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Dissolution of Biomass from Rubberwood with 1-butyl-3-methyl Imidazolium Acetate Ionic Liquid

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Biomass from rubberwood has been gaining interest in view of its availability and being relatively economical. However, due to its complex structure, it is difficult to separate biomass using common solvents. The recent application of ionic liquids as a reaction solvent has offered a new platform for its efficient utilisation. Different particle sizes of biomass in ionic liquid have been investigated to develop an optimum process. Pretreatment involved the biomass being ground into various particle sizes, dissolved in ionic liquid and the resulting mixture stirred at a high temperature in an inert atmosphere. The dissolution rate was dependent on particle size, thus, smaller particles dissolved easily in ionic liquid. Dissolution of rubber biomass was complete in ionic liquid. As an added advantage, the ionic liquid was also highly recoverable. Extracted materials were characterised using FESEM, FTIR and TGA. FESEM results have shown that morphology of the extracted material changed significantly after dissolution. FTIR and TGA are in line with changes in extraction of rubber biomass from the dissolution process.

Keywords: Ionic liquids; rubber; biomass; dissolution; pretreatment

Recently, interests in developing sustainable energy resources such as biomass have been increasing due to the decrease in fossil fuel resources. Biomass is a by-product generated from agricultural or industrial wastes. The main advantage of biomass is evident from its abundant availability and sustainability. Biomass is commonly found as wood chips, domestic wastes, animal wastes, effluent sludge and agricultural residues, which can amount to more than 150 million tonnes annually[1]. In the current hunt for greener technologies, biomass has become a highly in demand commodity. Rubber tree (*Hevea brasiliensis*) biomass is a promising candidate as an alternative renewable energy source[2] in years to come. Until now, the rubber industry has always relied heavily on latex for income, while trunks and branches are used for the wood industry. The alternative use of rubber as feedstock for biomass would provide a higher value-added material for smallholders.

Rubber tree biomass has been found useful in the wood industry, producing materials such as plywood, sawmill, timber and fibreboard.

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Biomass can be converted to thermal, chemical and biochemical forms, which have high potential in production and generation of value-added materials. Interestingly, biomass wastes can also be converted to feedstock fuels, organic acids[3], solvents[4] and chemicals[5]. In addition, it has good potential to be used as a material for insulation, filtration, activated carbons or carbon fibers.

Rubber biomass must be converted to lignocelluloses components in order to obtain renewable fuel or chemicals. There are a number of challenges related to the usage of lignocelluloses biomass as a source of bioethanol. However, a major problem in the hydrolysis of lignocelluloses biomass is due to cellulose components (35% – 50%) being protected by lignin (10% – 25%) and hemicellulose (20% – 35%). Therefore, ionic liquids need to be used to pretreat biomass before they are converted to value-added chemicals. Ionic liquids have gained popularity, because of their nature as an organic salt with a wide liquid range, high thermal stability, non-volatility and excellent dissolution capabilities for both organic and inorganic compounds[6].

Currently, ionic liquids are used as reaction solvents and are slowly replacing volatile organic solvents in synthesis, extraction and electrolysis processes. Due to their unique properties, ionic liquids can be recycled. This provides efficient product extraction for lignocellulose[7]. Conventional acidic and basic systems used in the lignocellulose industry are environmental pollutants and cannot be recycled. Previously, there were numerous researches on dissolution and regeneration of biomass by ionic liquids. However, there is yet to be any research or report with regards to dissolution of rubber biomass by ionic liquids. Since ionic liquids are environmentally friendly, reusable and can easily dissolve a large number of biomass, they will serve as the reaction media in effectively removing lignin and hemicellulose as well as in reducing cellulose crystallinity. The intention of this research is to study the dissolution effect of the particle size of rubber biomass in 1-butyl-n-3-methylimidazolium acetate, [BMIM][OAc] as well as to characterise the extraction after dissolution.

EXPERIMENTAL

Materials

[BMIM][OAc] (1-butyl-3-methylimidazolium acetate) was purchased from Sigma Aldrich and dried under vacuum at 60ºC prior to use. Rubber biomass (branch of rubber tree; RRIM Series 2020 clones) was supplied by the Malaysian Rubber Board (MRB), RRIM Sg Buloh. The size of biomass was reduced by using a pulveriser machine (Fritch Model Pulverisette 19, done in UTGT, MRB) to a mesh size of 50 – 300 μm.

