

# Dispersion evaluation of microcrystalline cellulose/cellulose nanofibril-filled polypropylene composites using thermogravimetric analysis

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**Abstract** Microcrystalline cellulose-filled polypropylene (PP) composites and cellulose nanofiber-filled composites were prepared by melt blending. The compounded material was used to evaluate dispersion of cellulose fillers in the polypropylene matrix. Thermogravimetric analysis (TG) and mechanical testing were conducted on composites blended multiple times and the results were compared with single batch melt blended composites. The residual mass, tensile strength, and coefficient of variance values were used to evaluate dispersion of the microcrystalline cellulose fillers in the PP matrix. The potential of using TG to evaluate cellulose nanofiber-filled thermoplastic polymers was also investigated and it was found that the value and variability of residual mass after TG measurements can be a criterion for describing filler dispersion. A probabilistic approach is presented to evaluate the residual mass and tensile strength distribution, and the correlation between those two properties. Both the multiple melt blending and single batch composites manufactured with increased blending times showed improved filler dispersion in terms of variation and reliability of mechanical properties. The relationship between cellulose nanofiber loading and residual mass was in good agreement with the rule of mixtures. In this article, the authors propose to use a novel

method for dispersion evaluation of natural fillers in a polymer matrix using TG residual mass analysis. This method can be used along with other techniques such as scanning electron microscope (SEM), transmission electron microscope (TEM), and X-ray diffraction (XRD) for filler dispersion evaluation in thermoplastic composites.

**Keywords** Microcrystalline cellulose · Cellulose nanofiber · Thermogravimetric analysis · Probabilistic approach · Reliability

## Introduction

### Why cellulose?

Early research for thermoplastic nanocomposites focused on inorganic nano-scale fillers such as nanoclay, montmorillonite, silica and mica, but interest in cellulose nanofibril-filled nanocomposites has increased in recent years [1, 2]. Considerable research activity about cellulose nanofibrils has been reported recently [3–6] because their overall properties are comparable to other inorganic fillers [7] and natural filler reinforced composites have desirable mechanical properties [8]. Cellulose represents a renewable, enantiomeric, and polymeric material with special properties including biocompatibility, biodegradation, long-term durability, and extreme-resistant raw materials to wide variations in temperature [9]. Industrial uses of these natural fiber-reinforced plastic composites are increasing including the automotive industry, packaging, construction, and furniture production and those composites are of interest as a replacement for synthetic fiber reinforced plastics because of their relative low price and their potential to be recycled.

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## Polymer matrix

Generally, because of their relative high-strength, high stiffness, and low density, cellulose-based biofibers, including cotton, flax, hemp, jute, sisal, and wood fibers are used to reinforce plastics [10]. However, polymer matrices such as epoxy or polyester in their solid form are both expensive and brittle. Therefore, there is an increased need for developing polymer composite materials for global industrial needs for an economical substitute having properties similar to those composites. In recent years, polypropylene (PP) has been used as a matrix polymer for several applications because of its favorable properties such as low density and good weatherability, design flexibility, stiffness, mechanical and thermal properties. In the field of bio-based composite materials, it is a viable option to combine the favorable performance and low cost attributes of both natural fillers and thermoplastic polymers [11–16].

