Research Article

Influence of Cellulose on the Mechanical and Thermal Stability of ABS Plastic Composites

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Microcrystalline cellulose was explored as possible biodegradable fillers in the fabrication of ABS plastic composites. TGA indicates that upon inclusion of cellulose microcrystals the thermal stability of the ABS plastics was improved significantly when compared to the neat ABS plastic counterparts. Furthermore, inclusion of extracted cellulose from plant biomass showed a higher thermal stability with maximum decomposition temperatures around 131.95°C and 124.19°C for cellulose from cotton and *Hibiscus sabdariffa*, respectively, when compared to that of the purchased cellulose. In addition, TMA revealed that the average CTE value for the neat ABS and 1:1 ratio of cellulose to ABS fabricated in this study was significantly lower than the reported CTE (ca. 73.8 $\mu\text{m}/\text{m}^\circ\text{C}$).

1. Introduction

Due to the rapid growth of waste from electrical and electronic equipment, a considerable amount of focus has been placed on exploring new sources that will allow the creation of unique polymeric materials that can be used in the development of biobased composites. Today, there are two categories of biodegradable polymers: synthetic and natural polymers. Though not all synthetic polymers portray such nature, upon the incorporation of additives these polymers mimic biodegradable behavior. Vroman and Tighzert [1] reported that natural polymers generally offer fewer advantages than synthetic polymers; however, natural polymers offer the key advantage of biodegradability. That being said, producing these composites with biodegradable nanomaterials will give rise to inexpensive, natural, renewable materials with little to no negative impacts on the environment.

Cellulose has been used to combat the issues of sustainability [2] and is a common biopolymer that is being used widely [3–8]. Cellulose is a complex carbohydrate made up of several thousand glucose molecules linked end to end, and due to its intra- and intermolecular hydrogen bonding various ordered crystalline arrangements are observed. Given

the abundance of natural resources available for cellulose and the unique mechanical properties of highly crystalline cellulose (micro- or nanocrystalline cellulose), it has great potential for use as fillers to increase composite material properties in comparison to unfilled polymer matrix counterparts. That is, cellulose composites have the potential to be light-weight, low-cost, and environmentally friendly with improved thermal and mechanical properties. Due to the incompatibility between generally hydrophobic host polymer matrix and hydrophilic natural fiber, combined with lower thermal resistance of the cellulosic material, most cellulose research has primarily focused on its extraction from different plants modification and its use in the reinforcement of various polymer matrices [9–16]. Common techniques for composites fabrication include but are not limited to casting, templating [6, 17, 18], and compounding or extrusion [8, 19].

Currently, acrylonitrile-butadiene-styrene (ABS) is one of the major components used in the fabrication of plastics casings for computers, monitors, keyboards, and other similar components. A life cycle assessment conducted in our group, but not discussed in this paper, has shown that the thermal processing of ABS has an impact on several environmental categories, having the greatest impact on

FIGURE 1: A typical flowchart depicting the method used to fabricate neat and cellulose-based ABS plastic composites for comparative analyses.

global warming. Though the monomers (acrylonitrile, butadiene, and styrene) of ABS may not be extremely harmful, this terpolymer possesses different properties and produces volatile organic compounds (VOCs) during pyrolysis, combustion, and extrusion [20, 21]. The list of possible VOCs includes hydrocarbons, aromatic hydrocarbons, alcohols, ketones, aldehydes, acids, and acrylonitrile. To conform to more biofriendly composites, micron-sized cellulose, a natural biopolymer, is used as filler for an acrylonitrile-butadiene-styrene (ABS) matrix. There are several challenges within cellulose particles, such as the capability to absorb moisture, but they have promising properties as a biofiller for polymers. Cellulose fillers have the potential of enhancing the composite properties (e.g., thermal or mechanical) of plastics formed using ABS, as well as increasing its biodegradation by organisms and recycling methods [11]. Hence, in this report, polymer dissolution and mold cast techniques were used for the fabrication of cellulose-based ABS composites as an alternative to a thermal process due to the volatile organic compounds (VOCs) released during thermal processing (i.e., recycling or extrusion).

