

Studies on Thermal Behavior, Moisture Absorption, and Biodegradability of Ginger Spent Incorporated Polyurethane Green Composites

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ABSTRACT: Ecological concern on accumulation of nutraceutical industrial waste material and the demands for newer composite materials have promoted extensive research on utilizing industrial wastes materials. Therefore, in the present study finely powdered ginger spent (GS), filled polyurethane (PU) green composites with varying amount viz., 0, 2.5, 5, 7.5, and 10 wt % of GS have been fabricated. The prepared PU/GS green composites have been characterized for their mechanical properties, density and void content. Interaction between filler and matrix has been confirmed from Fourier transform infrared spectroscopy studies. Moisture absorption and desorption studies have been performed at different relative humidity (RH). The moisture absorption and desorption studies, shows that as the hydrophilic GS content increases in the matrix the RH also increases. Water uptake behavior of PU/GS were measured in different chemical environments such as 5% sodium chloride solution, cold water at different temperature and in hydrochloric acid solution. The water uptake values increases as increase in GS concentration. Equilibrium water content, diffusivity and equilibrium time taken for all PU/GS composites have been investigated. Biodegradation studies reveals that as the GS content increases the weight loss also increases. Thermal properties have been performed using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). From DSC and DMA thermograms it is revealed that increase in T_g with increase in GS content. RH and contact angle measurement have been performed to understand the hydrophilic nature of the prepared composite. The morphological behavior of composites has been studied using scanning electron microscopy. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41614.

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INTRODUCTION

Bio-based fibers, fillers and resins are increasingly being developed for various applications. Green composites are replacing non-biodegradable materials derived from petroleum based products that are currently being used. Unlike petroleum, plant based materials such as proteins, starches and fibers are renewable. In addition, these green composites may be easily composted after their life time, completing nature's carbon cycle. Modification of the synthetic polymers into degradable polymer using natural filler, agricultural resources as filler materials and using industrial wastes as filler in to polymer matrix is becoming popular in recent years.^{1–3}

Although literature on use of mineral filler are most likely available than agricultural resources based fillers, Agro residues

interest has grown in recent years to use as an active filler in polymer. Agro residues are one of the most proactive systems of land management, the growing ecological consideration and stringent laws driving the whole world toward the aim of the land management is promoting the concept of biodegradable and recycling. Agro residues as fillers of reinforcements for polymers are currently gaining prominence as polymer additives.⁴ In recent years, automobile sector has ambitious plans and is aiming to fabricate biosourced polymers.⁵ Thus there is an ample scope to develop "green-composites" for different industrial sectors.⁶ Nutraceuticals are food or part of food that provide medical or health benefits including the prevention and treatment of disease. Literature survey reveals that, less attempts have been made so far to use nutraceutical industry residues having low specific gravity as filler materials.⁷ The nutraceutical

industrial residue based composites can take advantage of low cost and possibility to tailor the properties of plastics that can meet end-use specifications. These composites make it possible to explore new applications and new markets. The incorporation of low specific gravity nutraceutical residues vis-à-vis inorganic fillers into polymer matrix reduces the consumption of the petrochemical material and increases the bulk property of the polymer composites.⁸ Today's environmental waste management and social concerns point out increasing demands on bioresources, and to accomplish this the combination of agro waste based products and synthetic polymers, to produce cheap substitutes for traditional products, provides a promising way. Maiti and Subbarao⁹ incorporated Himalian soft wood up to 70 wt % and studied the mechanical properties of the polypropylene (PP)/wood composites. The positive and negative effects of adsorbed moisture within the wood flour filler filled PP composites on the mechanical and rheological behavior were evaluated by Rietveld and Simon.¹⁰ The use of polyurethane (PU) as a polymeric matrix for the preparation of composites have been well documented.^{11,12} High strength composites obtained from incorporation of wood flour on tung oil based PU has been studied by Casado.¹³ In response to the new challenges, the authors are reporting the use of ginger spent (GS) in PU matrix, because over 95% of the GS is considered as waste after the extraction from nutraceutical which is in high demand in western countries. Consequently, the E-factor, a metric used for "greenness"¹⁴ of the process, which is defined as "ratio of the total weight of waste produced to the total weight of the product obtained" assumes paramount importance. Literature survey revealed that, nearly 1329 tons of GS is produced by ginger oleoresin industry.^{15,16}

Development of technology relationship with consumer demands and expectation continues to increase demands on global resources, leading to major issues of material availability and environmental sustainability, provoked this work to choose castor oil based PU. It is known that lignocellulose filler contain hydroxyl groups. This unique nature draws interest to fabricate reactive PU based green composites.¹⁷ The objective of this research article focus on the PU obtained with castor oil and natural filler such as GS makes the polymer eco-friendly. The influence of GS content on water uptake behavior and thermal characteristics of PU green composites have been studied. Surface energy has been calculated for the green PU/GS composites using contact angle measurement and the hydrophilic natures are compared.

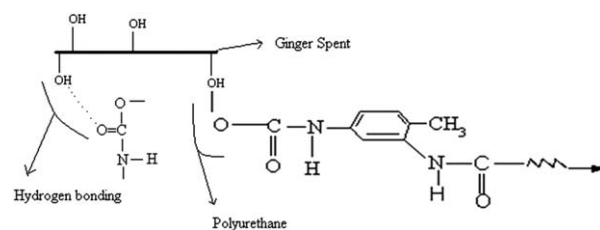
EXPERIMENTAL

Materials

Castor oil [molecular weight (M_n) is 930 and hydroxyl group/molecule is 2.24], toluene 2,4-diisocyanate (TDI), dibutyl tin dilaurate (DBTL) is used as catalyst and methyl ethyl ketone (MEK) used as solvent were obtained from Sigma. GS (moisture content 10.9%, density 0.85–87 g cm⁻³, and ash content 7.4%) was obtained from M/s. Sami Labs, India as gift sample. The particle size of the GS powder used in this investigation is ≈ 75 μ m. All the chemicals used in this study are analytical grades.

Filler Preparation

The GS is dried in sunlight for 2 days, and grounded to fine powder using pestle and mortar, the grounded GS was sieved



Scheme 1. Formation of hydrogen bond and polyurethane between toluene diisocyanate and ginger spent.

through mesh size of ≈ 75 μ m. This fine powder was dried again in hot oven with air circulation for 24 h at 60°C. Then treated with calculated amount of TDI and stored in desiccators in sealed polyethylene covers until further use.

FABRICATION OF PU/GS GREEN COMPOSITE

Previously dried castor oil (0.001 mol) and toluene diisocyanate (0.0015 mol) were dissolved in MEK along with two drops of DBTL were taken in a three-necked round bottomed flask. The contents were stirred continuously for 30 min under nitrogen gas purged atmosphere at 60–65°C. To the prepared isocyanate-terminated pre-PU the calculated amounts of TDI treated GS filler to match the NCO/OH ratio was mixed and stirring was continued for 1 h to form pre PU. This reaction mixture is then degassed under vacuum and poured on a clean glass mold, which is previously coated with releasing agent (small amount of glycerine). The glass mold is allowed to stay as such at room temperature for 12 h, and post cured at 60°C for 5 h. The sheet of PU/GS green composite formed was removed from the mold and all the films were stored in the controlled humidity in desiccators at 23°C until further tests. The varying amounts viz., 0, 2.5, 5, 7.5, and 10 wt % of GS with PU were fabricated using the same procedure. TDI being is strongly criticized in green or biodegradable materials. However, in the present study, it is used in minute quantity as compared to GS and castor oil, and isocyanides get converted to PU on treating with castor oil and GS hence TDI toxicity is reduced. The schematic representation of formation of hydrogen bond and PU is represented in Scheme 1.