## Dispersion evaluation

The dispersion of fillers in a polymer matrix is an important factor affecting the properties of the composite system [17, 18]. Evaluating a methodology to easily assess nanofiller dispersion in polymers is an important issue in nanocomposites research but only microscopic techniques such as SEM, TEM, and AFM are typically used for dispersion evaluation of reinforced polymer composites [17, 18]. A need exists to investigate the dispersion of fillers in composites using various methods. To our knowledge, no previous study has described a statistical analysis evaluation method of describing filler dispersion in polymers using thermogravimetric analysis (TG). Statistical evaluations are important because of inherent property variability among composite test samples. Analyzing the probability of well-dispersed fillers in composite materials is necessary because of the variability in filler dispersion and distribution after melt blending in the composite mixture. Thus, for improving composite material blending processes in industry as well as on the laboratory scale, filler dispersion and distribution must be understood and statistically analyzed. The statistical analysis used generally depends on the usual distribution of the mean value. The Weibull distribution has a more reliable value than other distributions in composite material property evaluations [19] and it has been proven that the Weibull distribution function is a useful and versatile means of describing composite material properties because the probability density function of the Weibull distribution exhibits a wide variety of shapes. When the shape parameter  $\beta$  equals to 1, it becomes a two-parameter exponential distribution. When the shape parameter is near 3, the coefficient of skewness approaches

zero and the function is capable of approximating a normal distribution [20–22].

In this study, the novel method of describing the dispersion of fillers in microcrystalline cellulose-filled polypropylene composites was evaluated by means of TG. A combined analytical and experimental approach was developed to characterize the residual mass of the composites after TG measurements. A series of experimental tests of the composites was conducted, and a two-parameter Weibull distribution function was adopted to establish a probability density function for the residual mass and tensile strength of composites using the test data. This investigation enables us to better understand the relationship between filler dispersion and mechanical properties of the resulting composite materials.

## Experimental procedure

### Materials

#### *Matrix polymer*

The polypropylene used as the thermoplastic matrix polymer was supplied by Polystrand Co. in the form of pellets with a density of  $0.90 \text{ g cm}^{-3}$  and a melt flow index of  $35 \text{ g } 10 \text{ min}^{-1}$  (503 K/2,160 g). The commercial product name is FHR Polypropylene AP5135-HS and the pellets were stored in sealed packs.

#### *Reinforcing fillers*

The cellulose materials used as natural reinforcing fillers in the composites were microcrystalline cellulose (MCC) and cellulose nanofibers (CNF). The product name of the MCC was Sigmacell<sup>®</sup> Cellulose Type 50 supplied by Sigma-Aldrich Co. and the product name of the cellulose nanofiber was Arbocel Nano MF 40-10 supplied by J. Rettenmaier & Söhne GMBH Co., Germany. The MCC was stored in sealed containers after being oven dried for 24 h at  $103 \text{ }^\circ\text{C}$  and the cellulose nanofibers were stored in a refrigerator in sealed packs containing preservatives.

### Sample preparation

Prior to compounding the MCC was dried to a moisture content of  $<1\%$  using a forced air oven at  $373^\circ\text{K}$  for at least 24 h and then stored in sealed containers in an environmental chamber. The cellulose nanofibers were stored in sealed containers in a refrigerator prior to compounding. A Brabender Prep-mixer<sup>®</sup> equipped with a bowl mixer was employed to compound the MCC and cellulose nanofibers with the polypropylene. The process temperature and

torque changes were measured in real time. The sample preparation procedure consisted of three general processes, viz. melt blending, grinding, and injection molding. Compounding was performed at 463°K for various blending times with a screw speed of 60 rpm. The blended mixture was granulated using a lab scale grinder, and the ground particles were stored in sealed packs to avoid moisture infiltration after first being oven dried for at least 24 h at 463°K. A fixed level of filler loading (10 wt%) for MCC and seven levels of filler loading (1, 2, 3, 4, 6, 8, and 10 wt%) for cellulose nanofibers were used in the sample preparation. MCC was blended with PP for 10 min, ground and then marked as 1st blended pellets. Part of the 1st blended pellets were melt blended again for 10 min, ground and then marked as 2nd blended pellets. Part of the 2nd blended pellets were melt blended once again for 10 min, ground and then marked as 3rd blended pellets. Moreover, 10, 20, 30, and 40 min blended single batches were produced, ground and then marked as 10–40 min blended pellets, respectively. The samples used for the TG measurements were selected from the ground particles and the samples used for the tensile tests were injection molded at 519°K and an injection pressure of 17.25 MPa. The width, length, and depth of the tensile test samples were according to ASTM D 638-03 Type I. The test samples were conditioned before testing at 296 ± 2°K and 50 ± 5% RH for at least 40 h according to ASTM D 618-99.

