

Use of Lignin Strengthened with Modified Wheat Gluten in Biodegradable Composites

Nahla A. El-Wakil

Department of Cellulose and Paper, National Research Center, Dokki-12622, Cairo, Egypt

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ABSTRACT: In this study, composites from alkali lignin and wheat gluten, modified with different percentages of sodium silicate, were prepared and characterized. Moreover, the addition of silica to the aforementioned composites was studied with the aim of improving the thermal and mechanical properties. The effect of wheat gluten percent and the extent of its modification on the blends properties were investigated via diametric tensile strength, thermomechanical analysis (TMA), scanning electron microscope (SEM), thickness swelling and thermogravimetric analysis (TGA). The results showed significant improvement in the diametric tensile strength, thickness swelling, uniformity in the fracture surface, and the shift of glass transition temperature (T_g) toward higher values with increasing wheat gluten percent and its modification extent. These results reflect the enhance-

ment of interaction between alkali lignin and wheat gluten. Alkali lignin/wheat gluten blends filled with silica possessed distinguishable characteristics and improved diametric tensile strength, low thermal expansion, and high T_g . Interestingly, TMA results showed that high dimensional stability against heating (thermal expansion percent) could be obtained using 60% wheat gluten modified with 15% sodium silicate and filled with 10% silica. This sample showed the highest T_g and the lowest thickness swelling in addition to smooth, uniform, and glossy surface as shown from the SEM images and TMA charts. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 793–801, 2009

Key words: alkali lignin; wheat gluten; thermo-mechanical analysis; biodegradable composite

INTRODUCTION

Lignin is a byproduct from the pulp-making industry, and every year about 50 million tons are accumulated. Blending lignin with natural resins yields composite; which is at high temperature can be processed to moldable form. A composite material can be described as a macroscopic combination of two or more materials to achieve a performance from the composite that was not available from the separate constituents.¹ Biocomposites (biodegradable composites) are obtained by blending together a biodegradable polymer and biodegradable filler; since both components are biodegradable, the composites as the integral parts are also expected to be biodegradable.² Natural polymers have been introduced in different kinds of composites to improve degradability. Thus, it has been supposed that the presence of a certain amount of natural polymers in blends with synthetic polymers can promote the degradation of the synthetic components.³

Materials such as renewable crops, agricultural wastes, and/ or byproducts are good sources of

natural polymers as they are comparatively less expensive in comparison to synthetic polymers. Blending of two natural polymers may result in poor adhesion between them. Various approaches have been explored to improve interfacial adhesion and thereby the properties of this type of composites. Utilization of compatibilizer⁴ is one of these approaches, for example, the addition of methylene diphenyl diisocyanate (MDI) caused a simultaneous enhancement of the modulus, strength, and elongation of kraft lignin and soy protein isolate blends. Also, maleic anhydride-modified polypropylene and silane coupling agents were used as compatibilizers to improve polymer–polymer interaction through covalent or hydrogen bonding between hydroxyl groups in lignocellulosic and compatibilizer.^{5,6}

Another approach is using a strengthening agent, such as cellulose powder, to improve the strength properties of composite plastic based on soy protein and lignosulphonate.⁷

Denaturation is one of the approaches explored in improving the adhesion between protein-based polymers and lignin. Blend plastics based on soy protein isolate (SPI) strengthened with alkaline lignin (AL)⁸ and lignosulfonate (LS)⁹ with different weight ratios were prepared. The results indicated that the introduction of AL could effectively increase the tensile

Correspondence to: N. A. El-Wakil (nawakil@hotmail.com).

strength, Young's modulus, thermal stability, and elongation of the composite plastics. Also, for the former. Also, the studies of the water sensitivity of the LS and SPI blends suggested that the strong interaction between them could restrict the effect of water on the swelling, thus limiting the damage of the composites. Our previous investigation showed that wheat gluten can be used as a binder, after denaturation with sodium hydroxide and urea, in reed based particleboard. It was found that a mixture of wheat gluten / urea formaldehyde in the ratio 80/20 improved the adhesion between the binder mixture and reed; which was sufficient enough to avoid addition of compatibilizer and thereby greatly improved the mechanical and physical properties of the produced particleboard.¹⁰ Since the mechanical properties were often the decisive factor in material selection, wheat gluten was chosen, with sodium silicate as a denaturing agent, to be blended with lignin. In this study, alkali lignin (natural biopolymer) isolated from the black liquor of rice straw pulping was strengthened with modified wheat gluten (byproduct of wheat starch production), to prepare biodegradable composites. The mechanical, physical, thermomechanical, and morphology of the prepared composites were studied. In addition, the effect of modification of wheat gluten and the use of silica on the aforementioned properties were also studied.

