples. It is obvious that molecular arrangement and interactions between the composite components are of the main factors controlling the polymer crystallinity. Moreover, the appearance of new peaks in the XRD patterns of the composites exhibits the creation of new crystalline area in the composites (**Table 2**). Some changes in XRD of PVP and PS have been observed after adding rice husk derivatives as can be seen in the literature [2,3].

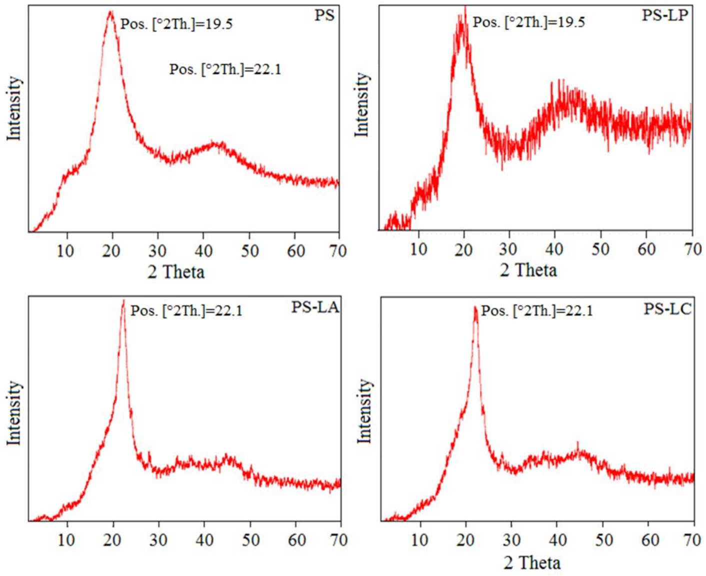

Figure 5. X-ray diffraction spectra of polystyrene and its composites.

Table 2. X-ray diffraction results of the PS samples.

	Peak	Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	*d*-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]
PS	1	9.895	86.72	1.92	8.93176	30.86	1.6
	2	23.0265	281.06	1.0184	3.86252	100	0.8487
PS-LP	2	19.743	281.1	1.0612	4.49685	100	0.8843
PS-LC	2	22.3645	1456.49	1.536	3.97203	100	1.28
PS-LA	2	22.289	1892.98	1.5744	3.98863	100	1.6

4. Conclusion

In this research study, polystyrene composites with *Buxus sempervirens* ingredients and the prepared carbon and ash materials were prepared via the solution casting method. The results of DRS and XRD investigations showed that incorporating the biomaterials into the polymer matrix leads to changes in their spectroscopic results. For example, in the DRS spectrum, polystyrene did not show absorption in the visible region, but the composites showed more absorption compared to the parent polymer. The composites of PS-LC and PS-LA showed a peak at around 400 nm that did not appear in the case of PS-LP composite. The XRD results exhibited that these additives cause shifting of 2θ values of the PS peaks as well as changes in the width of peaks and the d parameter. This indicates an alteration in the size of crystals and the morphology of the polymer. The study showed that the derivatives of *Buxus sempervirens* leaf ingredient prepared by pyrolysis can lead to the observable changes in DRS and XRD spectra of polystyrene. Thus, the effects of these additives on other properties of PS and other polymers can be considered interesting studies in the future.

Conflict of interest

The author declares no conflict of interest.

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