Test methods

*Thermogravimetric analysis (TG)*

The TG measurements were carried out using 8–10 mg of the composite samples at a heating rate of 283°K min<sup>-1</sup> in an N<sub>2</sub> atmosphere using a Mettler Toledo TGA/SDTA851° analyzer. The TG was conducted with the compounds placed in a high-quality nitrogen (99.5% nitrogen, 0.5% oxygen content) atmosphere with a flow rate of 20 ml min<sup>-1</sup>, to avoid unwanted oxidation. Each sample was scanned over a temperature range from 298 to 1073°K. The samples used for the TG measurements were 20 individual samples randomly selected from the ground particles.

*Tensile properties*

Tensile tests were performed to examine static tensile strength and modulus of elasticity of the composite samples using the ASTM D638-03 standard, and the loading rate was kept constant at 5 mm min<sup>-1</sup> (0.2 in min<sup>-1</sup>). An extensometer was employed to determine elongation of the

samples. Tests were performed in an environmentally conditioned room maintained at 294.1 K (70 F) and 50% RH. A 4,448 N (1 kip) load cell attached to a servo-hydraulic universal testing machine (Instron 8872) was used to collect stress–strain data of the corresponding samples. Static tensile loads were applied to 12 replicate samples for each series of prepared samples and then average, standard deviation, and coefficient of variance were calculated.

Probabilistic analysis of residual mass and tensile strength data

*Two-parameter Weibull distribution*

In this study, the statistical analysis of residual mass results was investigated using a two-parameter Weibull distribution function which is characterized by a probability density function  $f(x)$  defined as follows [23]:

$$f(x) = \frac{\beta}{\alpha} \left(\frac{x}{\alpha}\right)^{\beta-1} e^{-\left(\frac{x}{\alpha}\right)^\beta} \tag{1}$$

where  $\alpha$  is the scale parameter that locates the residual mass distribution and  $\beta$  is the shape parameter which is the inverse measure of the dispersion in the results.

*Cumulative density function*

By integrating the probability density function  $f(x)$  in Eq. 1, the associated cumulative density function  $P_c(x)$  can be determined as

$$P_c(x) = \int f(x)dx = 1 - e^{-\left(\frac{x}{\alpha}\right)^\beta} \tag{2}$$

$$1 - P_c(x) = e^{-\left(\frac{x}{\alpha}\right)^\beta} \tag{3}$$

where  $P_c(x)$  is the probability and the Eq. 2 can be rewritten as Eq. 3. The values of  $\alpha$  and  $\beta$  are determined by taking the natural logarithm twice in each side of Eq. 3 as

$$\ln \left[ \ln \left( \frac{1}{1 - P_c(x)} \right) \right] = \beta \ln(x) - \beta \ln(\alpha) \tag{4}$$

Equation 4 can be considered as a linear function in the form of  $Y = BX + C$ . The two variables  $\alpha$  and  $\beta$  in Eq. 4 can be determined by linear regression analysis of the experimental data of residual mass and tensile stress,  $x$  and the median rank,  $P_c(x)$ . The median rank used in this study is given as

$$P_c(x) = \frac{i - 0.3}{k + 0.4} \tag{5}$$

where  $i$  is the serial number of data and  $k$  is the total test number of samples.

