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MANUFACTURE OF NATURAL FIBER FILLED POLYSTYRENE COMPOSITES AND THEIR MICROCELLULAR FOAMS

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Abstract:

In this study, lignocellulosic filler (wood flour or wheat straw flour) and polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-graft-maleic anhydride (SEBS-MA) additive were used to manufacture polystyrene-based composites through compression molding. Some of the manufactured composites were foamed using microcellular foaming technology. Mechanical properties such as tensile strength, tensile modulus, elongation at break, flexural strength, flexural modulus and impact strength tests and prefoaming solubility and diffusivity values of composite samples were determined. Densities of the foamed samples were measured. Also morphologies of them were studied using scanning electron microscopy (SEM).

In the case of mechanical properties, filler type and filler loading had a significant effect on all mechanical properties investigated. Composites produced with wood flour provided better mechanical properties compared to the one with wheat straw flour. Regardless of filler type, with the increase of filler loading, tensile and flexural strength were reduced while modulus of elasticity and impact strength were improved. With the increase of additive loading, all properties except for elongation at break and impact strength were diminished. Density of composites were increased with filler loading but reduced with additive loading. In general, composites produced with wood flour provided higher densities than the ones produced with wheat straw flours.

Before foaming, solubility and diffusivity of manufactured composites were determined. Solubility of composites were reduced with filler loading but not affected by filler type and additive loading. However, at high filler loading, solubility was positively affected by additive loading. In the case of diffusivity, there was a more complex relationship. Diffusivity was significantly affected by all factors (filler type, filler loading and additive loadig).

The changes on density (before and after foaming) were also studied and density reductions were calculated. Regardless of filler type, with the increase of filler and additive loading, density reduction of the foamed samples was reduced. Additive had a deleterious affect on density reduction but at high filler loadings this reduction was less severe. Scanning electron microscopy (SEM) of the produced composites was taken. Samples having no filler and additive provided homogenously distributed fine cells. However, regardless of filler type composites with additive and filler provided cells in less number and bigger in size.

Key words: *Wwod composite; Polystyren; batch process microcellular foaming; foam; mechanical properties.*

INTRODUCTION

Even though polymer composites utilizing lignocellulosic materials as filler or reinforcer are present in the markets, their usages are still limited in areas requiring lower stiffness and high impact resistances (Matuana and Heiden 2004, Faruk *et al.* 2007, Mengeloglu and Karakus 2008, Mengeloglu and Kabakcı, 2008). Improving these drawbacks of polymer composites may extent the usage area of this type of materials. The idea of generating microcellular foams in this composite was considered and some studies in this area were conducted (Matuana *et al.* 1996, Faruk *et al.* 2007, Mengeloglu *et al.* 2009). Compare to unfoamed counter parts, foamed polymers provide lower weight and better performance-cost and strength-weight ratios. In foamed profiles, better surface properties, sharper edges and corners can be produced. In addition, foaming might provide economical advantages due to lower raw material utilizations. It should also be noted that, during process gas plasticizes the polymer matrix allowing lower temperature and higher speed for manufacturing. This also reduces the manufacturing costs (Faruk *et al.* 2007). For wood fiber filled polymer composites, it is reported that generating microcellular foams improved the specific mechanical properties (Matuana *et al.* 1996, Faruk *et al.* 2007).

There has been some research on the microcellular foaming of lignocellulosic material filled PS based composites. Doroudiani *et al.* (2002) studied the manufacture of wood flour filled PS based composites and determined their diffusivity and solubility values after they are saturated with CO_2 gas. The effect of gas pressure (CO_2) and filler loading on diffusivity and solubility of the composites were investigated. It is found that increasing gas pressure resulted in higher solubility and diffusivity values for composites while rising filler loading reduced these values. In another study, lignocellulosic fibre filled PS based composites were manufactured and their foaming was studied (Doroudiani and Kortschot 2004). Based on this study, density of the composites was reduced with increasing foaming time. In addition, raising the amount of fibre initially increased the density and then levelled off. Foaming temperature was also studied. Its effect on density was found to be less compared to foaming time and filler amount. Best impact strength result of the foamed composites was achieved when 60MPa foaming pressure, 110˚C foaming time and 20% filler loading were used.