Characterization Techniques

Fourier transform infrared spectroscopy (FTIR) spectra of PU and its green composites were recorded using FTIR (JASCO model made FT-IR 4100, Japan) spectroscopy. The IR spectrum was recorded in the wave number range 4000–400 cm⁻¹.

Density of PU/green composite specimens were measured according to ASTM D 792-86 (displacement) method using Metler Toledo electronic balance. The theoretical density was calculated for composites by weight additive principle, which states that

$$d = W_1 d_1 + W_2 d_2 \quad (1)$$

where d is the density of the composite, W_1 and W_2 are the weight fraction of the constituents and d_1 and d_2 are the corresponding densities.

The percentage of void content in the composites is obtained according to ASTM D 2734 by the following equation:

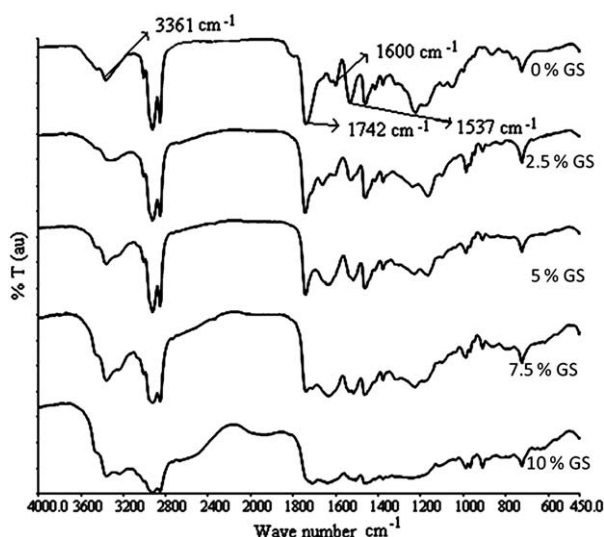


Figure 1. FTIR spectra of PU/GS green composites.

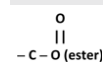
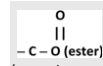
$$\text{Void content (\%)} = \left[\frac{T_d - E_d}{T_d} \right] \times 100 \quad (2)$$

where T_d is the theoretical density and E_d is the experimental density of the prepared PU composites

Resilience of the specimen is the ratio of rebounding height to drop height of a metal plunger of prescribed weight and shape which is made to fall on the specimen. Resilience of the specimens was recorded as per ASTM D 2632-88 method using Rebound Resilience tester, New Delhi, India. Aging test has been conducted as per the specification of ASTM D 3045 method, the samples were heated for 4 h.

Moisture sorption analysis was carried out using a moisture sorption analyzer (Q 5000 SA, TA Instruments) under controlled conditions of temperature and humidity. The stepwise adsorption and desorption of the samples were carried out from 10% relative humidity (RH) to 90% RH and back at a step interval of 10% RH at 25°C. At each RH level, equilibrium mass values was stopped when the relative change in sample mass remained below 0.01% for 5 min, and the next RH step was automatically applied.

Table I. Important Band Assignments of FTIR Spectra of PU/GS Green Composites

Group	Expected peaks (cm ⁻¹)	Observed peaks (cm ⁻¹) for PU/GS system				
		0	2.5	5	7.5	10
C=O	1630-1690	1600	1601	1601	1603	1608
N-H stretching with hydrogen bonding	3200-3400	3361	3351	3355	3355	3355
Aromatic C-H stretching	3000-3100	3010	3010	3009	3009	3010
C=C aromatic ring	1450	1456	1456	1455	1456	1455
1,4-substituted phenyl ring	860, 762	863, 724	866, 724	867, 724	865, 724	867, 724
 -C-O (ester)	1750-1700	1742	1740	1735	1734	1739
 -C-O (ester) (urethane peak)	1528	1537	1531	1538	1533	1538
Aromatic C-H bending	860	809	810	812	813	811

Procedure to measure percent water uptake behavior of PU/GS biocomposites at different environment is briefly explained as follows: a known weight of (W_1) dried PU and their composites were immersed in water at different environments, the specimens are removed individually, periodically from the specimen bottle, and gently wiped with tissue paper and reweighed. The procedure was repeated until a state of equilibrium was attained. When a sample swells, weight of the swollen sample is noted (W_2). The percentage of water uptake was calculated by the relation;

$$\text{Percentage uptake} = \left[\frac{W_2 - W_1}{W_1} \right] \times 100 \quad (3)$$

Thermal analysis was carried out using differential scanning calorimetry (DSC) Universal V4.3A (Q200), TA Instrument. Samples of about 5.0 ± 0.1 mg were sealed in aluminum pans. An initial heating to 180°C was carried out and held isothermally for one minute to erase all thermal history of the samples. Subsequent cooling (from 180 to -50°C) and heating from -50 to 200°C were carried out at $10^\circ\text{C min}^{-1}$. The second heating thermograms were recorded with an accuracy of $\pm 0.01^\circ\text{C}$. The dynamic mechanical properties of PU/GS green composites were carried out with dynamic mechanical analyzer (model Q 800).

Scanning electron micrographs were made with a JEOL JSM-5300 electron microscope to study the morphology. The specimens were frozen under liquid nitrogen, fractured, mounted, and coated with gold on a JEOL JFC-1100E ion sputter coater. The scanning electron microscopy (SEM) was operated at 10 kV. The biodegradability of materials based on weight loss method has been carried out as per ASTM D 5247 standard.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy

FTIR spectra of PU/GS green composites are shown in Figure 1. The observed and expected IR data for characteristic groups of GS filled PU green composites are addressed in Table I. From the table an observation was made that, PU/GS green composites showed all absorption bands corresponding to PU (Table I). The absence of peak at 2220 cm^{-1} clearly confirms

Table II. Density, Void Content, and Resilience Properties of PU/GS Green Composites

Ginger spent in PU (wt %)	Theore. density (g c m ⁻³)	Exptal. density (g cm ⁻³)	Void content	Resilience
0	-	1.048	-	12
2.5	1.043	1.039	0.38	13
5	1.038	1.027	1.25	13
7.5	1.033	1.016	1.93	14
10	1.028	1.008	2.04	14

that, there are no free -NCO groups in PU.^{18–20} The shifts in the observed band 3361–3351 cm⁻¹ are due to the formation of hydrogen bond between GS and PU matrix. The characteristic absorption peak is observed at 1455–1456 cm⁻¹ for C=C aromatic ring. All PU/GS exhibit the carbonyl absorption bands at an approximately the wave number range 1600–1608 cm⁻¹, which can be attributed to the stretching mode of the hydrogen bond. PU/GS exhibit the characteristic absorption bands at 1531–1538 cm⁻¹ which is due to >C=O group of urethane linkage.²¹ There is a variation in stretching frequencies as the filler concentration is varied; this is due to the change in degree of hydrogen bonding, and/or physical interactions between GS and PU.²²

Density

The measured density values for all PU/GS green composites (both experimental and theoretical) are given in Table II. Density of the pristine PU is 1.048 g cm⁻³ and the density values of PU/GS biocomposites lies in the range 1.039–1.008 g cm⁻³. The theoretical density values are calculated according to weight additive principle. From the table it can be noticed that, the density of the GS filled PU/GS green composites decreases as increase in GS content as expected. This is due to increase in low dense filler in high dense PU matrix. The experimental density values are slightly lower in comparison with theoretical values and also the difference between experimental and theoretical density values becomes wider at higher filler loading as compared to that at lower concentration.²³ As the filler content increases the void content also increases as shown in Table II, this intern attributed to that there is reduction in interaction between PU matrix and GS filler at higher filler content.