## Reliability

Probability of survival (reliability) in engineering refers to the probability that a composite sample will resist and maintain its structure under a given load. The probability of survival (reliability)  $P_s(x)$  and probability of failure  $P_f(x)$  can be described by combining Eqs. 3 and 5, and it results in an exponential function form of  $Y = e^{-X}$  as

$$P_s(x) = 1 - P_f(x) = 1 - \frac{i - 0.3}{k + 0.4} = e^{-\left(\frac{x}{\alpha}\right)^\beta} \quad (6)$$

where  $Y = 1 - \frac{i - 0.3}{k + 0.4}$  and  $X = \left(\frac{x}{\alpha}\right)^\beta$ . The diagrams of the probability of survival (reliability) are of considerable value to the designer where strength can be easily determined at any survival percent. For example, the 50% survival strength can be determined from the reliability diagrams by drawing a horizontal line that intersects with the curves. The strengths at the intersected points are the 50% survival stress levels. These values of survival strengths also can be determined from Eq. 6 and the values of  $\alpha$  and  $\beta$ .

## Results and discussion

If the filler is dispersed thoroughly, the individual TG results (residual mass) should exhibit little variation and this is an ideal boundary condition. Based on this concept, the authors developed a novel method for evaluating filler dispersion using thermogravimetric analysis.

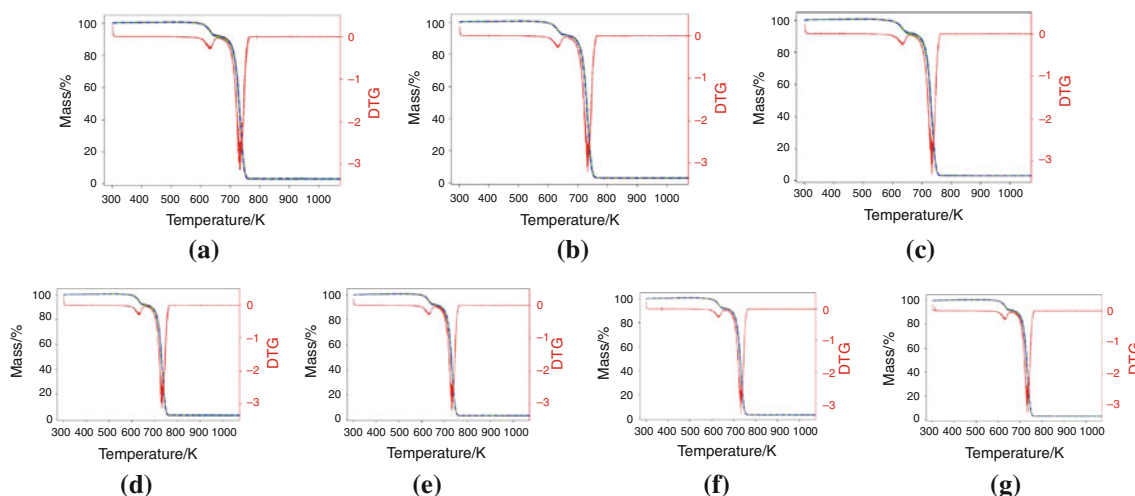
### Thermogravimetric analysis (TG)

A summary of individual TG curves of the MCC (10 wt%)-filled PP composites with different blending sequences and

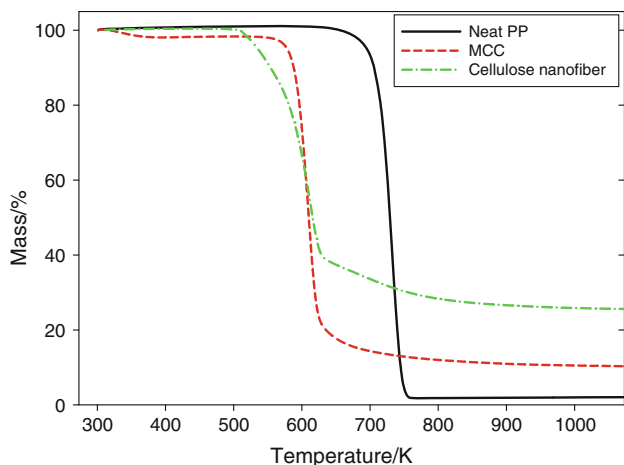
times is shown in Fig. 1. Generally, the curves exhibit two mass loss steps, an initial mass loss from 573 to 623°K, which is due to the decomposition of the cellulose which is chemically active and decomposes thermochemically in the range of between 548 and 623°K [13], and a second mass loss at approximately 723°K, which is due to the decomposition of the PP as shown in Fig. 2. From 773 to 1073°K, TG curves plateau and the mass percentage at 1073°K is defined as residual mass. The test results show that the residual mass value of the matrix polymer is negligible and the residual mass of MCC is more than 10%; therefore, the residual mass change is mainly attributed to the MCC content in the composite samples.