In this study, lignocellulosic filler (wood flour or wheat straw flour) and polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-graft-maleic anhydride (SEBS-MA) additive were used to manufacture polystyrene-based composites through compression molding. The manufactured composites were foamed using microcellular foaming technology. Mechanical properties such as tensile strength, tensile modulus, elongation at break, flexural strength, flexural modulus and impact strength tests and prefoaming solubility and diffusivity values of composite samples were determined. Densities of the foamed samples were measured. Also morphologies of them were studied using scanning electron microscopy (SEM).

EXPERIMENTAL

Polymer composites were manufactured utilising crystal Polistyrene (PS) as polymer matrix and wood flour (Turkish Red Pine) and wheat straw flour as fillers.

Materials

PS and additive Polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene-*graft*-maleic anhydride (SEBS-MA) were purchased from Guclu Plastik and Sigma Aldrich, respectively: they were used as received from the manufacturer. Short description of the SEBS-MA was presented in Table 1.

Table 1

Properties of Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-graft-maleic anhydride

MFI	~21 g/10 min (230°C/5.0kg)
Ingredients	maleic anhydrite, ~2 wt. %
Hardness	75 (Shore A)
Viscozity	12.5, %15 wt, toluen (25°C)
Density	0.91 g/mL at 25°C(lit,)
Elongation	ASTM D 412 - 500%

Composite manufacturing

Composite manufacturing was accomplished in a two stage process; production of pellets and production of composites. The experimental design of the study is presented in Table 2. In the first stage, crystallne polystyrene (PS), 60 mesh-size wood flour (WF) or wheat straw flour (WS), and additive (SEBS-MA) were dry-mixed in a high-intensity mixer to produce a homogeneous blend. This blend was then compounded in a laboratory-scale single screw extruder at 40rpm screw speed in the temperatures (barrel to die) of 170-180-185-190-200°C. Extruded samples were collected, cooled, and granulated into pellets. In the

second stage, these pellets were compression molded into 2mmx160mmx180mm dimension of panels using hot pres with cooling capabilities.

Table 2

Manufacturing compositions (%)

Grup ID	Polistiren (PS)	Filler (wood flour and wheat straw flour) (WF/WS)*	Additive (SEBS-MA)
1	98.25	0	1.75
2	94.50	5	0.50
3	92.00	5	3.00
4	83.00	0	17.00
5	79.50	17	3.50
6	81.25	17	1.75
7	70.50	29	0.50
8	68.00	29	3.00
9	64.25	34	1.75

*WF: Wood flour, WS: Wheat straw flour

Composite testing

Testing of the samples was conducted in a climate-controlled testing laboratory. Densities were measured by a water displacement technique according to the ASTM D 792 standard. Flexural, tensile, and impact properties of all samples were determined according to ASTM D 790, ASTM D 638, and ASTM D 256, respectively. Ten samples for each group were tested. Flexural and tensile testing were performed on Zwick 10KN while a HIT5,5P by Zwick™ was used for impact property testing on notched samples. The notches were added using a Polytest notching cutter by RayRan™.

Microcellular foaming of composites

During the batch microcellular foaming, determination of solubility and diffusivity is very important, Solubility was taken as the amount of gas (%) absorped by the sample. Diffusivity is calculated as diffusion rate of gas coming out of the sample using equation 1.

Samples with same dimensions were also used for microcellular foaming. Samples were first saturated with gas under pressure, then pressure chamber was opened and the samples were foamed in a hot gliserin bath. After foaming, foamed samples were dipped into cold water to stop cell coalescences. During foaming process, optimum foaming (foaming time and foaming temperatures) were determined.

$$D = \frac{\Pi}{16}\left[\frac{d\left(\frac{A_t}{A_\infty}\right)}{d\left(\frac{\sqrt{t}}{l}\right)}\right]^2 \qquad (1)$$

A_t – amount of gas absorped at time t, in sec;
A_∞ – amount of gas absorped at infinite time, in sec;
t – time, sec;
l – thickness of the sample, in mm.