Void Content

The calculated percentage of void content of the PU/GS green composites is given in Table II. The void content lies in the range 0.38–2.04.^{24,24} The void content of the composites increases as the percentage composition of the GS increases. This is due to the aggregation caused by the higher dosage of filler and at higher filler content, it is not completely wet by the matrix. The void content also reflects on the density.

Resilience

The resilience values (Table II) of all PU/GS green composites lies in the range 12–14. There is not much variation in resilience

with the composition of the composites. As the density of the films decreases the resilience values will increase.

Heat Aging

Polymeric materials exposed to heat aging undergo chemical and physical changes. The change in weight of the exposures depends on duration, filler content, and temperature range which determine the extent and type of changes that takes place. Extended periods of exposure of polymeric material to higher temperature will generally causes some degradation with progressive change in weight and physical properties which depends on the thermal stability of the polymer. The PU/GS green composites were exposed to hot air oven at temperatures 100, 150, and 225°C for 4 h and the loss of weight is measured to probe the thermal stability. The weight loss results obtained are tabulated in Table III. It is evident from the data, that there is slight reduction in weight of PU/GS green composites at different elevated temperatures under investigated and obtained values falls less than 4.26%. The weight loss is slightly higher at 225°C as compared to 100 and 150°C. The weight loss in the composites may be due to moisture content, low volatile impurities and oligomers of PUs present in the system. This result indicates that, there is no systematic variation in weight loss with the composition of filler loading.^{25,26}

Moisture Adsorption and Desorption Studies

Moisture sorption is an important parameter that determines the polymer interaction with moisture. By determining moisture sorption isotherm, the water adsorption behavior of a material can be studied at various RH conditions. In the present investigation, the moisture sorption behavior of PU/GS green composite was evaluated. The PU composite membranes were subjected to different RH conditions and the resultant weight gain/loss were measured as a function of time. Figure 2 shows the moisture sorption and desorption experiments of these sheets, where weight change in percent is plotted as a function of time. The results clearly showed that with an increase in RH, the membranes tend to absorb more moisture. From this experimental data, moisture sorption and desorption isotherms as a function of RH for PU/GS green composites were plotted as shown in Figure 3.

The moisture sorption isotherm obtained can be typically divided into three regions.²⁷ The initial region of the isotherm represents the bound water, which includes hydrogen bonded

Table III. Weight Loss Data Obtained After Heat Aging of PU/GS Green Composites

GS content in PU (wt %)	Weight loss at different temperatures (±3%)		
	100	150	225
0	0.95	2.21	3.82
2.5	1.15	2.25	4.23
5	1.19	3.0	4.02
7.5	1.48	2.91	4.22
10	1.35	2.94	4.26

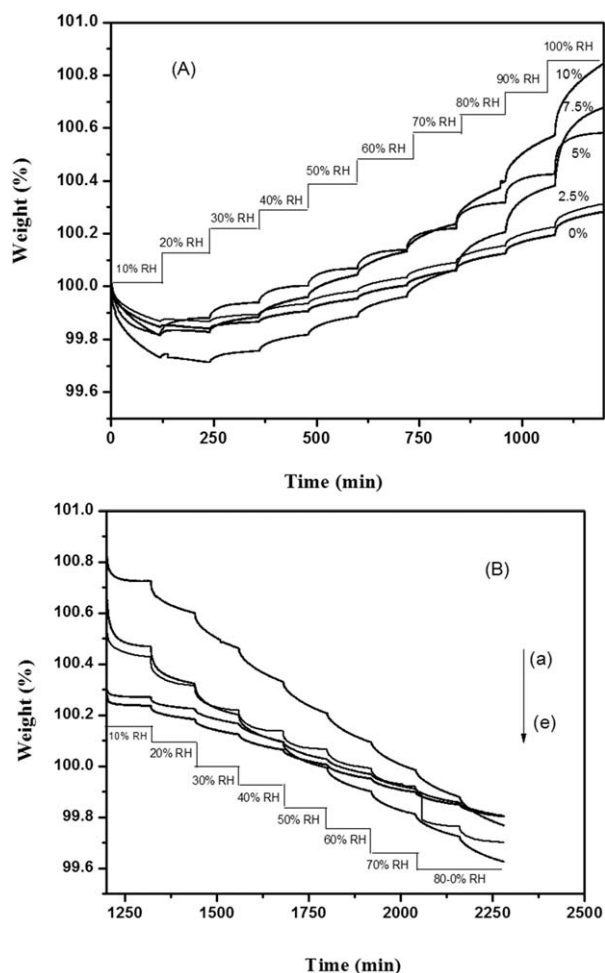


Figure 2. Moisture (A) sorption and (B) desorption plots for PU containing (a) 0 wt %, (b) 2.5 wt %, (c) 5 wt %, (d) 7.5 wt %, and (e) 10 wt % of ginger spelt filled PU green composites.

water and monolayer water that is sorbed by the hydrophilic and polar groups of solids. Bound water is unfreezable and it is not available for chemical reactions. In the second region, water molecule bind firmly than the first zone, they usually present in small capillaries. The vaporization enthalpy of this molecule is slightly higher than that of pure water. This class of water can be considered as the continuous transition from bound to free water. The properties of water in third region where RH is very high are similar to those of the free water that is held in voids, large capillaries etc., and the water in this region loosely binds to materials. Moreover, hysteresis is related to the nature and state of water in the region reflecting their potential for structural and conformational rearrangements, which alters the accessibility of energetically favorable polar sites. The presence of capillaries in any material can result in considerable increase in water activity.²⁸

At RH above 70%, the sorption isotherm shows increase in moisture content. A similar trend can be observed for desorption curves also. Moisture sorption isotherms can be generated from an adsorption process or a desorption process. The curve showed an increase in equilibrium moisture content with

increasing RH, at a constant temperature of 25°C. The curves display a sigmoid shaped profile, which is very common for hydrophilic polymers. At low and intermediate humidity ranges, moisture content increases linearly, whereas at higher humidity ranges, moisture content increases rapidly. The increase in GS content in PU increases the water binding capacity by the composites. This could be due to the hydrophilic nature of natural filler. Moreover, the absorbed water, due to its interference with intermolecular hydrogen bonding of lignocellulose, induces relaxation of polymer chains.