Preparation of Purified and Dried Ionic Liquid

Ionic liquid was purified and dried using the Schlenk technique. It was necessary to remove water and several undesirable side products from ionic liquids as they are highly hygroscopic. The process of drying the [BMIM][OAc] was done with continuous stirring under vacuum on a standard Schlenk line. Water or contaminants in [BMIM][OAc] were evaporated off and collected in cooling traps.

Mechanical Pulping on a Sample Biomass

Mechanical pulping using a pulveriser was needed to breakdown the biomass sample. The untreated biomass (control) was separated by passing them through the pulveriser with

different mesh sizes of 50 – 300 µm. The average particle size of the biomass sample was measured by FESEM.

Pretreatment of Biomass in Ionic Liquid: Dissolution and Extraction

[BMIM][OAc] was added into a 100 mL dry flask equipped with a magnetic stirrer under nitrogen flow in an oil bath. The biomass sample (particle sizes of 10 – 300 µm) was then rapidly added into [BMIM][OAc] (biomass/IL 5 wt%), and heated at 130ºC with vigorous stirring. The brown/black solution formed was gradually added into an excess of rapidly stirred regeneration solvent (distilled water) resulting in the precipitation of the extracted biomass. The precipitated material was filtered using a Buchner funnel and washed thoroughly with distilled water to remove the ionic liquid. The extracted material was dried in an oven at 80ºC. The flowchart for the dissolution process of rubber biomass in ionic liquid is illustrated in *Figure 1*.

Field Emission Scanning Electron Microscopy (FESEM)

Morphology of both control and extracted biomass from various sizes was observed with field emission scanning electron microscopy (FESEM, Supra 35 VP-24-58) at an acceleration voltage of 5.0 kV. Samples were mounted on copper and carbon adhesive tape sample stubs and sputter coated with a thin layer of gold before the analysis was performed.

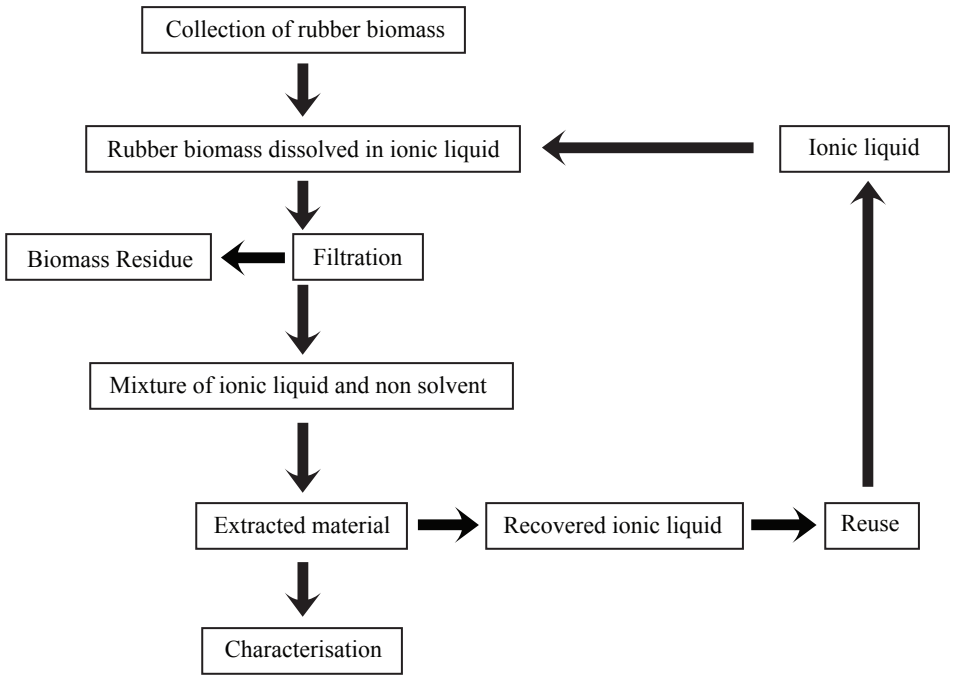


Figure 1. Flowchart for the dissolution process of rubber biomass in ionic liquid.

Fourier Transform Infrared (FTIR)

The spectra of control and extracted biomass were measured using an FTIR Spectrometer-equipped Thermo Nicolet 6700 with an ATR attachment. Each spectrum was averaged from thirty two scans in the range of 800 cm^{-1} to 4000 cm^{-1} with resolution of 4 cm^{-1}.