Scanning electron microscope (SEM) study

Fractured surfaces of the samples were studied using a JEOL scanning electron microscope (SEM, Model JSM 5500LV) at 15kV accelerating voltage, First, samples were dipped into liquid nitrogen and then broken in half to prepare the fractured surfaces, Finally, samples were mounted on the sample stub and were sputtered with gold to provide electrical conductivity.

Data analysis

Design-Expert® Version 7,0,3 statistical software program was used for statistical analysis.

RESULTS AND DISCUSSION

PS based wood flour or wheat straw flour filled composites were produced in the density range of 1,04-1,13g/cm^3, Mean density values are presented in Table 3. Statistical analysis was performed using central composite design (CCD). Filler type, filler loading and additive loading were find to be statistically important

on density values (p<0,0001). Composites with wood flour provided slightly higher density values compared to wheat straw ones. In addition, density of the composites was increased with filler loading. This increase was believed to be due to the higher cell wall density of lignocellulosic materials (Mengeloglu and Karakus 2008). It should also be noted that density of the composites was lower when more additive was present in the formulations.

Table 3

Density of the manufactured composites

Grup ID	Density (g/cm^3)	Grup ID	Density (g/cm^3)
O1	1.04 (0.01)*	B1	1.04 (0.01)
O2	1.06 (0.04)	B2	1.05 (0.01)
O3	1.04 (0.01)	B3	1.04 (0.01)
O4	1.09 (0.02)	B4	1.09 (0.00)
O5	1.08 (0.01)	B5	1.06 (0.01)
O6	1.06 (0.04)	B6	1.06 (0.02)
O7	1.13 (0.01)	B7	1.11 (0.01)
O8	1.12 (0.01)	B8	1.10 (0.02)
O9	1.13 (0.01)	B9	1.11 (0.01)

* Values in parenthesis are standard deviations,

Mechanical properties of the polymer composites produced with wood flour (WF) and wheat straw flour (WS) were presented in Table 4 and Table 5, respectively. Both filler and additive loadings had significant effect on mechanical properties. Composites produced with wood flour provided better mechanical properties compared to the one with wheat straw flour. Regardless of filler type, with the increase of filler loading, tensile and flexural strength were reduced while modulus of elasticity and impact strength were improved. Reduction in strength values was caused by the incompatibility of the polymer matrix and fillers. Presence of fillers in the matrix improved the modulus values. With the increase of additive loading, all properties except for elongation at break and impact strength were diminished. These poor mechanical properties of the composites might be caused by the poor performance of additives in the matrix.

Table 4

Mechanical properties of wood flour (WF) filled polymer composites

Örnek No	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (J/m)
WF/WS1	13.76 (2.7) *	603 (244)	2.66 (0.62)	37.6 (5.7)	2420 (146)	10.3 (1.28)
WF2	27.05 (0.4)	1019 (36)	3.20 (0.22)	51.4 (1.9)	3051 (69)	11.3 (0.75)
WF3	20.31 (0.8)	936 (28)	3.01 (0.47)	46.1 (0.9)	2845 (54)	11.7 (0.91)
WF4	27.94 (1.7)	1142 (22)	2.74 (0.15)	47.4 (2.6)	3640 (85)	12.1 (1.21)
WF5	19.13 (0.2)	1009 (16)	2.86 (0.20)	41.2 (1.6)	3101 (111)	12.8 (1.28)
WF6	20.79 (0.3)	979 (118)	3.09 (0.22)	40.3 (4.4)	3095 (352)	11.7 (1.36)
WF7	20.89 (0.9)	1153 (42)	2.37 (0.24)	43.7 (1.7)	4022 (100)	17.3 (3.40)
WF8	16.13 (0.9)	975 (46)	2.25 (0.19)	34.4 (3.0)	3322 (254)	16.2 (2.04)
WF9	16.38 (0.6)	1025 (25)	2.19 (0.17)	36.4 (1.3)	3731 (82)	15.5 (0.87)

*Values in parenthesis are standard deviations.