EXPERIMENTAL

Materials

Lignin was precipitated with 10% H₂SO₄ from rice straw black liquor, which was delivered from RAKTA Company for paper industry, Alexandria, Egypt. After precipitation, lignin was washed till neutrality and dried in vacuum oven at 65°C. Wheat gluten was delivered from Cerestar Company, France. It has the composition of 79.0% protein, 12.0% carbohydrate, 2.0% fat, 5.0% moisture, 1.0% fiber, and 0.1% ash.

Sodium silicate was delivered from Sigma Aldrich Laborchemikalien GmbH.

Silica gel was delivered from Sisco Research Laboratories, Mumbai 4000, India, Mesh 60-120.

Lignin and wheat gluten were sieved to pass from a sieve of 160 μm.

Preparation of samples

Wheat gluten was modified with sodium silicate in two ratios, 10 and 15% based on wheat gluten weight; they were blended mechanically in 3 mL ethyl alcohol at room temperature for 10 min. Wheat gluten was added to lignin in 2 wt % ratios, i.e., 35% (series I) and 60% (series II) and blended mechani-

cally for 15 min. The resulting blend was placed in a polished stainless-steel mold and then compression-molded using a hot press. The disc was molded at 100°C for 5 min and pressure of 3.9 N/mm² and then cooled at about 40°C for 20 min under the same pressure. Each blend was molded with and without 10% silica gel based on sodium silicate.

Characterization

1. Diametric tensile strength was carried out using LLOYD INSTRUMENTS LR 10K Universal Testing Machine.
2. Thickness swelling was determined according to EN (317-1993).
3. Thermomechanical analysis (TMA) was carried out with TMA-50-Shimadzu 50 made in Japan, heating rate 5°/min, initial load 5 g, atmosphere air.
4. Scanning electron microscopy (SEM): The fracture surface of molded neat lignin and some selected samples were examined with JXA-840A Electron Probe Micro Analyzer SEM.
5. Thermogravimetric analysis (TGA): Thermal analysis was carried out using Perkin-Elmer thermogravimetric analyzer. Heating rate set at 10°C/min over temperature range between 50 and 500°C. Measurements were carried out in nitrogen atmosphere; the rate of nitrogen flow was 50 cm³/min.

RESULTS AND DISCUSSION

The idea of using a pair of materials, each of the known properties, to obtain a product of high performance led to using lignin and modified wheat gluten to obtain such product. Lignin is characterized by softening on pressing under controlled relatively high temperature and its capability of interaction with other functional groups.

Since the ratio and the inherent properties of the reinforcing agent (wheat gluten) as well as the interaction with the matrix (lignin) are important parameters controlling the properties of the produced composites, two ratios of modified wheat gluten were used mainly 35% (series I) and 60% (series II) based on lignin weight. For each composite type, there were two batches at 10 and 15% sodium silicate based on wheat gluten weight. Overall, each aforementioned composite was tested with and without 10% silica gel based on the sodium silicate weight. The samples under investigation are denoted and tabulated in Table I.

The study has been focused on identifying trends rather than a detailed study of the bonding between phases. Like all the filled polymer composites, the

TABLE I
Sample ID of the Investigated Blends

Sample	Constitution
B	Neat lignin
II	3 g lignin + 35% WG + 10% sodium silicate
I2	3 g lignin + 35% WG +10% sodium silicate + 10% silica gel
I3	3 g lignin + 35% WG + 15% sodium silicate
I4	3 g lignin + 35% WG + 15% sodium silicate + 10% silica gel
II1	3 g lignin + 60% WG + 10% sodium silicate
II2	3 g lignin + 60% WG + 10% sodium silicate + 10% silica gel
II3	3 g lignin + 60% WG + 15% sodium silicate
II4	3 g lignin + 60% WG + 15% sodium silicate + 10% silica gel

strength properties are related to the adhesion between the phases and consequently the bonding between the phases. The bonding between the phases will be a factor governing the degree of stress transfer from the matrix to the filler. Stress transfer between the phases is important as noted by Shenoy.¹¹