The residual mass value in each series of prepared samples from Fig. 1 appeared to be similar on the macro-scale, but the individual residual mass was different in a magnified scale. Figures 3 and 4 show that as the melt blending process sequences are increased from one to two and three times, the residual mass of the individual TG samples shows less variation from 5.08 to 3.14 and 1.81 of coefficient of variance (COV), respectively. As melt blending time increased from 10 to 40 min for the single batches, the results also show less variation from 5.08 to 1.86 of COV, respectively. The lower variability indicates that dispersion of filler in the matrix polymer was improved. The average, standard deviation, and COV from residual mass results are summarized in Fig. 4. It can be shown that as the melt blending process sequences and blending times increased, the standard deviation and COV of TG samples were significantly reduced.

The residual mass of the composites made using cellulose nanofiber as the reinforcing filler and PP as the matrix polymer at different filler loadings is shown in Fig. 5. As the filler loading increased, the residual mass of the



**Fig. 1** TG and DTG curves of 10 wt% MCC-filled polypropylene composites with different blending sequences and times. **a** 1st blended, **b** 2nd blended, **c** 3rd blended, **d** 10 min blended, **e** 20 min blended, **f** 30 min blended, **g** 40 min blended



**Fig. 2** TG curves of MCC, cellulose nanofiber and polypropylene

composites also increased, and residual mass data were in good agreement with the rule of mixtures. As can be seen in Fig. 2, the residual mass of cellulose nanofiber is two and a half times the residual mass of the MCC. These results suggest that the TG evaluation method is also

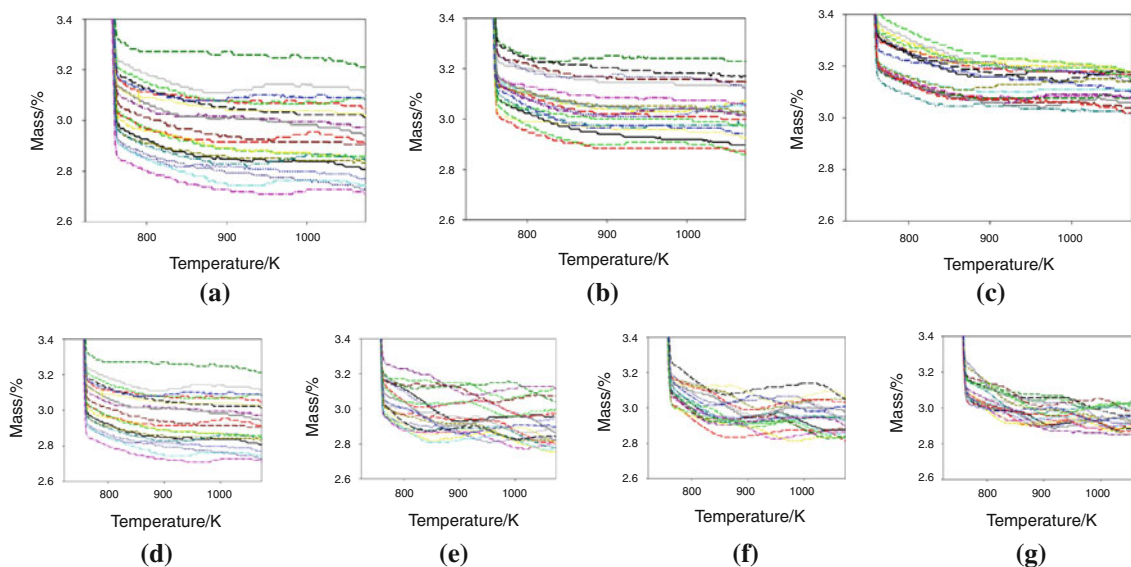
feasible for cellulose nanofiber-filled thermoplastic composite materials.