Table 5

Mechanical properties of wheat straw flour (WS) filled polymer composites

Örnek No	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (J/m)
WF/WS1	13.76 (2.7) *	603 (244)	2.66 (0.62)	37.6 (5.7)	2420 (146)	10.3 (1.28)
WS2	23.71 (0.5)	979 (29)	2.98 (0.17)	49.0 (2.3)	3038 (73)	10.3 (1.06)
WS3	18.65 (1.2)	924 (23)	2.79 (0.20)	42.8 (1.3)	2697 (77)	10.2 (1.50)
WS4	22.16 (1.2)	1059 (17)	2.49 (0.11)	43.5 (1.9)	3609 (113)	12.9 (2.01)
WS5	17.39 (0.5)	914 (40)	2.70 (0.20)	37.1 (1.5)	2886 (94)	14.5 (1.96)
WS6	16.95 (0.6)	970 (34)	2.42 (0.13)	38.4 (3.1)	3207 (136)	14. (3.55)
WS7	17.76 (0.5)	1040 (17)	2.33 (0.17)	38.5 (0.9)	3776 (50)	17.4 (2.55)
WS8	16.15 (0.5)	940 (19)	2.35 (0.16)	36.0 (1.1)	3263 (113)	17.6 (3.23)
WS9	15.24 (0.5)	968 (21)	2.06 (0.09)	34.3 (1.3)	3463 (112)	19.0 (2.05)

* Values in parenthesis are standard deviations.

Solubility and diffusivity values of the produced samples were also determined. Samples were saturated with CO_2 gas under 34.5bar pressure over 12 hours. Maximum absorbed gas was presented in percentages as a solubility value of sample. Diffusivity of the samples were calculated based on the equation 1 using desorption curves of the samples. Summary of the results are presented in Table 6. Typical desorption curves for wood flour and wheat straw four filled PS based polymer composites were shown in Fig. 1 and 2. respectively. Solubility of the samples was not affected by filler type but it is significantly affected by filler amount. The increase of filler amount in the matrix reduced the solubility of the samples. Similar results for different polymers were reported in previous studies (Matuana *et al.* 1998, Faruk *et al.* 2007, Mengeloglu *et al.* 2009). In the case of additive loading, when higher filler was present in the matrix, additive had positive affect on solubility. However, this positive effect was limited when small amount of filler was used in the composites. When a sample was produced using only SEBS-MA and tested for solubility, its solubility was three times higher than solubility of PS. It is believed that presence of SEBS-MA in the matrix might be improved solubility of the composites.

Table 6

Solubility and diffusivity values of the samples

Grup ID	Solubility (%)	Diffusivity ($x10^{-6}$ cm^2/sn)	Grup ID	Solubility (%)	Diffusivity ($*10^{-6}$ cm^2/sn)
WF/WS1	3.45 (0.16)	632.3 (57.97)	WF/WS1	3.45 (0.16)	632.3 (57.97)
WF2	3.10 (0.14)	461.2 (58.89)	WS2	3.33 (0.01)	523.5 (24.80)
WF3	3.15 (0.04)	519.3 (23.11)	WS3	3.34 (0.07)	499.2 (16.95)
WF4	2.91 (0.53)	202.6 (6.45)	WS4	2.68 (0.06)	328.0 (18.41)
WF5	2.850 (0.14)	467.2 (18.20)	WS5	2.77 (0.09)	474.5 (45.88)
WF6	2.68 (0.12)	566.5 (35.83)	WS6	2.54 (0.20)	520.9 (40.29)
WF7	2.10 (0.11)	412.8 (49.53)	WS7	2.07 (0.04)	497.5 (5.00)
WF8	2.47 (0.21)	292.1 (22.43)	WS8	2.38 (0.04)	413.0 (50.93)
WF9	2.41 (0.29)	302.5 (60.79)	WS9	2.27 (0.04)	446.0 (17.33)

*Values in parenthesis are standard deviations.