Thermogravimetric Analysis (TGA)

The decomposition temperature was carried out on a Perkin Elmer Pyris Diamond TGA. Samples with an average weight of *ca*. 5 mg were placed in a ceramic pan and heated from 40ºC to 900ºC at a rate of 20ºC/min.

RESULTS AND DISCUSSION

Morphology of Biomass

The surface morphology of biomass at various sizes was investigated using FESEM. *Figure 2* shows the FESEM micrograph of biomass after pulverisation. Four filters with mesh sizes of 0.2, 0.4, 0.8 and 1.0 mm were used during pulverisation and the average particle sizes were deduced from FESEM. The FESEM image (a) exhibits the average particle size (100 – 300 µm) obtained by mesh size of 1.0 mm, (b) 80 – 150 µm from mesh size of 0.8 mm, (c) 20 – 100 µm from mesh size of 0.4 mm and (d) 10 – 50 µm from mesh size of 0.2 mm.

In *Figure 2(a)* and *(b)* the individual fibre is clearly visible as the largest wire mesh of pulverising was used. However, the particle sizes of biomass in *Figure 2(c)* and *(d)* are small because the smallest mesh was used during the pulverisation process. The powder had formed for particle sizes with an average of 10 – 50 µm compared to particle sizes with an average of 20 – 100 µm.

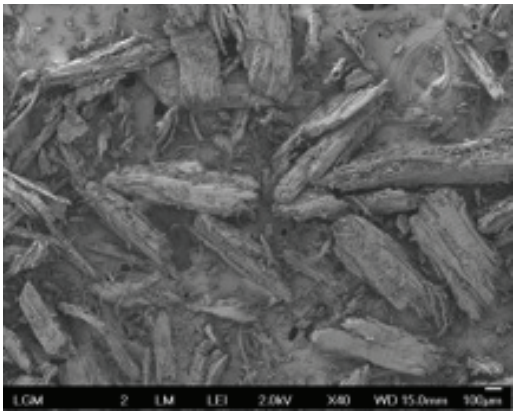
Dissolution of Biomass in Ionic Liquid

The dissolution of biomass in [BMIM][OAc] was investigated as a function of various particle sizes. Biomass with various particle sizes was dissolved in [BMIM][OAc] and the mixture was stirred at 130ºC under inert atmosphere. Temperature in a range of 100 – 130ºC was used to study the dissolution of rubber biomass in [BMIM][OAc]. It was found that a high temperature of 130ºC can promote rubber biomass to dissolve in ILs and this temperature was used to enhance the dissolution. 1-butyl-3-methyl imidazolium acetate [BMIM][OAc] was selected as it provided good solubility in the biomass sample[7].

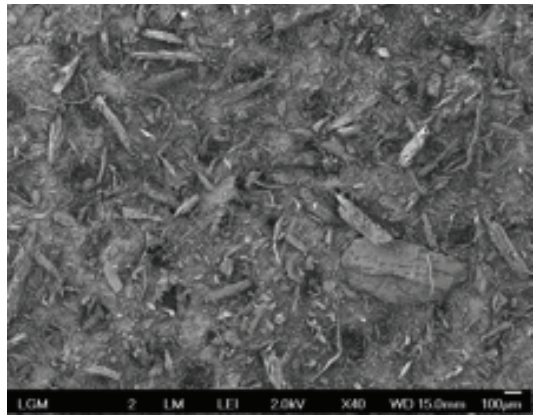
Data in *Table 1* indicates that smaller biomass particles are easier to dissolve in [BMIM][OAc] and dissolution rate is dependent on particle size of the biomass sample. The change of colour and viscosity in the IL/biomass indicated the dissolution of wood. No fibre or smooth surface was observed when the biomass was completely dissolved in [BMIM][OAc].

Biomass with smaller particles requires a shorter time to dissolve. Conclusively, the grinding of biomass by pulverisation helps to disrupt some of the fibrous structures in rubber biomass to obtain smaller particles[8]. Solutes with smaller particle size have larger surface area resulting in a higher rate of dissolution compared to solutes with larger particles.