Water Uptake Behaviors in Different Environments

All natural polymers and natural filler or filler loaded polymer composites have a tendency to absorb moisture in humid atmosphere. Natural fillers absorb more water as compared to synthetic filler/fibers. GS and other natural fillers are highly hygroscopic and possess low wettability with hydrophobic resins mainly due to hydroxyl groups of cellulose, hemicellulose, and lignin.^{29–32} In GS, lignocellulose is mainly responsible for water absorption. Adsorbed water causes swelling of fillers and it continues till the cell walls are saturated with water. Beyond saturation point, water exists as free water in the void structure

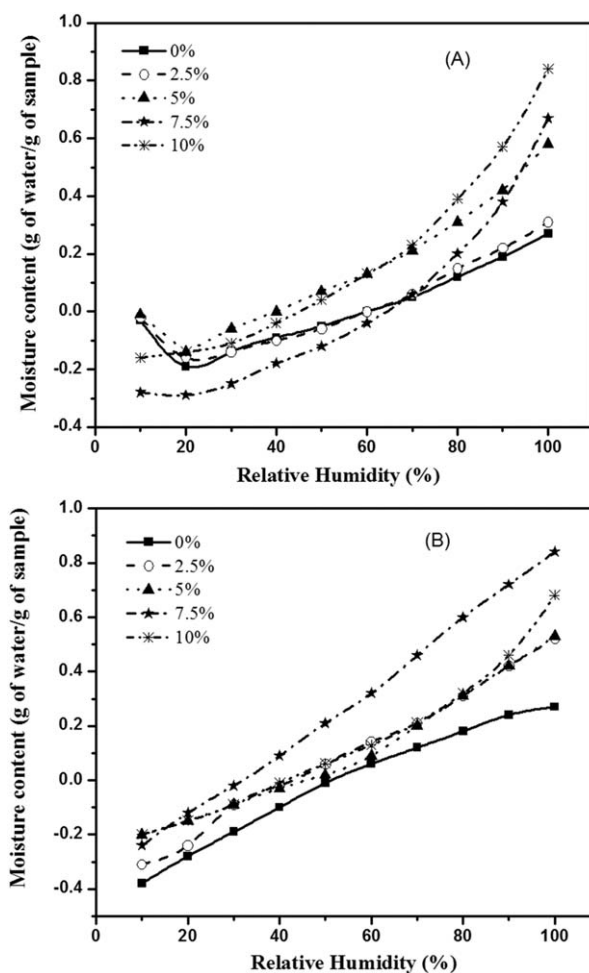


Figure 3. The plots of moisture uptake as a function of relative humidity for different compositions of PU/GS green composites (A) sorption and (B) desorption curves.

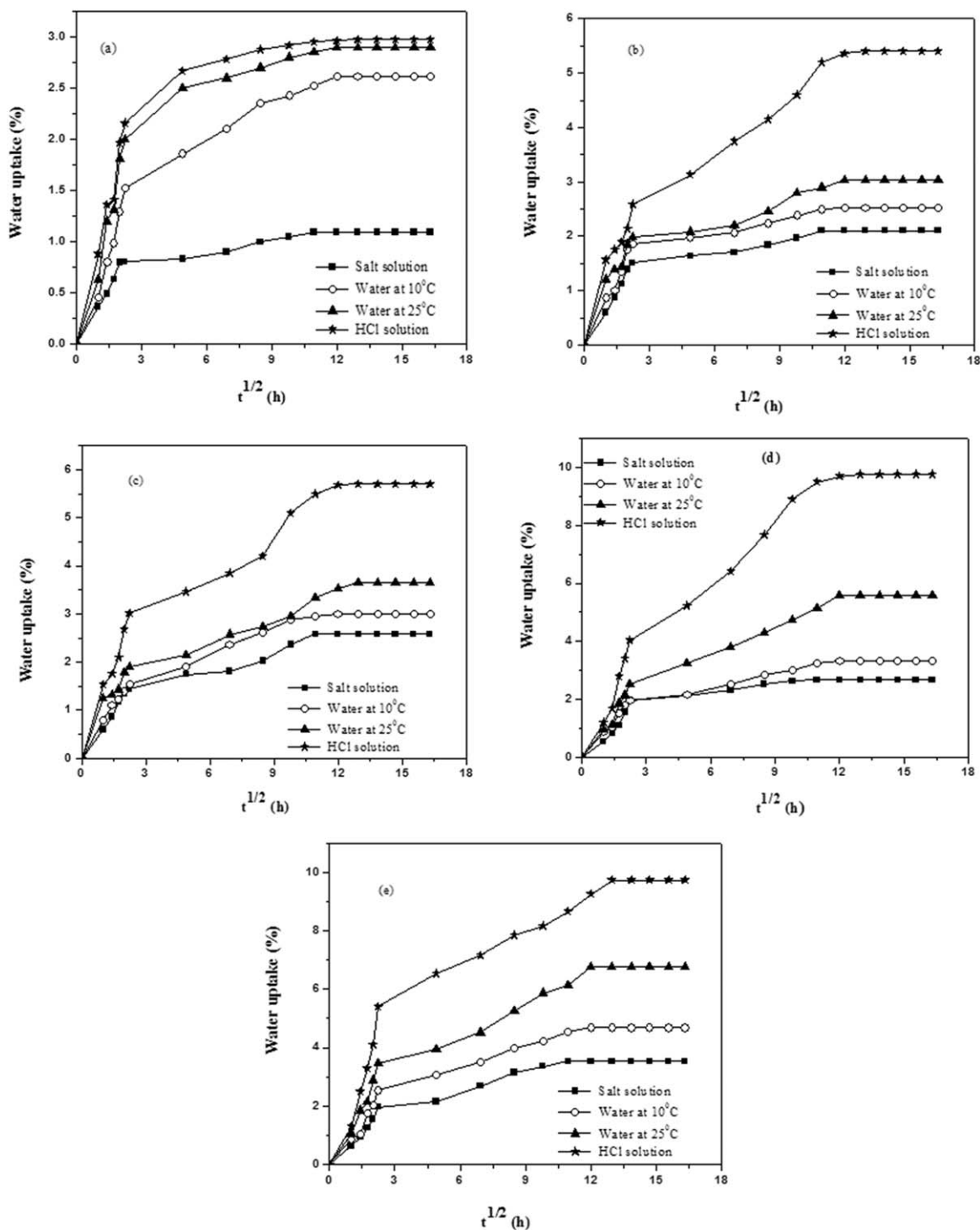


Figure 4. The plots of change in weight against square root of time for (a) 0 wt %, (b) 2.5 wt %, (c) 5 wt %, (d) 7.5 wt %, and (e) 10 wt % GS filled PU green composites in different environments.

leading to composite delamination or void formation.^{30,31} Absorbed water leads to weakening of interface and accelerates delamination and hence, decreases the strength of the composites,^{32,33} additionally absorbed water causes hydrolytic degradation of both matrix and interface during service.^{34,35} Water absorption in composites depends upon amounts of fillers, interaction between filler and polymer, void content, additives,

humidity and temperature. In present case water absorption by PU/GS followed by one dimensional Fickian diffusion. The water sorption studies have been carried out with pure water, water at 10°C, 10% HCl, and 10% NaCl at room temperature by gravimetric method. The study is also carried out in boiling water. The percent of water uptake by PU/GS in different environments (water at 25°C and 10°C, 10% HCl and 10% NaCl)

Table IV. Water Uptake and Diffusivity Data of PU/GS Green Composites at Different Environments