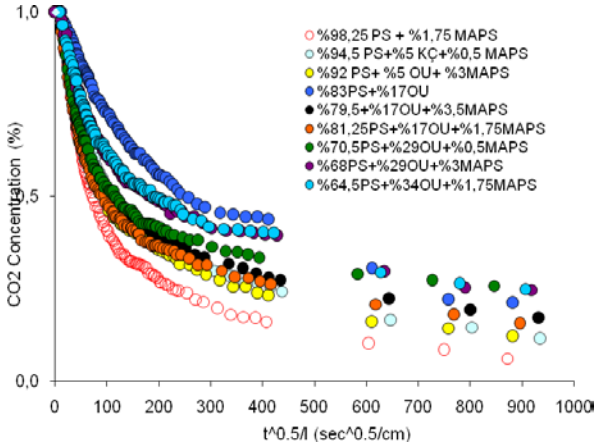


Fig. 1

Desorption curves of the wood flour (WF) filled samples.

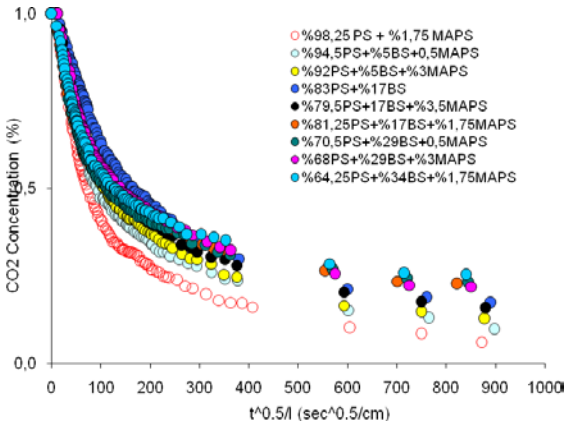


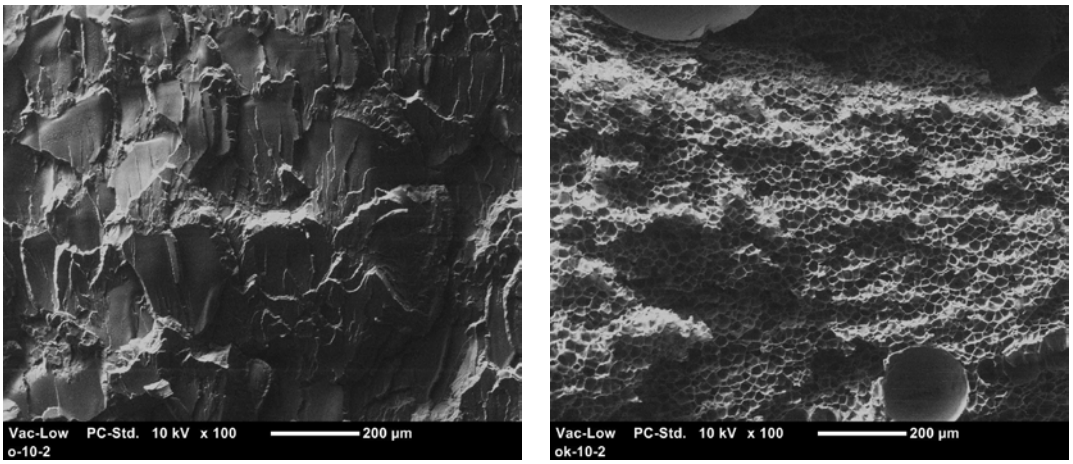
Fig. 2

Desorption curves of the wheat straw flour (WS) filled samples.

Diffusivity of the samples was also affected by filler and additive loadings. Diffusivity of composites were increased with additive amounts. Increased filler loadings, gas diffusion from the samples were reduced.