2. Materials and Methods

2.1. Materials. Dichloromethane $\geq 99.5\%$ ACS reagent was purchased from Sigma-Aldrich while the Lustran ABS 552 (ABS) was purchased from PolyOne Corporation. The manufactured microcrystalline cellulose (MMCC) was received from CreaFill Fibers Corp. as TC40 CreaTech. For the extraction of cellulose, acetic acid, acetone, sodium chlorite, sodium hydroxide, and sulfuric acid, ACS reagent grade chemicals were purchased from Sigma-Aldrich and used as received. *Hibiscus sabdariffa* was obtained from the local farm. The cotton was purchased from the local convenience store.

2.2. Sample Preparation. Cellulose extracted from *Hibiscus* and cotton was carried out using the experimental procedures as described by Huntley et al. [17]. In short, solutions of acetic acid (90 wt%), sodium chlorite (9 wt%), a buffer solution, and sulfuric acid (32 vol%) were prepared for cellulose extraction. Acetic acid was used for a pretreatment process followed by bleaching. The resulting product was then hydrolyzed using sulfuric acid. Following hydrolysis, centrifugation and sonication were performed for the complete extraction of crystalline cellulose. The flow chart in Figure 1 depicts the method utilized to fabricate neat ABS, as well as composites reinforced with MMCC and extracted celluloses. This method has been found to be beneficial due to the method being carried out at room temperature, which increases the cost effectiveness during production [18]. The ABS pellets and cellulose were added to a plastic mixing cup in varying ratios; see Table 2. As-received dichloromethane was added to dissolve the ABS pellets. Utilizing a stir stick, a manual mixing method was used. The ABS and cellulose ratios were mixed for several minutes to achieve uniform distribution of the cellulose fibers. The resulting paste was poured in a metal flexure mold and allowed to dry at room temperature for 48 hours or longer [22]. (Cellulose dispersion studies need to be conducted due to a lack in mechanical mixing procedures to ensure homogeneous mixing of the materials.)

2.3. X-Ray Diffraction (XRD). XRD analyses were performed using a Rigaku D/MAX 2200 X-ray diffractometer using $\text{CuK}\alpha$ radiation with wavelength $\lambda = 1.54 \text{ \AA}$ and 40 kV and 30 A. Analyses of dried celluloses were performed on a glass slide from 0° to 50° of 2θ angle at a rate of $5^\circ\text{C}/\text{min}$. Proceeding data collection, the results were characterized utilizing PDF data base of Joint Committee on Powder Diffraction Standards (JCPDS) along with literature findings.

FIGURE 2: XRD spectra revealing the CI structure for purchased MMCC (a) and cellulose extracted from cotton and *Hibiscus* (b) and (c), respectively, via strong acid hydrolysis.

2.4. Scanning Electron Microscopy (SEM). SEM images were collected from a Zeiss EVO 50 VP SEM operating at an acceleration voltage of 3 keV for the purchased cellulose and 20 keV for the extractions. Additionally, gold sputter coating was achieved on an EMS 550X sputter coating device.

2.5. Modulated Differential Scanning Calorimetry (MDSC). Thermal analysis was carried out using custom MDSC heat only, with sample sizes remaining in a range of 10–13 mg. These analyses, for the dried celluloses along with the composites and pellets, were carried out on TA Instrument DSC Q2000 equipped with aluminum hermetic pans. The samples were analyzed under nitrogen gas at 50 mL/min. While the cellulose and pellet samples were ramped to 400°C and 300°C at a rate of 5°C/min, the composites were subjected to a different method to determine the glass transition temperature (T_g) after thermal stresses were relieved. The ABS composite samples were ramped from 30°C to 140°C, cooled to 30°C, and ramped again to 150°C.

2.6. Thermogravimetric Analysis (TGA). TGA analyses were performed using a TA Instrument TGA Q500 under a nitrogen atmosphere. The mass of all samples ranged from 13 to 15 mg and they were tested using pretared platinum TGA pans. The samples were purged with nitrogen at a rate of 40 mL/min. After drying the extracted cellulose samples, these samples along with the purchased cellulose were analyzed at a rate of 5°C/min from 30°C to 400°C. On the other hand, the composites samples were analyzed at an identical rate with a ramping range of 30°C to 300°C.