Properties (values in brackets are standard deviation)	Composition of PU/GS green composites (wt/wt %)				
	100/0	97.5/2.5	95/5	92.5/7.5	90/10
Diffusivity in 5% NaCl solution 10^{-12} ($\text{m}^2 \text{s}^{-1}$; $\pm 0.4\%$)	4.12	4.52	5.95	5.48	6.97
Equilibrium water content for 5% NaCl solution (%; $\pm 0.6\%$)	1.09	2.10	2.58	2.66	3.52
Equilibrium time for 5% NaCl solution (h)	120	120	120	119	120
Diffusivity in water at 10°C 10^{-12} ($\text{m}^2 \text{s}^{-1}$; $\pm 0.4\%$)	6.39	4.31	6.19	5.78	6.92
Equilibrium water content for water at 10°C (%; $\pm 0.6\%$)	2.61	2.52	3.0	3.33	4.68
Equilibrium time in water at 10°C (h)	144	144	143	144	144
Diffusivity in water at 25°C 10^{-12} ($\text{m}^2 \text{s}^{-1}$; $\pm 0.4\%$)	4.96	4.59	5.72	7.53	7.11
Equilibrium water content for water at 25°C (%; $\pm 0.6\%$)	2.9	3.03	3.66	5.57	6.77
Equilibrium time in water at 25°C (h)	148	144	150	147	144
Diffusivity in 5% HCl solution 10^{-12} ($\text{m}^2 \text{s}^{-1}$; $\pm 0.4\%$)	4.39	6.64	6.38	8.37	7.79
Equilibrium water content for 5% HCl solution (%; $\pm 0.6\%$)	2.97	5.4	5.7	9.76	9.73
Equilibrium time for 5% HCl solution (h)	168	168	168	167	169

as a function of time is presented in Figure 4. From Figure 4, it is evident that water absorption behavior is quite different in different environments supporting different diffusion behaviors. The calculated equilibrium water content and the time taken to reach equilibrium data are addressed in Table IV. From Table IV, it is noticed that the equilibrium water content (1.09–3.52%) in salt environment are lesser than water uptake at 25°C , water uptake at 10°C and in acid environments. The water uptake sequence of the composites followed the following order, i.e., acid medium > water at 25°C > water at 10°C > salt medium. The lower water uptake behavior of composites in salt medium serves the utility in marine applications. The water uptake phenomenon at 25°C is more than at 10°C , due to kinetic energy of the water molecule increases with temperature. Water sorption into composite is mainly by diffusion mechanism. The penetration of water in composites also occurs through capillary flow along the filler interface followed by diffusion from the interface in to the bulk resin. Adsorbed water may induce irreversible changes like chemical degradation, cracking, and debonding. Cracking and blistering cause high water absorption, while leaching of small molecules results in decrease in weight.³⁶

Diffusivity

It is well established that absorbed water in polymers and composites plays a significant role in mechanical behavior and long-term durability. Assuming one-dimensional Fickian diffusion in composite, an attempt has been made to determine diffusivity (D) in different environments. Diffusivity is assumed to depend only on temperature and independent of the moisture content as well as stress levels in composites. The amount of water absorbed is given by the following equation³⁷:

$$D = \pi \left(\frac{h\theta}{4 M_m} \right)^2 \quad (4)$$

where θ is the slope of the linear portion of the sorption curves, h is the initial thickness of the sample, and M_m is the mass

uptake value at equilibrium. The diffusivity of water in PU/GS composites in all chemical environments was determined from Figure 5 and using eq. (1), and obtained results are reported in Table IV. From table it was noticed that diffusivity is different in different environments and diffusivity value increases with increase in the concentration of GS content. This increase in diffusivity with increase in GS content is due to the increase in void formation, which provides more space between the molecular entanglement for the water to penetrate. The diffusivity value is lower in salt solution and higher in acidic media. The presence of electrolyte in water breaks water structure and hence, diffusivity. High diffusivity in acid solution supports more structure breaking tendency as compared to salt solution. The lower water uptake in salt solution might be due to electrostatic repulsive forces acting among electronegative groups present in PU/GS green composites. Ionic size has also affected water structure in diffusion process. H^+ ions have high tendency to break water structure as compared to Na^+ ions. The size of the hydrated Na^+ ions is greater than that of H_3O^+ ions leading to low diffusivity. Thus, smaller is the penetrant molecules size, greater is the diffusivity.

Water Absorption in Boiling Water

Water absorption in composites strongly depends on temperature, nature of filler, filler content and it is independent on amount of water content around the composite. In boiling water the interaction between hydrophilic component (filler) and water molecules in the PU matrix increases, this leads to higher water uptake (Figure 5). At higher temperature free volume in the composites increases due to thermal expansion, this increases water uptake behavior of the composites. The effect of boiling water on PU/GS green composites as a function of time is shown in Figure 5. From figure it is evident that the rate of water uptake behavior in boiling water strongly depends on filler content. Higher filler loading shows higher water uptake behavior as compared to lower dosage filler loaded composites. This process is due to increase in the number of $-\text{OH}$ groups in

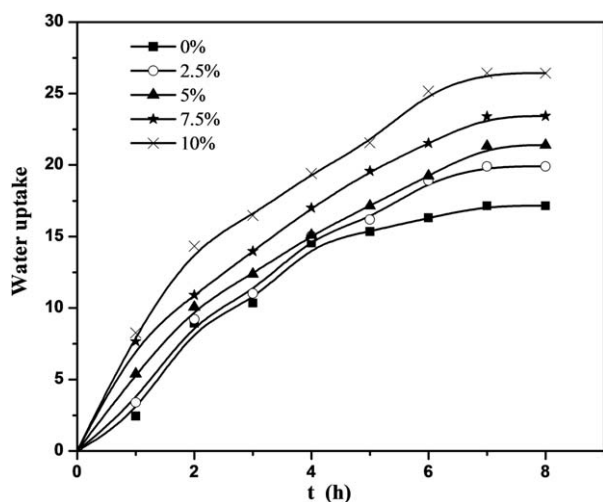


Figure 5. The plots of percent weight change against time for PU/GS green composites in boiling water.

the composites. It is evident from the figure that equilibrium water adsorption in boiling water is increased two times, than at room temperature. Water absorption is maximum (23.5%) within an hour and then it gradually reached an equilibrium with in 7 h.

Thermoanalytical Studies

Differential Scanning Calorimeter. DSC was used to study the effect of filler loading on the glass transition temperature (T_g) of the composites. The DSC thermograms of the PU/GS green composites are presented in Figure 6. The variation in T_g as a function of GS content is shown in Figure 6. An increase in the GS content leads to an increase in T_g . T_g of pristine PU and PU/7.5% GS are -28 and -12°C , respectively. Similar observation was made by El Miloud et al.³⁸ Moreover, T_g of the composites rises steadily with the amount of lignocellulose (Figure 7). In general the increase in T_g of the composites indicates the presence of interactions between the matrix and reinforcement due to hydrogen bond and physical interaction which enhances the interfacial adhesion between matrix and filler. The increase in T_g values may be also due to reduction in chain mobility of PU network with the addition of GS content. This is in consistent with FTIR analysis, where the hydrogen bond formation and physical interaction between PU matrix and GS filler was observed.

Dynamic Mechanical Analysis. The dynamic mechanical analysis (DMA) properties such as storage modulus (G'), loss modulus (G'') and loss tangent ($\tan \delta$) are recorded as a function of temperature and shown in Figures 8–10, respectively. The effect of GS content on storage modulus of PU systems is shown in Figure 8. All the specimens showed a glassy state that is followed by a rubbery state. In general, the storage modulus, G' is found to increase after incorporation of GS below the T_g . This indicates that incorporation of the GS filler has improved the stiffness of the PU and the dependence of G' on filler loading is more pronounced around the glassy region.³⁹

It is well known that the information about the polymer–filler interaction can be obtained from the analysis of the loss modu-