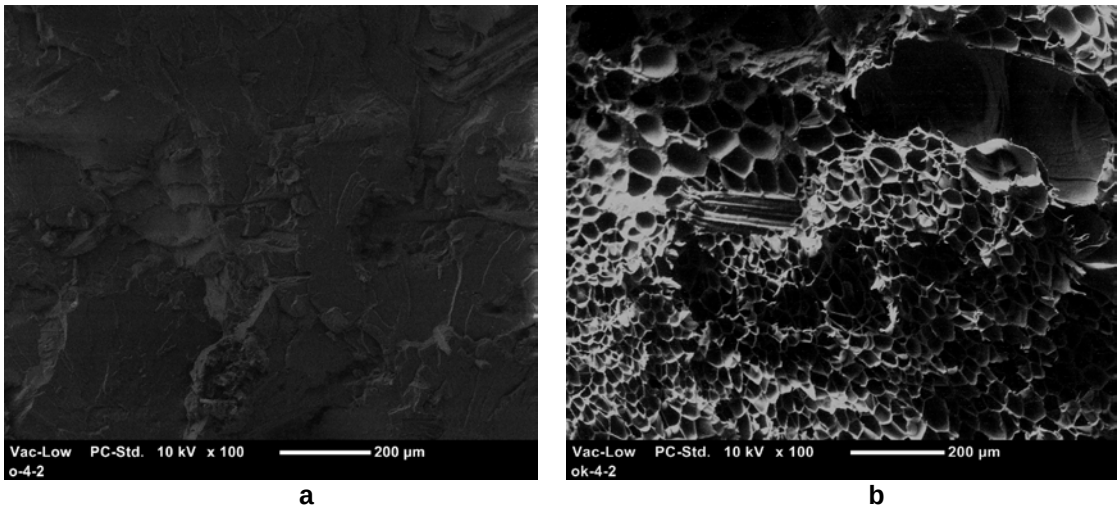
Microcellular foaming of the samples was accomplished using foaming temperatures in the range of 100-150°C and foaming time in the range of 60-240sec. Best results were achieved when 120°C as foaming temperature and 180sec as foaming time were chosen. During this study over 80% density reduction was achieved. Additive and filler loadings significantly affected the density reduction of the samples. Composites with high filler and additive amount provided lower density reductions. Increasing the amount of filer in the matrix reduces the amount of plastic in the matrix to be foamed. That's why this result was expected. Additive amount had also negative effect on foaming. It is believed that higher diffusivity of samples with additives resulted in a quick gas loss and not leaved enough gas for proper foaming.

Morphology of the foamed samples was also studied. SEM images of PS samples without filer and additive was presented in Fig. 3. SEM images of composites (WF-6) was shown in Fig. 4.



a **b**

Fig. 3
SEM images of PS samples
a - un-foamed; b – foamed.



a **b**

Fig. 4
SEM images of polymer composites (WF6)
a - un-foamed; b – foamed.

From these images, it is clear that microcellular foams are successfully produced. Foams with smaller in size and homogenous in distribution were produced in PS samples. In composites, on the other hand. foams in various sizes and heterogeneous distribution were observed.

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CONCLUSIONS

Polymer composites with lignocellulosic materials were produced and the effect of filler type, filler loading and additives amount on composites properties were determined. These composites were also foamed using microcellular foaming technology. Following conclusions were driven.

Polymer composites with wood flour provided better mechanical properties than wheat straw flour filled ones. Overall, increasing filler loading reduced the tensile strength, elongation at break and flexural strength while improving the tensile modulus, flexural modulus and impact strength. However, there was no significant effect on elongation at break and impact strength. In the case of additive amount, there were significant effects on tensile strength, tensile modulus, flexural strength and flexural modulus. All of them were reduced by increasing the mount of (SEBS-MA). There was no significant effect on elongation at break and impact strength.

Solubility and diffusivity of the polymer composites were affected by filler and additive amounts. Increasing filler amount reduced the solubility and increased the diffusivity of the polymer composites. Additive amounts also had deleterious effect on diffusivity of the composites.

Microcellular foaming of the samples was accomplished through microcellular foaming. Density of the samples was reduced as much as 70% depending on the formulation. The more the filler present in the formulation lesser the density reduction was observed. When SEB-MA additive was used, foaming was negatively affected especially at lower filler loadings.

SEM images of the composite foams showed that composites samples produced bigger and heterogeneous cells compared to unfilled PS samples. Also use of SEB-MA reduced the number of cells produced and increased the size of the cells.

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