2.7. Thermomechanical Analysis (TMA). TMA were completed on TA Instrument TMA Q400. The samples were

analyzed at 5°C/min at 30°C to 90°C under thermal expansion mode, with a force of 0.3 N in a nitrogen atmosphere.

3. Results and Discussions

3.1. XRD Analysis of the Manufactured and Extracted Microcrystalline Cellulose. Figures 2(a)–2(c) display the crystalline structure for MMCC and cellulose extracted from cotton and *Hibiscus*. In Figure 2(a), XRD analysis verifies cellulose I (CI) polymorph structure. As can be observed, the existence of peaks with 2θ values of 15°, 22°, and 35° is shown. These results match well with previously reported results on the structure of native cellulose [2]. In addition, in previously reported literature for different biomass sources by Contos et al. [21], Ford et al. [23], and Kargarzadeh et al. [24], similar structural arrangements of the extracted cellulose were observed when analyzing by XRD.

Likewise, the extracted celluloses featured in Figures 2(b) and 2(c) exhibit similar XRD behavior patterns to that shown in Figure 2(a). This report is made evident due to the corresponding 2θ values of 15°, 22°, and 35°. For the extracted cotton spectra, the peak at 15° portrays two peaks overlapping which is usually observed in a CI α /CI β mixed XRD pattern as well as mercerized cellulose that has not been fully converted to cellulose II [23, 25]. O'Sullivan [26] reports that native cellulose, cellulose I, only exists in a mixture (I α and I β). A true conversion of CI to CII occurs through mercerization [26, 27] (swelling due to sodium hydroxide) or regeneration (solvent solubilization and reprecipitation by water dilution [28]). Meanwhile, the peak at 22° is more defined in comparison to the MMCC spectra which we attribute to the smaller diameter fibers and increased shape uniformity of the cotton fibers versus its MMCC and *Hibiscus*

FIGURE 3: Scanning electron micrographs revealing the shape and size for purchased cellulose, MMCC (a), and cellulose extracted from cotton (b) and *Hibiscus* (c).

counterparts; see Figures 3(a)–3(c). In addition, based on the peak height XRD method reported in the literature [28] for calculation of cellulose crystallinity, we have determined that the cellulose extracted from cotton has the highest crystallinity (ca. 88.46%) based on our method of extraction. Moon et al. [2] and Kargarzadeh et al. [24] reported similar values for the microcrystalline cellulose dimensions [2] and crystallinity [2, 24].

3.2. SEM Analysis of the Manufactured and Extracted Microcrystalline Cellulose. Scanning electron micrographs are presented in Figures 3(a)–3(c) revealing the size and shape of MMCC and extracted celluloses. Figure 3(a) shows that the MMCC crystals are rod-like fibers with diameters and lengths in the micron-size range. These cellulose fibers appear to be free of agglomeration and not uniform in length; that is, longer and shorter length scale fibers are observed. However, the cotton extracted cellulose counterpart featured in Figure 3(b) apparently exhibits similar fiber-like crystals with increased uniformity in its shape when compared to the manufactured microcrystalline cellulose in Figure 3(a). Furthermore, the length of the cotton extracted cellulose appears longer than that of the MMCC with lengths of approximately 100 μm and 200 μm , respectively.

Similar results are observed for cellulose extracted from *Hibiscus*; see Figure 3(c). *Hibiscus* extracted cellulose exhibits rod-like fibers with lengths and diameters on the micrometer scale. Furthermore, large scale aggregation of cellulose fibers is observed for *Hibiscus* extracted cellulose, which is attributed to the larger fiber sizes ($\geq 300 \mu\text{m}$) observed when compared to its cotton extracted or purchased cellulose

counterparts. It has been reported that, depending on the mechanistic nature of the drying process and extraction methodology used, induced large scale aggregation of cellulose fibers will be observed [6, 19, 29]. Thus, based on reports from the literature and previous findings reported by our group [17, 25], we propose here that a similar mechanism of induced aggregation is occurring due to a combination of both processing and drying methodologies.