Mechanical properties

The effect of wheat gluten percent (35 and 60%) modified with 10 and 15% sodium silicate with and without silica as well as neat lignin on the diametric tensile strength is illustrated in Table II. Blending of lignin with modified wheat gluten enhanced the diametric tensile strength of all the blends. This enhancement is pronounced with increasing the wheat gluten percent from 35 to 60%, i.e., as the reinforcement volume fraction increases, the strength increases. High molecular weight and limited reactivity of wheat gluten restrict the ability to develop crosslinking with other polymers. Raising pH is one of the reported methods for protein denaturation; alkaline medium is expected to unfold protein molecules and expose the function groups (COOH and NH₂) to stronger adhesion. Mo et al.¹² showed that protein molecules are hydrolyzed in alkaline medium producing peptide chains with suitable molecular weight, which could further enhance bonding. In this respect, sodium silicate has double effect for improving the strength; the first is the contribution of its alkalinity in protein hydrolysis and the second is the role of silica as a strengthening agent. The gradual increase in diametric tensile strength reflects the extent of crosslinking formation between the lignin and modified wheat gluten with increasing the sodium silicate percent from 10 to 15%. The increase of diametric tensile strength with the introduction of silica has been attributed to the increased stiffness. Also, silica is expected to deposit at the lignin/

wheat gluten interface and block the voids thereby improving stress transfer across the interface itself, similar to compatibilizer.¹³ The role of silica can also be clarified from the SEM images as will be discussed later.

Thermomechanical properties

The thermomechanical properties of a filled polymer composite are critically important for design purpose as they define to which application the material can be used for. The TMA thermograms of lignin as well as all the previously mentioned blends with and without silica are shown in Figure 1(A,B). The related data, T_g , linear expansion coefficient, and percent expansion are tabulated in Table III. Neat lignin thermogram is characterized by the lowest T_g (103°C), the highest linear expansion coefficient (39708.6×10^{-6}), and the highest percent expansion (97.37%). All the thermograms are characterized by the presence of a single T_g for each. This single T_g is an indication to the pronounced compatibility between the matrix and the reinforcing agent. Blending of lignin with modified wheat gluten resulted in T_g shift toward higher values. Also, blending shifted the percent of expansion and the linear expansion coefficient to lower values.

Balasuriya noted that glass transition temperature, typically of the lignin, has no effect on the mechanical properties but it is often studied as an indicator of the adhesion between the phases.¹⁴ However, for these blends there is accordance between the T_g and the mechanical properties.

These shifts are more pronounced for the samples filled with silica, which is located at the lignin/modified wheat gluten interface and improved the stress transfer across the interface. The thermomechanical properties of sample II4 in this study exhibit unexpected characteristics when compared with conventionally studied blends because of the high volume fraction and modification of the reinforcing agent. This sample possesses high T_g (152°C), very low expansion coefficient (-855×10^{-6}), and no expansion (-2.01%). These characteristics reveal that some

TABLE II
Diametric Tensile Strength of the Investigated Blends

Samples	Diametric tensile strength N/mm ²
B	2.80
II	4.60
I2	5.96
I3	7.25
I4	7.55
II1	7.98
II2	8.03
II3	8.44
II4	8.54