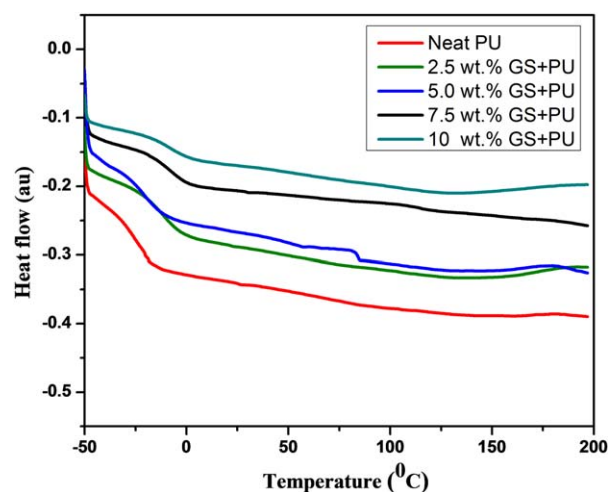


Figure 6. DSC thermograms of PU/GS green composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lus of a filled compound in the T_g region as a function of temperature.⁴⁰ Loss modulus plots of the composites are shown in Figure 9. From figure it was noticed that loss modulus of all filled PUs are higher than pristine PU, except for 2.5 wt % filled PU. The area of the maximum peak of the loss modulus indicates the dissipated energy by volume unit of a sample during the transition from the glassy region (rigid) to the flexible stage. If the polymer–filler interactions are present, in a polymer system, a fraction of the polymer chain is immobilized at the interface of polymer and filler. Therefore, the dissipated energy during the T_g increases above the level of the sample without filler, due to the contribution of the fixed polymer chain. For this increase, there are two main contributions, the volume fraction of the immobilized polymer layer and the polymer–filler interaction.⁴¹

The incorporation of rigid fillers and fibers usually decreases the damping as expressed by $\tan \delta$.⁴² The obtained $\tan \delta$ values along with T_g which was represented by the peak temperature of the $\tan \delta$ curve (Figure 10) is summarized in Table V. This confinement the effect of reinforced filler on PUs and the strong

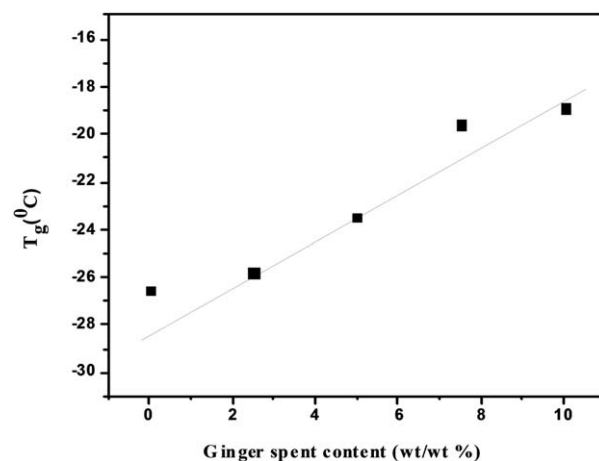


Figure 7. Plot of T_g as a function of GS content for PU/GS composites.

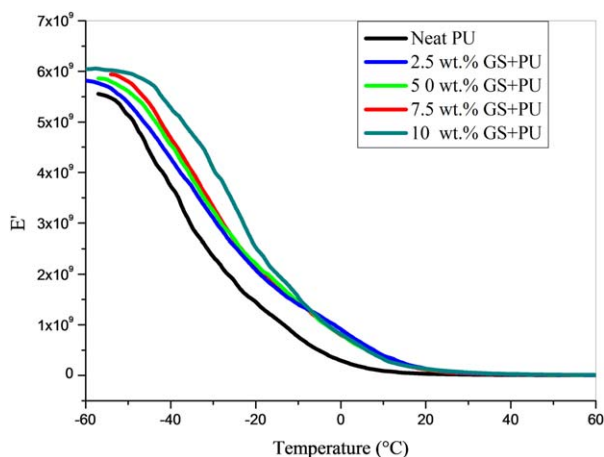


Figure 8. Plots of storage modulus versus temperature for PU/GS green composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interactions such as hydrogen bonding between the urethane groups of PU molecules and the hydroxyl groups of lignocellulose (GS). The DMA results were supported by the T_g data obtained from DSC thermograms. From the results it can be seen that the incorporation of GS into PU matrix, leads to gradual enhancement in the T_g . From table it was noticed that there is no systematic variation in $\tan \delta$ values with composition. However, $\tan \delta$ values are lower for GS filled systems than pristine PU and lies in the range of 0.57–0.63. This may be due to the presence of GS, the composites structures became more tightly constrained.

Tensile Properties

Stress versus strain curves (Figure 11) indicates increase in tensile strength and tensile modulus with the increase in GS content upto 7.5 wt % and on further loading the tensile property decreases. This improvement in mechanical property is attributed to the formation of PU formed by reaction with hydroxyl group of GS and diisocyanate and also formation of hydrogen bond. Elongation at break decreases as increase in filler loading

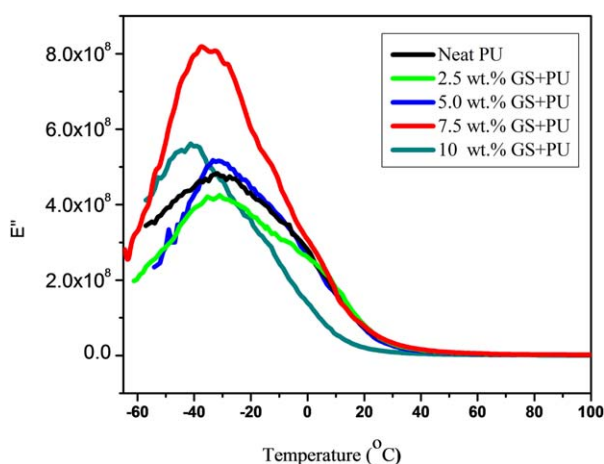


Figure 9. Plots of loss modulus versus temperature for PU/GS green composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

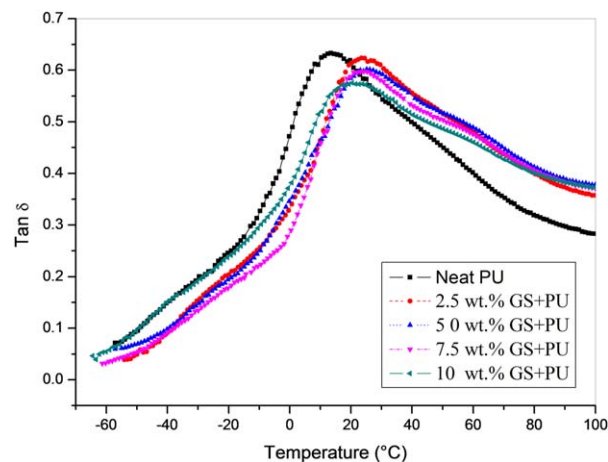


Figure 10. Loss tangent as a function of temperature for PU/GS green Composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

an increase in chain rigidity seems to decrease the elongation property.¹⁷

Contact Angle Measurement

The surface hydrophilicity characteristics of the composite membranes were investigated by contact angle measurements. Figure 12(a–e) shows the contact angle as a function of GS content in PU. Pristine PU films show hydrophobicity with contact angle of 82.2 and surface energy of 81.72 mJ m⁻². The GS filled PU surface poses higher water contact angle and lower surface energy indicating hydrophilic nature and wettable surface of PU/GS composites. As the filler content increases the contact angle decreases and the surface energy increases as shown in Table VI due to the hydrophilic nature of the GS filler.⁴³