3.3. Thermal Analysis of the Manufactured and Extracted Microcrystalline Celluloses. Figure 4 reveals the DSC curve showing the thermal behavior of MMCC. This analysis reveals exothermic as well as endothermic peaks corresponding to water vaporization, degradation, char formation, and oxidation (90–150°C, 262°C, 275°C, and 337°C, resp.). Similar results were observed by Sinha and Rout [30]. Here it is reported that water vaporization appears as a broad endothermic peak in the range of 60–140°C, another small endothermic peak present is indicative of the thermal degradation of hemicelluloses and the glycosidic linkages of cellulose at 290°C, and further decomposition of cellulose occurs around 365°C causing char formation. The char is later oxidized along with the remaining mass being consumed, around 431°C. As can be seen, similar results are observed in Figure 4 with a broad endothermic peak appearing with a range between 90 and 150°C but centered at around 115°C and corresponding small endothermic and exothermic peaks, 262°C, 275°C, and 337°C, respectively, indicating hemicellulose and glycosidic linkages decomposition, continuing with further cellulose degradation causing char formation, followed by the oxidation of char. In addition, temperature

TABLE 1: Tabulated DSC and TGA values for both purchased and extracted cellulose.

Name	DSC		TGA		
	T_g (°C)	Residue (%)	Onset (°C)	Rate (%/°C)	Max decomp (°C)
MMCC	N/A	14.01 ± 0.22	257.88 ± 8.62	1.75 ± 0.07	333.37 ± 0.61
<i>Hibiscus</i>	N/A	28.68 ± 0.91	165.82 ± 2.87	0.57 ± 0.09	252.08 ± 5.64
Cotton	N/A	32.97 ± 0.15	131.90 ± 2.83	0.36 ± 0.00	207.31 ± 2.53

FIGURE 4: DSC curve showing the thermal behavior of MMCC.

ranging between 200 and 250°C apparently reveals a high thermal stability region for the MCC. That is, once the absorbed water has been driven off, the cellulose structure exhibits high resistance to degradation between 200°C and 250°C.

The thermogravimetric analysis, TGA, of the MMCC and extracted celluloses can be observed in Figure 5 while the corresponding tabulated values that were obtained from both TGA and differential scanning calorimetry, DSC, analyses are provided in Table 1. The onset of degradation for the manufactured cellulose is higher than that of the extracted cellulose, with an approximate value of 258°C; see Table 1. The maximum decomposition temperature for the MMCC was observed at 333°C at a rate of 1.75%/°C. However, the TGA for the extracted celluloses exhibited significantly lower onset and maximum decomposition values (i.e., *Hibiscus* and cotton, 166°C and 132°C and 252°C and 207°C, resp.) when compared to their manufactured counterpart. We attribute the significant difference in TGA values exhibited for the comparison of manufactured and extracted cellulose to the extraction methodology. That being said, the *Hibiscus* and cotton exhibited similar rates of mass loss at the maximum decomposition values when compared. Similar results have been observed for cellulose extracted from *Hibiscus cannabinus* (kenaf bast fibers). Kargarzadeh et al. [24] reported a sharp weight loss at 300°C for unhydrolyzed cellulose, which can be observed in Figure 4 for the MMCC due to its undergoing the pulping process which does not utilize hydrolysis [31]. According to the manufacturers, MMCC was produced by micronization of hardwood pulp. Kargarzadeh et al. [24] also reported that longer hydrolysis time makes for shorter fibers. Huntley et al. [25] reported that acids used during hydrolysis affect the thermal stability of extracted celluloses. The functional groups attached to the active sites on cellulose

FIGURE 5: TGA percent weight loss curves for purchased and extracted cellulose.

are determined by the acids used, which in turn degrades at varying times and temperatures. It can be observed in Figure 5 and Table 1 that the extracted celluloses begin to degrade at lower temperatures than the MMCC but the rate of decomposition is more favorable for the extractions. Hence, the hydrolysis caused the extracted celluloses to become more thermally resistant at higher temperatures in comparison to the manufactured cellulose. In Table 1, at 400°C, MMCC has a residue of 14%, which is lower than that exhibited for its extracted cellulose counterparts. It can be observed that the residues for the extractions are comparable (*Hibiscus* and cotton, 28.68% and 32.97%, resp.) but, in comparison to the manufactured, are both approximately doubled in value. It was reported by Kargarzadeh et al. [24] that char percentage increased with acid hydrolysis along with the increase in hydrolysis times. This was said to be ascribed to the increase in the amount of sulfate groups, which acted as flame retardants.