**Tensile strength**

The average tensile stress and standard deviation of the MCC-filled PP composites were evaluated, and the coefficient of variance of the tensile stress is also shown in Fig. 6 with different process sequences and blending times. There is almost no difference in terms of mean tensile stress value as the melt blending process sequences and times increased, but the variation of strength was significantly reduced. This result suggests that improved filler dispersion leads to better uniform stress transfer in the composite system and more consistent quality of the composite materials.

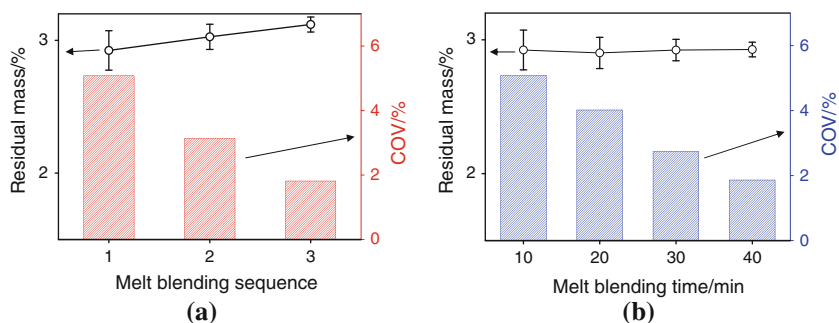
**Probabilistic analysis**

Because the test data of composite materials are scattered, a reliability analysis is necessary to better describe the test

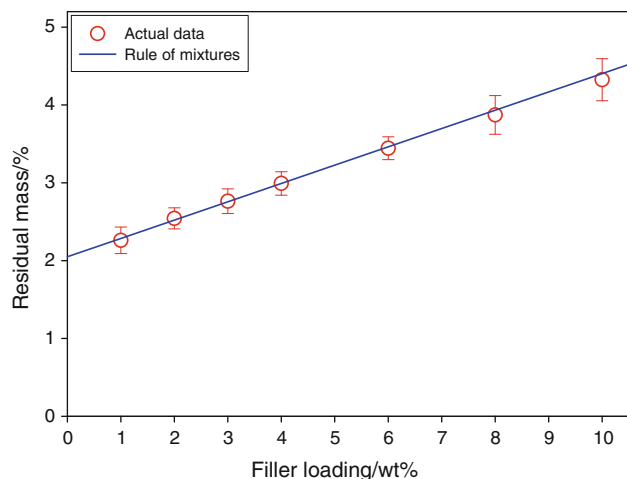


**Fig. 3** TG curves of 10 wt% MCC-filled polypropylene composites with different blending sequences and times (magnified view). **a** 1st blended, **b** 2nd blended, **c** 3rd blended, **d** 10 min blended, **e** 20 min blended, **f** 30 min blended, **g** 40 min blended

**Fig. 4** Average residual mass, standard deviation (line and symbol), and coefficient of variance (bar) of 10 wt% MCC-filled polypropylene composites with different blending sequences (a) and times (b)