Morphological Analysis

In order to know the degree of dispersion of filler in PU matrix and its interaction with polymer matrix SEM images of the composites are recorded. Both surface morphology of the cryo-fractured PU/GS biocomposite specimens surface have been studied using SEM technique. Figure 13(a–e) shows the surface morphology of the composites, there is a finer dispersion of the filler particles in the PU matrix which demonstrated a good interfacial bond between PU and GS powder. Scanning electron photomicrographs of cryofractured surface of PU/GS are shown in Figure 14(a–d) for 2.5, 5, 7.5, and 10 wt % filled systems, respectively. These figures clearly indicate that there is an effective interaction between GS filler and PU matrix. As the

Table V. Thermal Data Obtained from DMA Thermograms for PU/GS Green Composites

GS content in PU (wt %)	Tan δ (peak max.)	T_g (°C)
0	0.63	15.3
2.5	0.57	20.4
5	0.59	21.9
7.5	0.62	22.5
10	0.60	23.2

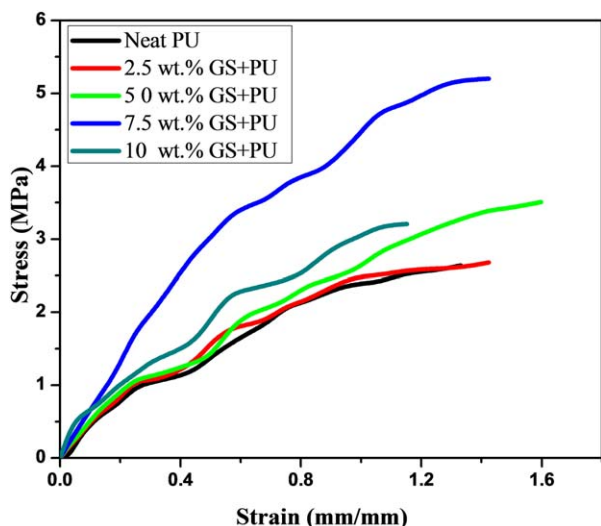


Figure 11. The plots of stress versus strain curves for PU/GS green composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

percentage composition of GS is raised the agglomeration of filler takes place and the microcracks are developed due to over loading of filler. These can be attributed to the existence of polymer–filler and filler–filler interactions.

Biodegradation Studies

The specimens exposed to *Aspergillus niger* in potato dextrose broth [PDB] showed change in surface appearance. The previously weighed polymer composites were placed in a 250 cm³ Erlenmeyer flask with 60 cm³ of PDB. The mixture was sterilized in autoclave and it was inoculated with 2 cm³ of *A. niger* spore suspension (1×10^6 spores cm⁻³). The flasks were placed on rotary shaker at 100 rpm for 7 days at 30°C in the incubator. After 7 days it was taken out and kept at this temperature without shaking for another 23 days. After 30 days the broth was sterilized in autoclave, polymer composite samples were taken out, washed gently with distilled water, surface adhering water was wiped out gently and weighed. After weighing these

Table VI. Contact Angle and Surface Energy Values at 25°C for PU/GS Green Composites

Ginger spent content (wt %)	Water contact angle (°)	Surface energy (mJ m ⁻²)
0	82.2	81.72
2.5	77.4	87.65
5	76.8	88.36
7.5	71.5	94.79
10	70.1	96.42

samples were dried under vacuum at 60°C. The control experiment was also done in the same way but without fungi *A. niger*. The experiment was conducted in triplicate and the mean value is taken for calculation by incorporating the error bar.

The digital photographs of degraded samples were given in Figure 15. The figure shows that as the GS content increases the *A. niger* growth also increases on the surface of the PU/GS bio-composite. The GS being natural product is more proven for biodegradation hence incorporation of GS in castor oil based PU increases the activity of degradation. The pure GS exposed to *A. niger* for 30 days had weight loss of $\approx 38\%$. The measured weight loss of specimens with *A. niger* media is given in Table VII. From the table it was observed that weight loss in GS filled PU composites were more than pristine PU. Literature survey revealed that, *A. niger* has tendency to attack galactomannan a major storage polysaccharide in seeds of leguminous plants.⁴⁴ There are literature that were reported the growth of *A. niger* on the surface of polymer films.⁴⁵

CONCLUSIONS

PU/GS green composites with different weight fraction of GS content were successfully fabricated. A significant improvement in mechanical properties such as, tensile strength, tensile modulus, percentage elongation at break, and surface hardness with increase in GS content from 2.5 to 7.5 wt % in PU matrix was noticed. This result can be attributed to good physical

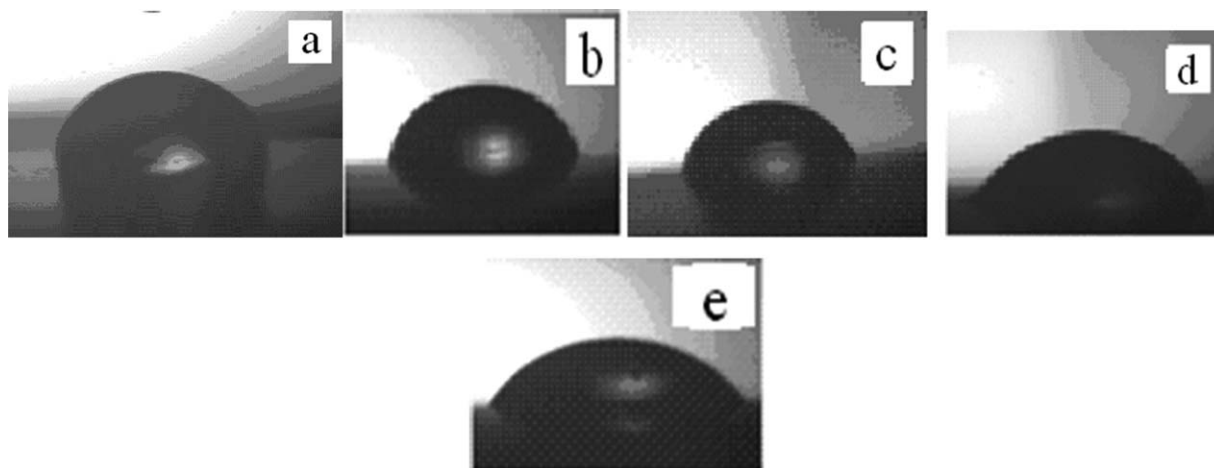


Figure 12. Photographs of contact angle and the shape of water droplets on the surface of (a) 0 wt %, (b) 2.5 wt %, (c) 5 wt %, (d) 7.5 wt %, and (e) 10 wt % of GS filled PU green composites.