For the extracted celluloses, TGA revealed a slightly higher onset of degradation and maximum decomposition for the *Hibiscus* in comparison to the cotton, as previously stated. Contrarily, this was not observed for the percent of residue remaining for the extractions. As stated previously, the residues for *Hibiscus* and cotton extractions are 28.68% and 32.97%, respectively. Other analysis values may portray a higher stability for the cotton extraction at 400°C; per the maximum decomposition temperatures, this is not the case.

According to TGA, MMCC is an ideal candidate for filler due to the thermal stability at high temperatures (i.e., onset

FIGURE 6: TGA weight loss curves revealing the thermodynamic behavior of neat and MMCC-based ABS plastic composites at various filling ratios (a) and (b).

temperature and maximum decomposition temperature). Onset and maximum decomposition are very important properties when determining thermal stability of materials. Hence, the values presented in Table 1 for MMCC are the determining factors for considering the manufactured cellulose as filler. The T_g was not revealed in DSC for the celluloses.

3.4. Thermal Analysis of Cellulose-Based ABS Composites. Figures 6(a) and 6(b) show thermal graphs for the cellulose filled at different ratios of ABS to cellulose and neat ABS. Upon initial observation of the thermal graphs featured in Figures 6(a) and 6(b), the neat polymer sample has an onset temperature higher than that of the as-received ABS pellet. Based on this observation, we must note that the method utilized for the fabrication of the neat ABS and cellulose-based ABS composites apparently has a small initial effect on their thermal stability [18, 32]. In the case of the neat ABS, the slight improvement in thermal stability when compared to the pellet ABS form can be attributed to the decrease in density of dangling bonds of the ABS structure. Nishi et al. [18] reported that molecules of the solvent used in the solvent casting process of ABS can be absorbed by the ABS polymer causing segments of ABS polymer structure with dangling bonds to be attracted to the solvent molecules leading to improvements in its impact strength. In addition, it is proposed in this study that the same weak intermolecular attractions between the absorbed solvent molecules and the dangling bonds of the ABS provide a mechanism for a slight instantaneous improvement in the thermal stability of the ABS composite. That is, due to the increased intermolecular

attractions, a slight increase in the thermal energy needed to promote degradation is observed. However, the residue and rate of degradation for the pellet are more favorable characteristics in comparison to the composites. This could be due to, in the neat ABS case, observance of solvent absorption for the ABS composites. Furthermore, the rate of residue and moisture loss (weight loss) increased as the amount of cellulose increased, with decreasing ABS, proving that the ABS moisture absorbance significantly impacts the thermal stability of the composite material (data not shown).

It can be observed that the incorporation of cellulose microcrystals does not significantly change the initial onset of degradation and the maximum decomposition temperature at low concentrations of cellulose fillers added to the ABS matrix when compared to its neat ABS counterpart; however, significant changes in the thermal stability are observed when the concentration of cellulose fillers is increased. A more quantitative view can be observed from Table 2, which consists of a list of tabulated values for the thermal analyses depicted in Figures 6(a) and 6(b). It must be noted that the onset temperature is significantly higher than that of the as-received pellet in all samples where cellulose has been added. However, upon comparison to neat ABS samples with the cellulose filled composites, the onset temperatures recorded for the higher ratios of ABS to cellulose (e.g., 32:1, 16:1, 8:1, 32:5, and 16:1) exhibit values that are similar to the average onset temperature of 100.90°C measured for its neat ABS counterpart. Furthermore, increasing the concentration of cellulose in the ABS matrix (e.g., 4:1, 23:10, 8:5, 6:5, and 1:1) exhibits a significant decrease in the onset temperature when compared to the neat ABS.

TABLE 2: Tabulated DSC and TGA values for neat and cellulose-based ABS composites.