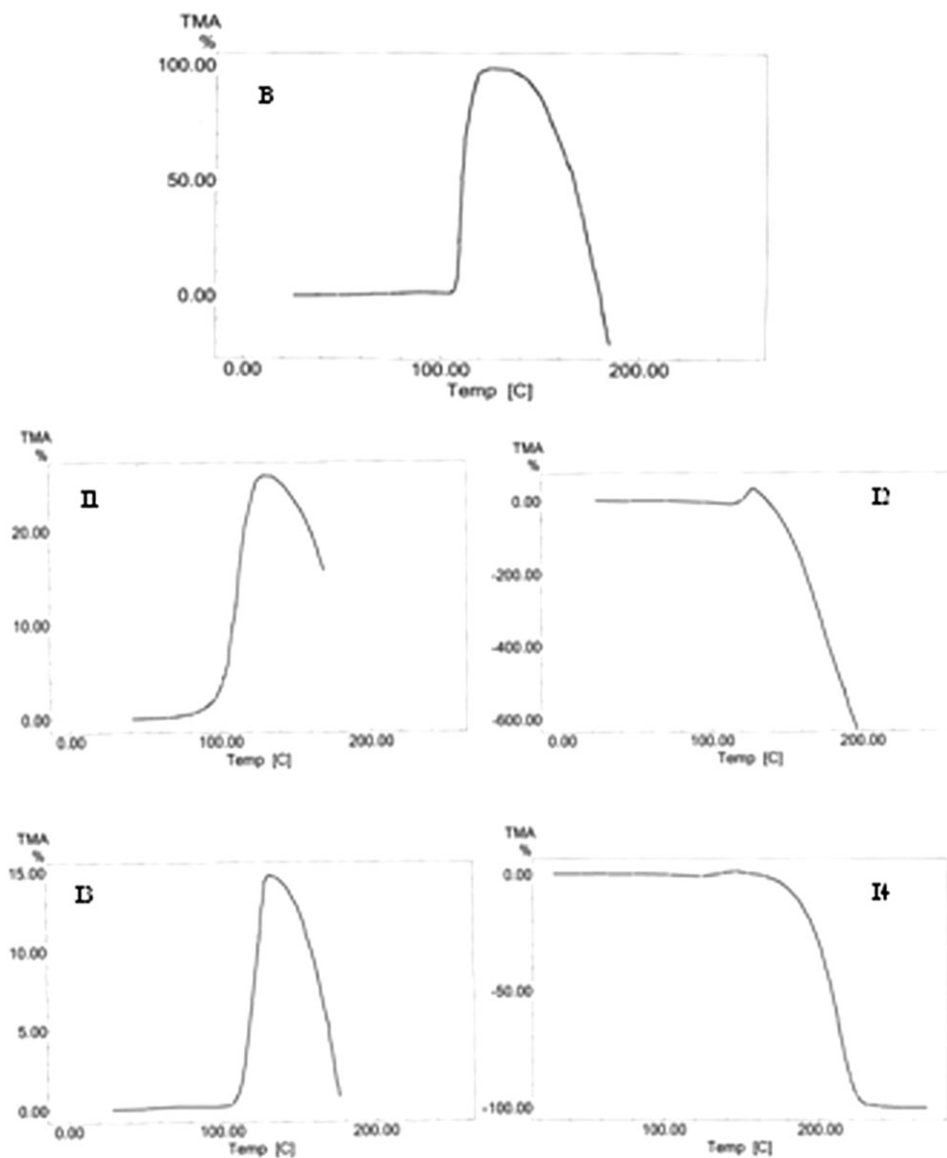


Figure 1 (A) TMA curves of lignin and lignin filled with 35% modified wheat gluten; (B) TMA curves of lignin and lignin filled with 60% modified wheat gluten.

sort of contraction or shrinking existed at T_g within a range of thermal stability 14°C. This behavior, which is exhibited only in this case, may be attributed to reorientation of the wheat gluten chains.

Thickness swelling

The percent of thickness changes, of the previously mentioned blends, due to swelling after soaking in water for 2 h are shown in Table IV. The decrease in thickness change, due to swelling, with increasing wheat gluten percent from 35 to 60% may be attributed to the predominance of modified wheat gluten, which contain relatively small proportion of carbohydrate (12%) when compared with soy protein, which can be used in similar fields (35% carbohydrate), in addition to the hydrophobic nature of alkali lignin.⁴

Also, the decrease of thickness change, due to swelling, may be attributed to the formation of crosslinked structure based on the strong physical interaction between alkali lignin and modified wheat gluten. As can be viewed from the results, the use of silica as an adhesion promoter additive has furnished composite of lower water absorption relative to lignin alone.

Morphology

To show the role of wheat gluten percent, modified with both sodium silicate ratios, and the role of silica on the phase separation of alkali lignin and modified wheat gluten blends, some selected samples were chosen to account for these effects. These samples are B, I3, I4, II3, and II4. The fracture surfaces of the studied samples are shown in Figure 2. The fracture