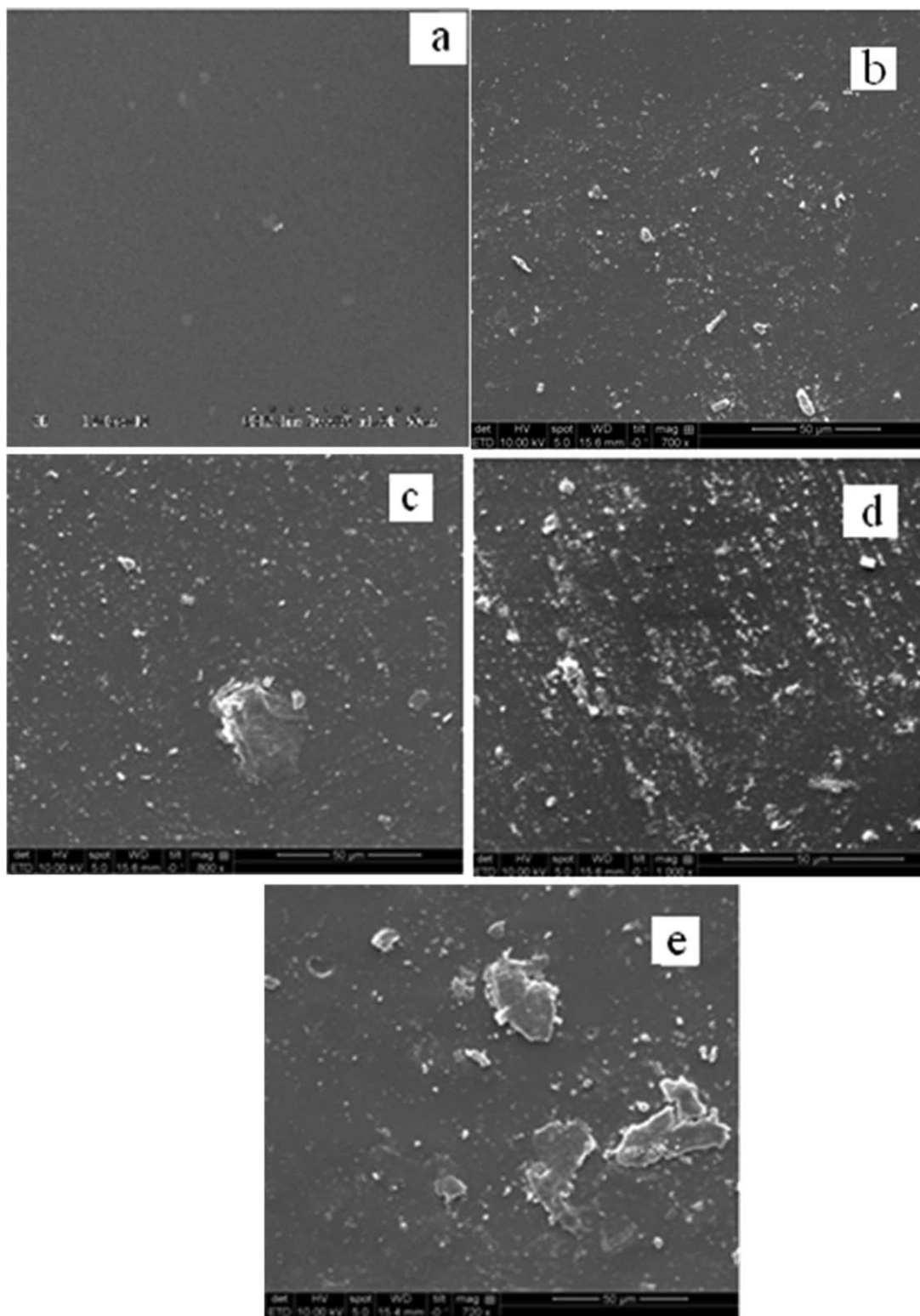


Figure 13. Scanning electron photomicrographs of (a) 0 wt %, (b) 2.5 wt %, (c) 5 wt %, (d) 7.5 wt %, and (e) 10 wt % of GS filled PU green composites.

interaction between PU matrix and GS filler. Water uptake behaviors of composites strongly depend on GS content. The water uptake behavior increases with increase in GS content, which is due to the hydrophilic nature of the GS filler. The

water uptake behavior of the composites has been studied in different chemical environments. The water uptake sequence of the composites followed the following order, i.e., acid medium > water at 25°C > water at 10°C > salt medium. The water

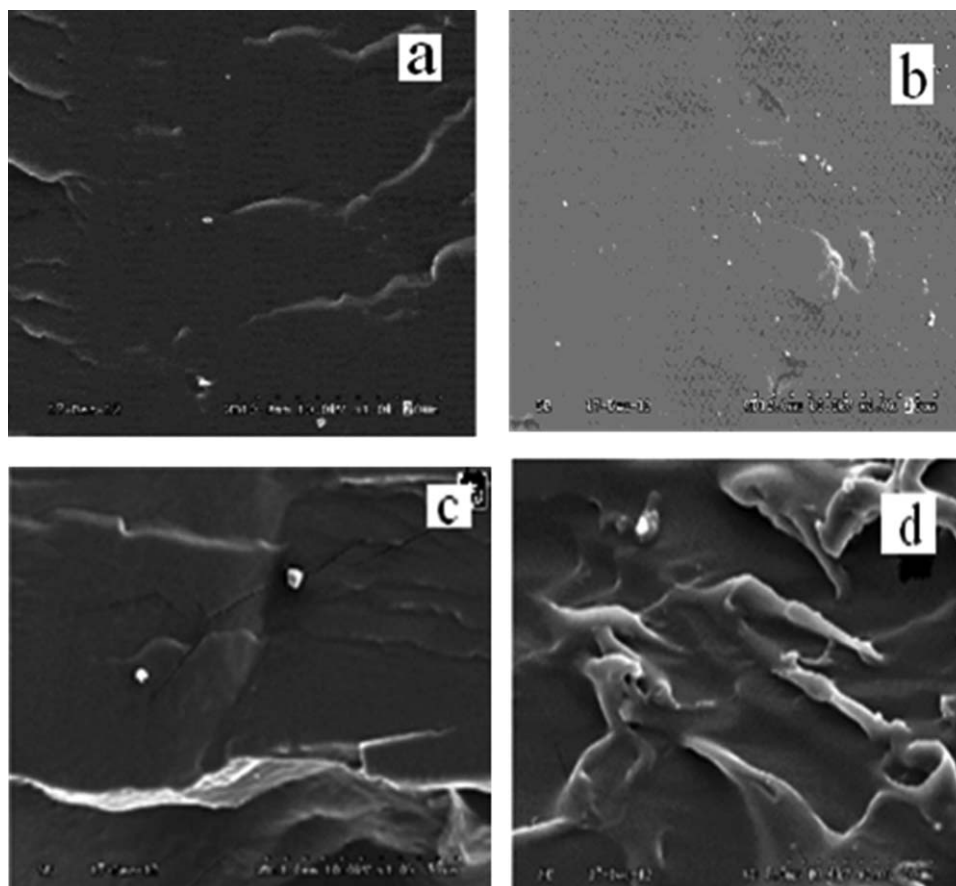


Figure 14. Scanning electron micrographs of (a) 2.5 wt %, (b) 5 wt %, (c) 7.5 wt %, and (d) 10 wt % of GS filled PU green composites.

uptake in boiling water was greater than all the media. The water uptake behavior strongly depends on the nature of the medium; weight fraction of natural filler, RHs and temperature. DSC results show single T_g and as the filler content increases

the T_g values also increases slightly due to the strong physical interaction between polymer and filler. T_g obtained from DMA thermograms supported the DSC results. Though there is slight reduction in $\tan \delta$ values with increase in filler loading, there is no systematic variation in $\tan \delta$ values. Contact angle images also support moisture sorption studies. SEM images indicate the uniform dispersion of GS filler in PU matrix. It can also be seen that, the filler particles are embedded in PU matrix. Biodegradation studies reveals that as the GS content increases the weight loss also increases. Resulted PU/GS composites showed that the use of nutraceutical waste fillers allows the development of competitive, powerful products, which are ecofriendly, consumer-friendly, low density and low toxicity as filler.



Figure 15. Images of *Aspergillus niger* growth on PU/GS green composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VII. Weight Loss of PU/GS Biocomposites in *Aspergillus niger* Medium

Ginger spent content (wt %)	Weight loss in <i>Aspergillus niger</i> medium (%)
0	2.47
2.5	4.58
5	6.63
7.5	7.75
10	9.72

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