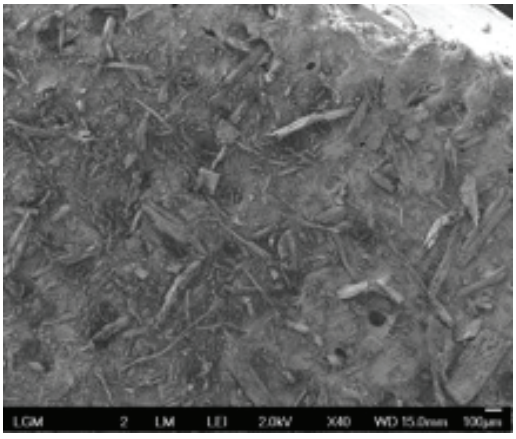
It is noteworthy that [BMIM][OAc] exhibits superior ability to dissolve biomass for all particle sizes, including larger particles (100 – 300 µm). In this study, [BMIM][OAc] shows better performance to dissolve biomass. Anion of acetate, OAc^- associated with cellulose hydroxyl proton from wood, has the capability to break the lignocellulose complex as well as



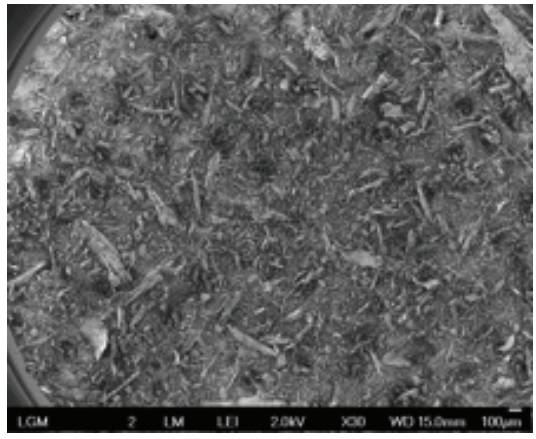
(a) 100 – 300 µm



(b) 80 – 150 µm



(c) 20 – 100 µm



(d) 10 – 50 µm

Figure 2. Field Emission Scanning Electron Microscopy (FESEM) of biomass at various particle sizes (a) 100 – 300 µm (b) 80 – 150 µm (c) 20 – 100 µm and (d) 10 – 50 µm.

TABLE 1. DISSOLUTION TIME OF RUBBER BIOMASS IN [BMIM][OAc]

Average particle size, µm	Dissolution time, h
10 – 50	8
20 – 100	24
80 – 150	48
100 – 300	72

inter and intra-molecular hydrogen bonding interactions in the biomass matrix. As a result, cellulose crystallinity was decreased and good dissolution of biomass was achieved.

Characterisation

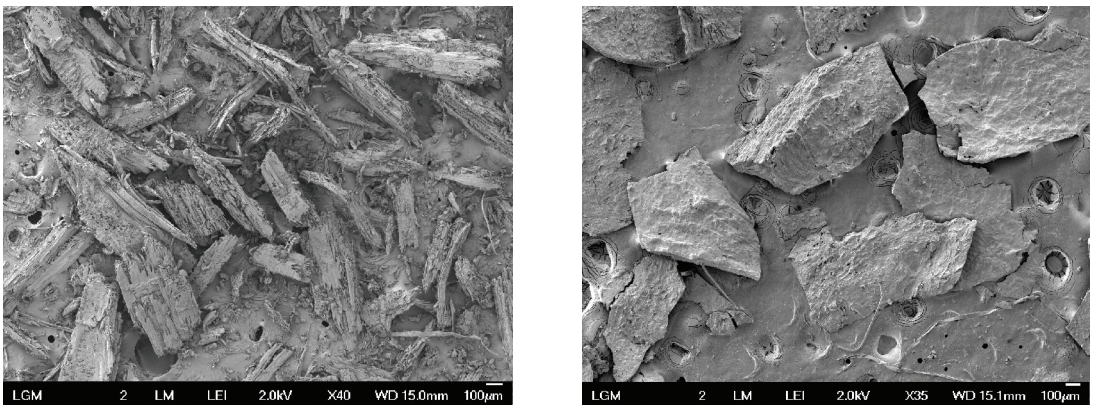
Field Emission Scanning Electron Microscopy (FESEM). The changes in the morphology of extracted material with [BMIM][OAc] were determined using FESEM. Micrographs in *Figure 3a* and *b* are FESEM images for control or original biomass at particle sizes 100 – 300 μm and extracted material at particle sizes 100 – 300 μm, respectively.

The micrograph clearly displays that ionic liquid pretreatment could modify the biomass morphology through dissolution and extraction of biomass. The fibrous look of the control in *Figure 3* significantly changed, giving rise to a conglomerate and homogeneous texture in *Figure 3b* after the ionic liquid treatment.