Ratios (ABS : cellulose)	T_g (°C)	Residue (%)	Onset (°C)	Rate (%/°C)	Max decomp (°C)
Pellet	104.45 ± 0.22	98.75 ± 0.08	62.86 ± 2.97	0.003 ± 0.001	162.79 ± 4.33
Neat	93.20 ± 5.07	91.59 ± 0.33	100.90 ± 2.48	0.21 ± 0.02	108.27 ± 3.21
32 : 1 MMCC	93.02 ± 6.34	90.37 ± 1.14	91.90 ± 3.40	0.22 ± 0.06	100.16 ± 4.85
16 : 1 MMCC	91.48 ± 7.07	90.49 ± 1.10	97.03 ± 3.50	0.19 ± 0.04	104.02 ± 3.49
8 : 1 MMCC	88.46 ± 1.99	91.59 ± 1.01	103.69 ± 1.88	0.13 ± 0.04	111.63 ± 5.69
32 : 5 MMCC	92.10 ± 6.65	88.33 ± 0.66	93.87 ± 1.57	0.18 ± 0.04	98.67 ± 1.17
16 : 3 MMCC	93.05 ± 7.65	87.48 ± 1.39	97.63 ± 3.41	0.18 ± 0.07	103.07 ± 5.31
4 : 1 MMCC	95.87 ± 2.64	81.42 ± 1.26	82.86 ± 1.47	0.26 ± 0.07	90.62 ± 3.41
23 : 10 MMCC	98.07 ± 1.77	77.86 ± 0.93	85.33 ± 2.11	0.29 ± 0.02	282.74 ± 1.47
8 : 5 MMCC	98.55 ± 5.23	73.99 ± 0.44	87.00 ± 1.10	0.32 ± 0.01	281.91 ± 2.10
6 : 5 MMCC	97.13 ± 1.12	71.75 ± 0.59	87.52 ± 0.50	0.37 ± 0.01	283.39 ± 0.69
1 : 1 MMCC	105.67 ± 0.09	75.06 ± 1.08	59.21 ± 6.07	0.50 ± 0.01	282.29 ± 1.87
32 : 1 cotton	94.55 ± 6.59	93.04 ± 0.90	109.45 ± 6.99	0.09 ± 0.02	131.95 ± 9.43
32 : 1 <i>Hibiscus</i>	98.39 ± 6.69	92.40 ± 0.42	116.07 ± 4.84	0.10 ± 0.04	124.19 ± 2.93

Unlike the onset temperature trend, the complete opposite is observed for the maximum decomposition temperature of the cellulose filled ABS composites. Although the maximum decomposition temperature is similar for both the neat and cellulose filled ABS composites at the lower concentration of MMCC, as the MMCC concentration increases, the thermal stability “maximum decomposition temperature” increases by a two-fold excess. In fact, at a ratio of 1 : 1, ABS : MMCC, respectively, the onset temperature is lower than the neat ABS but the decomposition temperature is maximized. Given that the MMCC exhibits high thermal stability (ca. 333.37°C), it can be extrapolated that the increase in thermal stability here corresponds closely to that of the thermal properties of MMCC shown in Figures 4 and 5 and, more closely, Table 1. That is, the increased thermal stability here is surely attributed to the larger amount of cellulose inducing a composite effect when trapped in the ABS matrix. Šišáková [33] and Xanthos [34] have reported that the addition of reinforcements along with the stage of mixing and distribution of fillers within the polymer matrix will significantly impact the thermal and mechanical properties. El-Shekeil et al. [35] found that an increase in filler content decreased the thermal stability of kenaf fiber (*Hibiscus cannabinus*) reinforced thermoplastic polyurethane composites. At lower temperatures, this was said to be attributed to dehydration from cellulose and thermal cleavage of glycosidic linkage, caused by transglycosylation and scission of C–O and C–C bonds. At higher temperatures, aromatization, involving dehydration reactions, was said to have caused decomposition. Furthermore, it has been reported by Xue et al. [36] that excessive dosages of additives no longer fulfill their purpose and perform counterproductively.

Sanaeepur et al. [22] reported a T_g value of 108.98°C for pure ABS which is shown to be comparable to our ABS pellets. In Table 2, it can be observed that the process described in this paper does not significantly reduce the T_g value for ABS; in fact, in every composite the T_g value is

shown to be comparable. In comparison to the pellet, the 1 : 1 ratio is almost identical to T_g of the pellet.