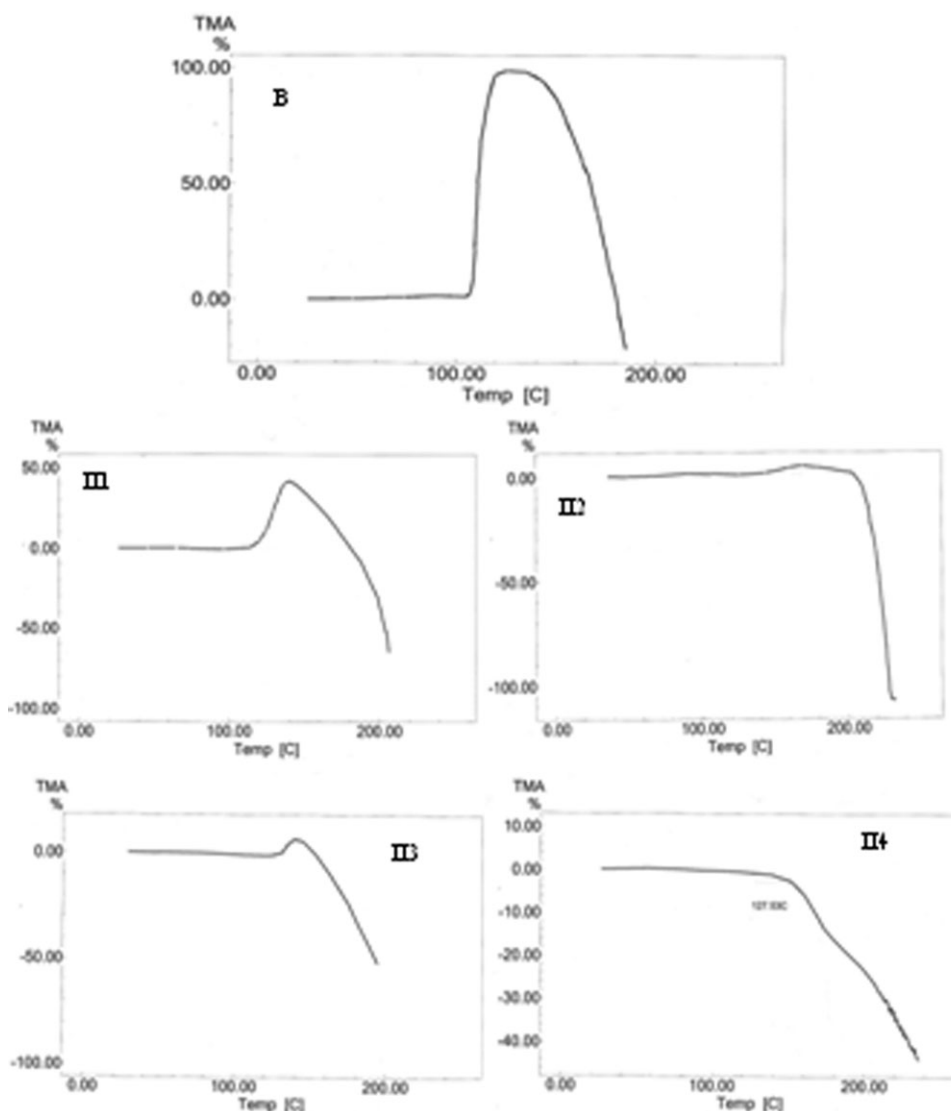


Figure 1 (Continued from the previous page)

surface of lignin (sample B) shows a clear coarse texture. The pores formed will act as stress concentration points of the composite during loading, which then lead to an early failure. Addition of modified

wheat gluten resulted in smoothness and more uniform surface with increasing gluten percent. The presence of some cracks indicating phase separation are noticed for some alkali lignin/wheat gluten blends; this phase separation may be due to the

TABLE III
Expansion Coefficient, T_g and % Expansion of the Investigated Blends

Sample	Expansion Coefficient $\times 10^{-6}$	T_g	% Expansion
B	39708.6	109.3	97.37
II	4622.6	100	25.42
I2	3344.6	119	37.76
I3	5139.7	112	4.47
I4	923.76	133.3	1.95
II1	13768	120	41.43
II2	993.51	144	4.06
II3	4652.11	126.6	7.80
II4	-855.16	152	-2.01

TABLE IV
Thickness Swelling Percent of the Investigated Blends

Samples	Thickness swelling
B	-
II	-
I2	-
I3	16.9
I4	11.1
II1	14.3
II2	14.5
II3	10.9
II4	10.6