The extracted material is substantially amorphous by showing no identifiable fibre structure. In this new state, this biomass is physically made more susceptible and easily accessible towards various chemicals and enzymes[9].

FTIR. FTIR studies were carried out to confirm changes in strength of functional groups in the sample upon the pretreatment process. The spectrum of control demonstrated characteristic peaks of wood samples: discrete absorptions in the region from 1000 to 1750 cm^{-1}, C–H stretching in methyl and methylene groups (2800 – 3000 cm^{-1}) and strong broad OH stretching (3300 – 4000 cm^{-1})[10,11]. The appearance of a band near 1600 cm^{-1} is attributed to the pure ring stretching mode while the C=O stretch conjugated or aromatic ketones absorbs at 1700 cm^{-1}. As expected, the main structural framework for the whole range of particle sizes (10 – 50 μm, 20 – 100 μm, 80 – 150 μm and 100 – 300 μm) was notably similar. It has been validated that particle size would not affect chemical change during the dissolution of biomass.

The spectra of (a) control (original rubber biomass) and (b) extracted material, were compared to that of (c) commercial lignin



(a) (b)

Figure 3. Micrographs of (a) control and(b) extracted material at particle sizes 100 – 300 μm.

and (d) cellulose in *Figure 4*. Compared to the FTIR spectra of control, the stronger carbonyl band at 1750 cm^{-1} confirmed the disappearance noticed in the FTIR spectra of extracted material. It is important to note that the C=O absorption band changed to O-H and conjugated C-O compared with control, suggesting ionic liquid extracted some material from the raw material of biomass[11].

Vibrations located at 1380 cm^{-1} and 895 cm^{-1} were attributed to the C-H cellulose and hemicellulose in *Figure 4(a)*. After dissolution in [BMIM][OAc], the extracted material showed the characteristics of cellulose bands, further indicating that the extracted material was enriched in carbohydrates.

Lignin-related absorbance band at 1590 cm^{-1} (C=C stretching), 1450 cm^{-1} (CH asymmetric bending), 1320 cm^{-1} (CO in syringyl ring) and 1260 cm^{-1} (CO stretching) were noted. Also important in this study, is the fact that the extracted material shows characteristics of cellulose and lignin peaks, indicating that [BMIM][OAc] has successfully extracted the main components of biomass which are cellulose and lignin[12].

Thermogravimetric Analysis (TGA). TGA curves shown in *Figure 5* are of control and extracted material of particle sizes 10 – 50 μm. For all particle sizes *e.g.* 50 – 80 μm, 80 – 100 μm and 100 – 300 μm the TGA curves were the same as those of 100 – 300 μm, probably because the reduction of physical size does not affect thermal decomposition in rubber wood.

For both samples, control and extracted material, the first stage at temperatures below 200ºC corresponds to the drying period where light volatiles, mainly water, were released throughout the procedure. A small initial drop in sample weight observed in *Figure 5*, due to weight loss was less than 10% at this early stage.

A rapid decrease at the second stage of decomposition occurred at temperatures between 200 – 400ºC, corresponding to a

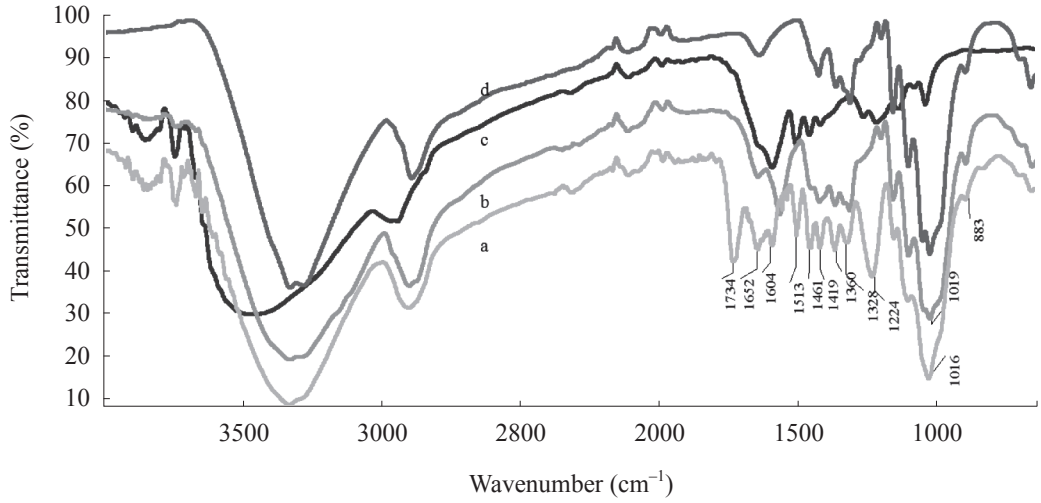


Figure 4. FTIR of (a) control, (b) extracted material, (c) commercial lignin and (d) commercial cellulose.