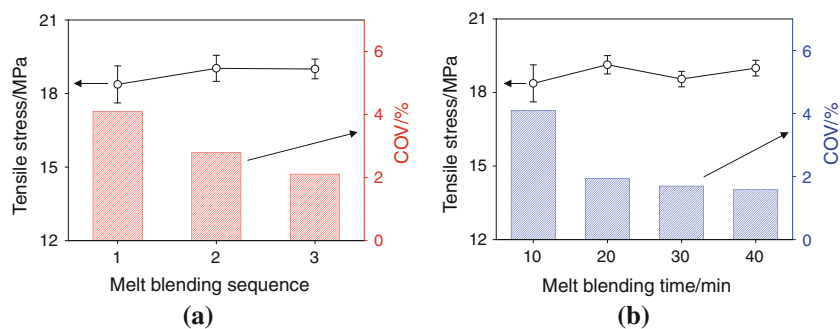


**Fig. 5** The residual mass of cellulose nanofiber-filled polypropylene composites with different filler loadings

results. Among the statistical analysis distributions, the Weibull distribution has more reliable values than other distributions in mechanical data evaluations [19]. In assessing the probability of survival (reliability), the two-parameter Weibull distribution is commonly used to represent mechanical data [22, 24]. A two-parameter Weibull distribution probability and cumulative density function for the test data are given in Eqs. 1 and 2. The experimental test results were used to determine the values of  $\alpha$  and  $\beta$  in Eq. 4 using a linear regression and these values are shown in Table 1.

The bounds with 95% confidence for the Weibull distribution parameters are shown in Figs. 7 and 8 for residual mass and tensile stress, respectively. As indicated in Figs. 7 and 8, the scattered data are well distributed within a 95% confidence range, therefore the test results could be analyzed using a Weibull distribution. Figure 9 shows probability density of residual mass results calculated by Eq. 1 with different process sequences and blending times. The area under each curve can be described as a cumulative density and always converges on 1. A sharp and high peak means that the results are more consistent and exhibit less variation. As can be inferred from Fig. 9, as the melt blending process sequences are increased from one to three

**Fig. 6** Average tensile stress, standard deviation (line and symbol), and coefficient of variance (bar) of 10 wt% MCC-filled polypropylene composites with different blending sequences (a) and times (b)