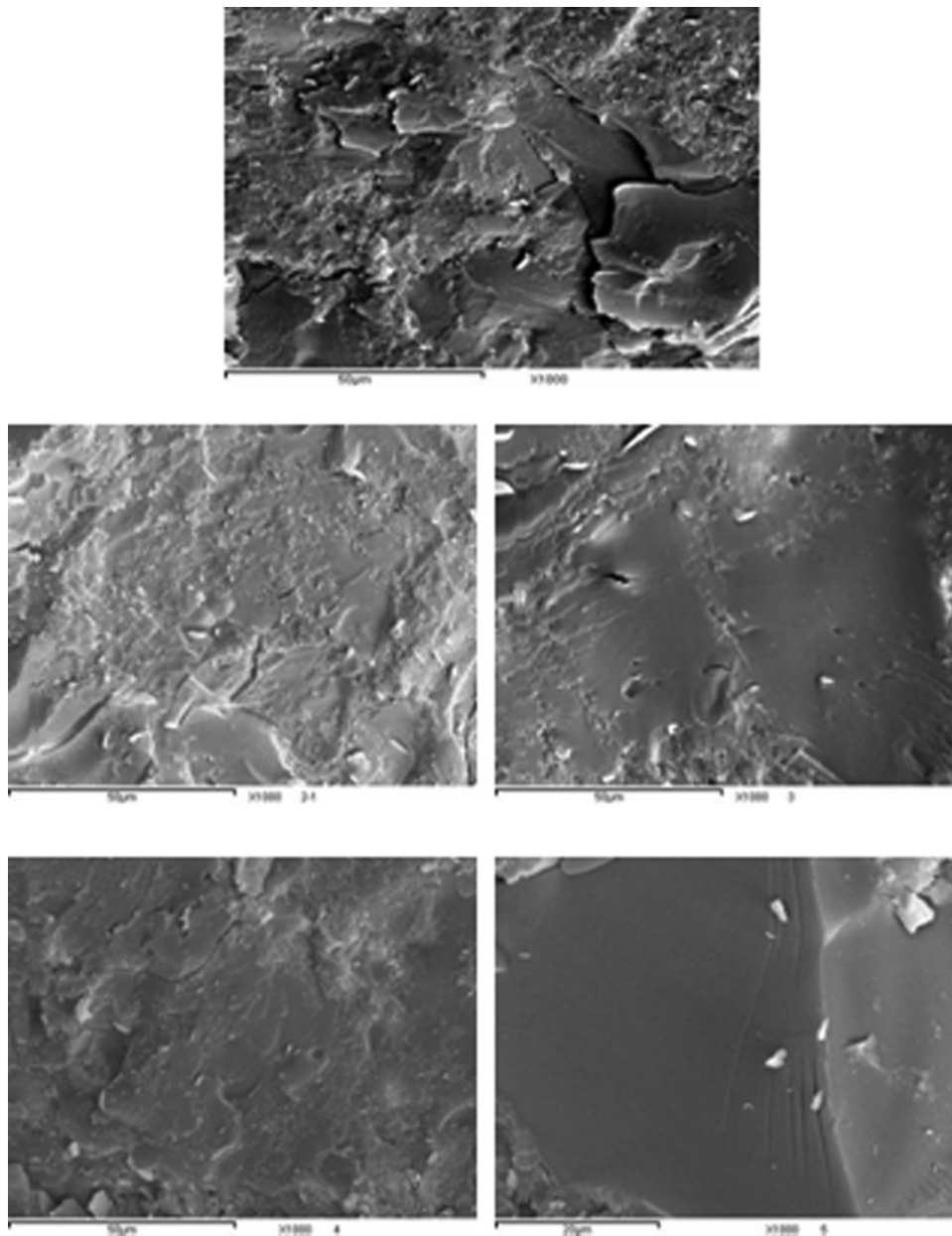


Figure 2 SEM of lignin and blends under investigation.

method of processing, which led to certain degree of in homogeneity; consequently, the cracks may lead to inferior mechanical properties.

However, these cracks were filled to some extent on adding silica. As shown before, silica acted as filler and strengthening agent. Additional identified factors in the presented blends, which can significantly affect the polymer composite strength, are the particle size and the presence of agglomerates and voids. The strength of filled polymer composites has been reported¹⁵ with the reduction in the particle size. This increase is due to increasing the interfacial area per unit volume between the composites components, hence increasing sites for adhesion and hence strength. Agglomerates have been noted to act

to decrease the strength of filled polymer composites as they are weak points within the composite and become stress concentration points and can lead to a greater probability of large voids within the matrix. The appropriate particle size of lignin and wheat gluten and the absence of agglomerates in these blends led to the improved properties.

Thermogravimetric analysis

The same selected samples to study the morphology of the blends were subjected to TGA. The thermal degradation patterns are shown in Figure 3, and the derived data from the TG and DTG are illustrated in Table V and Figure 4.