significant drop in weight for both samples due to liberation of volatile hydrocarbons from thermal decomposition of hemicellulose and cellulose. Results obtained were consistent with previously published data[13]. For extracted material, the weight percentage was reduced to below 50% followed by a rapid decomposition at 400ºC corresponding to the remaining heavy components from lignin. TGA curves of the control showed two different stages of decomposition.

It is important to note that, in the case of the extracted material, after pretreatment with ionic liquids the decomposition temperature decreases. Ionic liquid successfully extracted lignin from rubber biomass[14]. As can be seen from *Figure 5*, the control sample has two stages of decomposition due to decomposition of lignin. Lignin is difficult to decompose, hence the potential of designing a dissolving solvent such as ionic liquids could be to break up intra and inter hydrogen bonding of biomass. High residual masses after the decomposition step show a high yield of ash content, primarily due to the fact that 80 wt% of biomass is formed by volatile fraction and only approximately 20 wt% is in the form of solid carbonaceous residue[15].

CONCLUSIONS

Three main biopolymers; cellulose, hemicellulose and lignin were successfully extracted and separated from various particle sizes of rubber biomass by dissolution in ionic liquid, [BMIM][OAc] followed by precipitation in water. The dissolution of rubber biomass in small particles was found to

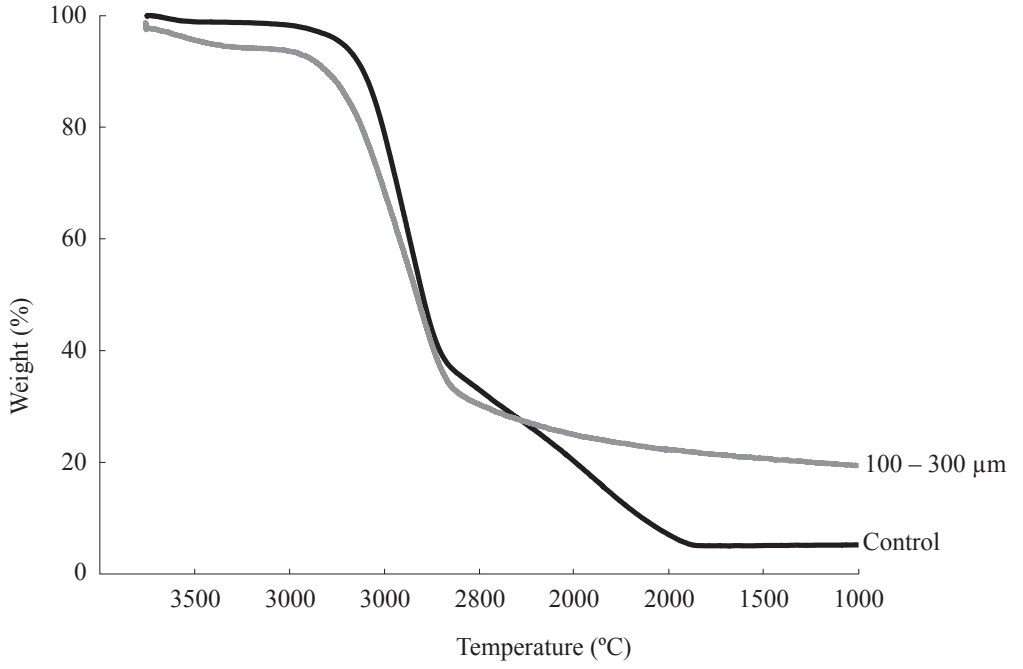


Figure 5. TGA of control and extracted materials with particle sizes 100 – 300 µm.

be better compared to the larger counterparts. FESEM confirmed that the extracted material completely dissolved in ionic liquids. FTIR of extracted materials showed the existence of cellulose, hemicellulose and lignin peaks. TGA proved that ionic liquid was successful in extracting cellulose, hemicellulose and lignin from rubber biomass.

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