Upon incorporation of cellulose fibers from different biomass sources (see Table 2), a significant change in the T_g and maximum decomposition temperature is observed. In the case of cellulose fibers extracted from cotton and *Hibiscus*, T_g was very comparable. The maximum decomposition temperature is observed at 131.36°C, 124°C, and 100.16°C for the cotton fiber, *Hibiscus* fiber, and MMCC composites, respectively. This could be explained in terms of fiber uniformity and dispersion within the polymer matrix [33]. In the case of the extracted cellulose, it is observed that the cellulose crystals are slightly more uniform in shape and size for both of the cotton and *Hibiscus* fibers; see Figures 3(b) and 3(c). Irregularities in the shape and size of fillers will impact the uniformity of the fiber dispersion within the polymer matrix during mixing. Furthermore, for the composites consisting of extracted celluloses (see Figure 7), they have the greatest thermal characteristics when compared to neat and 32 : 1 MMCC counterpart samples in Table 2 and Figure 7. The sulfate groups [2] introduced onto the surface of the celluloses extracted from cotton and *Hibiscus* are the cause behind the improved thermal properties. These sulfate groups are known to produce charged surfaces that stabilize [2] dispersion. The MMCC composites are expected to have poorer dispersion of particles due the lack of hydrolysis being performed. Without hydrolysis or another form of chemical functionalization, cellulose naturally undergoes hydrogen bonding due to the three hydroxyl groups located on each glucose monomer, causing nonuniform dispersion [25]. As chemical functionalization has the ability to disrupt the strong hydrogen bonding behavior [25], the extracted celluloses have the ability to disperse more uniformly, hence causing a more thermally stable composite.

3.5. Thermomechanical Analysis of ABS Composites. Figure 8 shows the coefficient of thermal expansion (CTE) trend

FIGURE 7: TGA weight loss curves revealing the thermodynamic behavior of ABS plastic composites as a function of the ratio of cellulose additive (purchased or extracted).

FIGURE 8: TMA bar graphs revealing the thermomechanical behavior of neat and cellulose-based ABS plastic composites.

observed for the ABS composites filled with MMCC. The initial CTE of the neat ABS is observed at around $20 \mu\text{m}/\text{m}^\circ\text{C}$. Upon the addition of 3% MMCC, the CTE increases dramatically. Further increases in the amount of MMCC dispersed within the polymer matrix yield a decrease in the measured CTE values. However, after the addition of 25% MMCC fillers (i.e., 4:1 ratio), a dramatic increase in the CTE values is observed with a continued decrease as the amount of cellulose fillers is increased within the polymer matrix. It is well known that the shape and the dispersion of fillers in the polymer matrix significantly impact its effect on the measured CTE of its polymer host composite. DeSarkar and coworkers [37] reported that upon the addition of various inorganic fillers a dramatic change was observed for the polycarbonate matrix and effectiveness of the impact of the fillers on the measured CTE values of the polymer matrix was dependent upon filler type and degree of dispersion. That is, better dispersion of the fillers within the polymer matrix allowed

for greater interaction with the matrix, thereby decreasing the CTE value. In this study, mechanical methods were not used to mix the cellulose-based ABS composites, but rather a rudimentary method was used such as wooden stir sticks. The uniformity of the dispersion during this process is unknown and questionable in its dispersion homogeneity. Thus, we speculate that the dispersion of the MMCC within the ABS matrix governs the CTE trends observed for the cellulose-based composites. (Note that investigations to determine the nature of the dispensability of our cellulose fillers within ABS polymer network via mixing method used here are currently in progress.) Furthermore, the CTE value improves significantly for the 1:1 ratio of ABS to cellulose when compared to the neat ABS. Cellulose and wood pulp has been found to have a low CTE, as well as having the capabilities of reducing the CTE of composites [38–40]. The CTE for the cellulose in this paper needs to be determined for a conclusive answer but the large values and variations in the composites observed can be attributed to the possible heterogeneous mixture of the MMCC within the matrix. Additionally, the presence of moisture and thermal stresses play a vital role in the properties of these composites.

4. Conclusions

In this paper, we have found that extraction and drying procedures of cellulose have a dramatic effect on dispersion and thermal stability of polymer matrices. We have also discovered that polymer dissolution is a very useful technique for the improvement of cellulose filled ABS composites. With cellulose having an effect on the properties of ABS, T_g was not dramatically lowered, which is a great quality for manufacturing. Although the CTE does not have a distinct trend, the average minus the standard deviation (STD) for all samples falls below that which is reported.

Competing Interests

The authors declare that they have no competing interests.

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