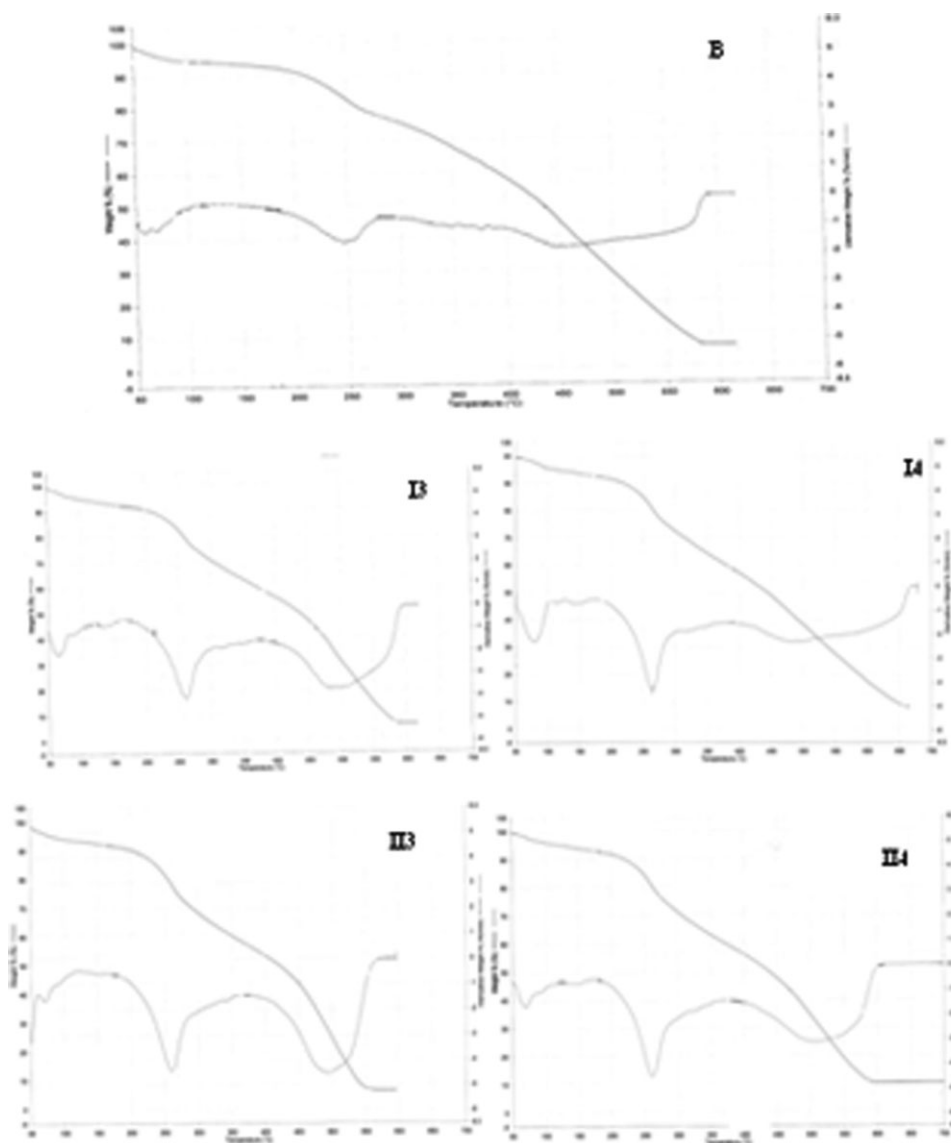


Figure 3 TGA and DTGA curves of lignin and blends under investigation.

The thermographs indicates initially a stage of mainly moisture loss followed by two distinctive weight loss stages indicative of the degradation of first three composites. The second weight loss stage is splitted into two substages in case of sample II4. This splitting may be attributed to the reorientation of the wheat gluten chains as mentioned before. The kinetics of thermal degradation of the previously mentioned blends was studied using the Friedman equation¹⁶:

$$\ln d\alpha/dt = \ln Z + n \ln(1 - \alpha) + E/RT$$

where α is the fractional weight loss and R is the gas constant. The value of $\ln d\alpha/dt$ can easily be obtained from the DTG curve. The value of $\ln(1 - \alpha)$ can be obtained from the TG curve. The values of $\ln d\alpha/dt$ were plotted against $1/T$, and then E can be

determined from the slope of the plot. Finally, the $\ln Z$ (the frequency factor) can readily be calculated through the equation at certain temperature. As shown from the results, lignin showed the lowest onset degradation temperature when compared with all the other blends.

TABLE V
Effect of Thermal Stability of the Investigated Blends

Sample	Onset degradation temperature	Activator energy KJ/mol
B	211°C	44.7
I3	225°C	48.8
I4	230°C	53.1
II3	227°C	47.6
II4	235°C	54.9

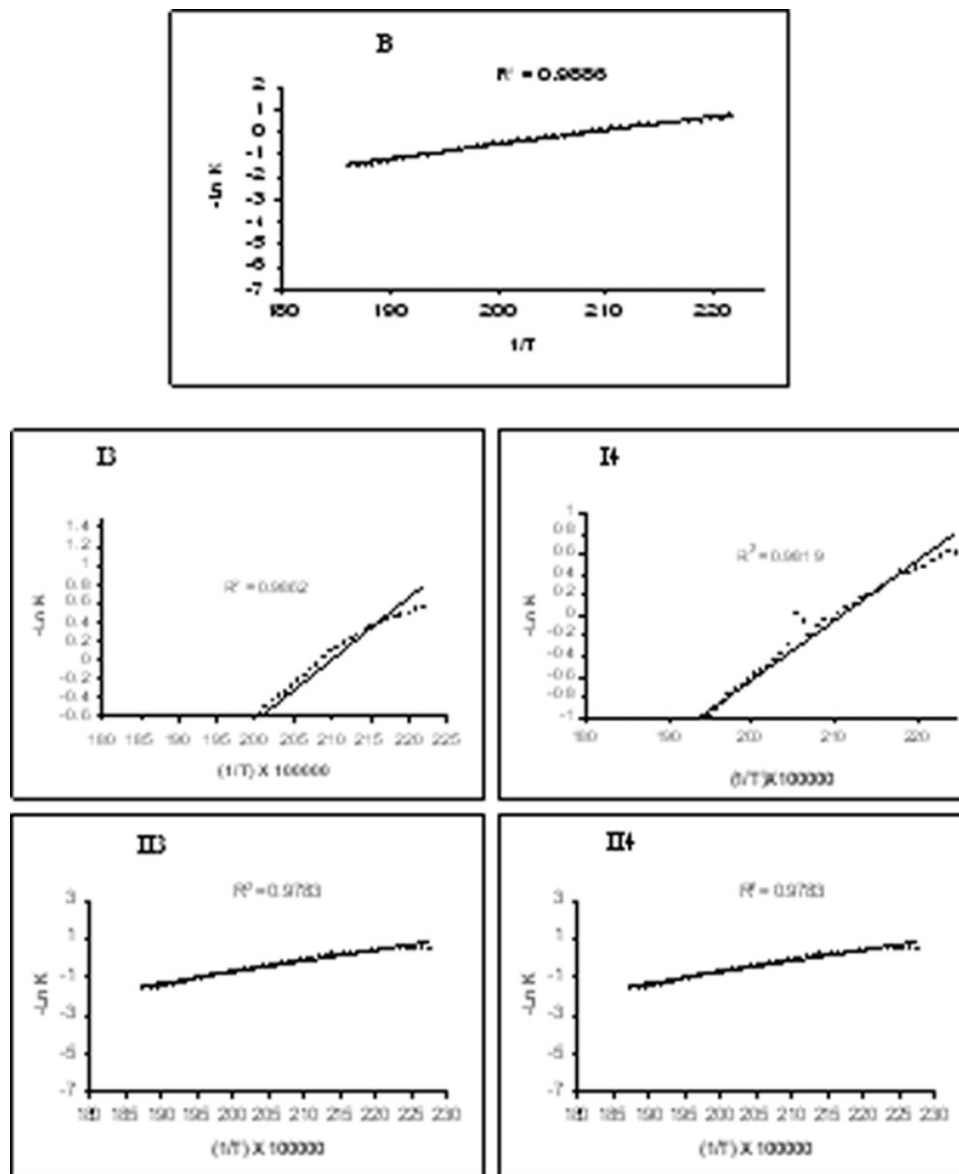


Figure 4 Friedman plots for the determination of kinetic parameters of the thermal degradation of lignin and blends under investigation.

All the investigated samples possess two main degradation stages except sample II4 where its degradation is performed via three degradation stages. The splitting of the second degradation stage into two stages may be ascribed to the reorientation of the modified wheat gluten chains, which is responsible for the increase in mechanical and thermomechanical behavior.

The increase in the onset degradation temperature from 210°C for lignin to 240°C for lignin/60% wheat gluten modified with 15% sodium silicate and filled with 10% silica blend confirm the strong interaction between lignin and modified wheat gluten, which could resist the effect of thermal degradation at relatively high temperatures.

CONCLUSION

1. The results have shown that blends of lignin and wheat gluten, modified with sodium silicate and filled with silica, have the following characteristics:
 - a. Pronounced high mechanical properties (diametric tensile strength).
 - b. Reduced thickness swelling.
 - c. Smooth and continuous fracture surface.
 - d. Decrease in linear expansion coefficient and expansion percent.
 - e. The blends reveal single T_g for all the compositions considered in this study probed by TMA. However, in all the blends, the

T_g increases with the incorporation of modified wheat gluten and silica.

2. The blends of lignin and 60% wheat gluten modified with 15% sodium silicate and filled with 10% silica showed unexpected behavior, significant diametric tensile strength and no expansion upon heating under load. This behavior qualifies this sample to be applied in some industrial applications.
3. It could be concluded from the SEM and TMA results that the interactions between lignin and modified wheat gluten are sufficient to avoid the addition of compatibilizer.

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