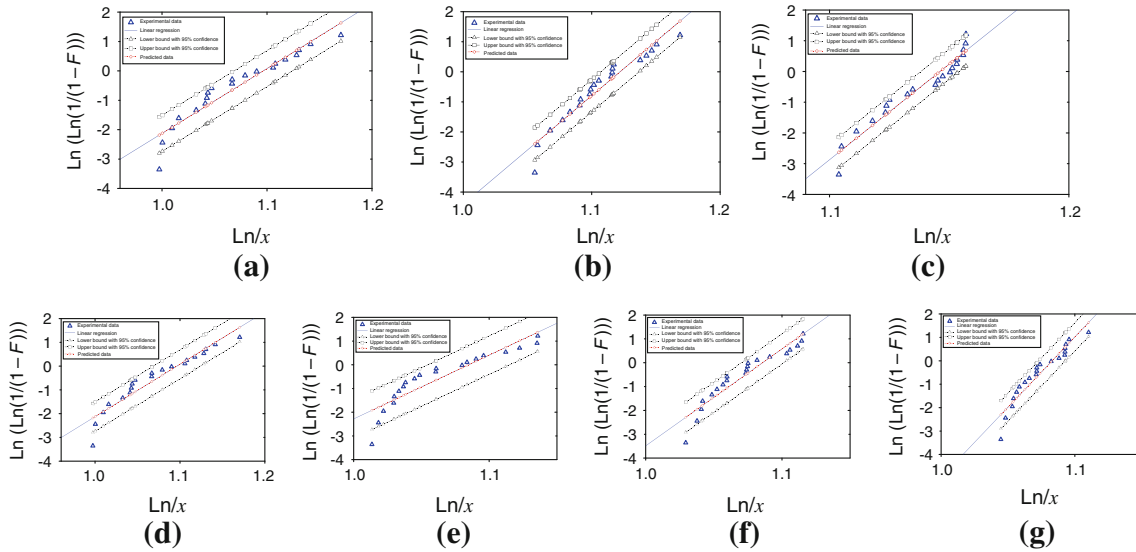


**Table 1** Weibull parameters of residual mass and tensile stress results

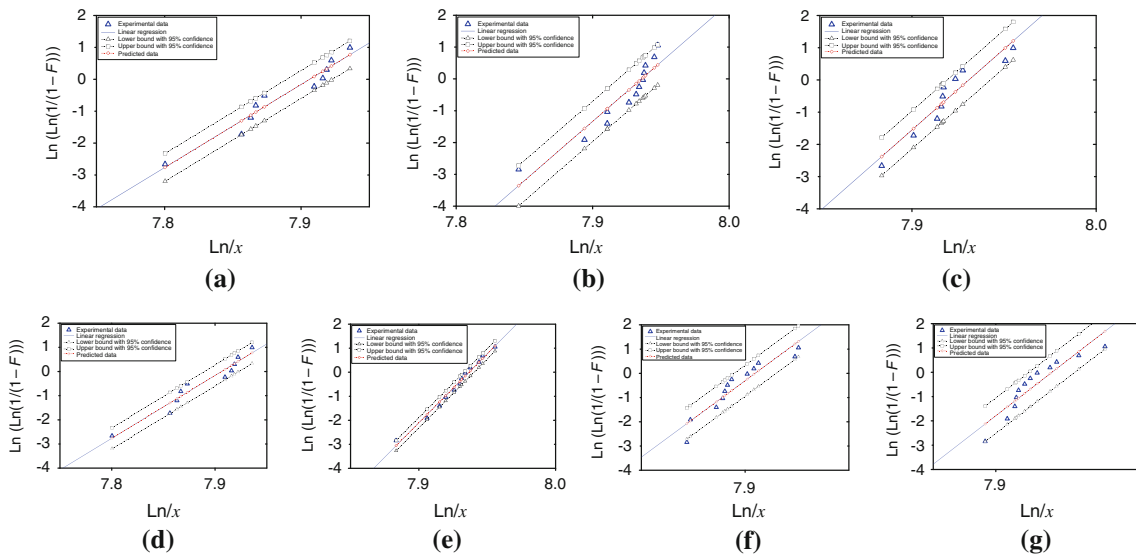
Test data	Sample preparation	Weibull Parameters	
		$\alpha$	$\beta$
Residual mass	1st blended	2.99	22.06
	2nd blended	3.07	36.08
	3rd blended	3.15	62.24
	10 min blended	2.99	22.06
	20 min blended	2.96	26.88
	30 min blended	2.96	40.63
	40 min blended	2.95	59.99
Tensile stress	1st blended	2714.2	26.06
	2nd blended	2795.8	37.27
	3rd blended	2782.0	50.29
	10 min blended	2714.2	26.06
	20 min blended	2797.9	57.39
	30 min blended	2710.4	63.06
	40 min blended	2771.0	66.37

times and melt blending times increased from 10 to 40 min, the residual mass of the individual TG samples shows less variation from 2.70 to 7.27 and from 2.70 to 7.47 of probability density, respectively. This result agrees with the results in Fig. 3 and suggests that the dispersion of filler in the matrix polymer was improved. Increasing the blending time with single batches might be recommended because there is no shift in average values.

The probability density and reliability versus tensile stress distribution for the 10 wt% MCC-filled polypropylene composites are shown in Fig. 10. In this figure, the tensile stress probability density and reliability of the composites were calculated using the Weibull function (see Eq. 6) and represented as distribution curves. As shown in Fig. 10c and d, under a given reliability, e.g., by drawing a horizontal line at reliability index of 0.9 that intersects with the curves which means 90% reliability, the increased melt blending process sequences and blending times, the higher tensile stress. This means that 90% of the material will survive under higher tensile stresses. Moreover, under a given survival strength, reliability can be determined from the diagrams by drawing a

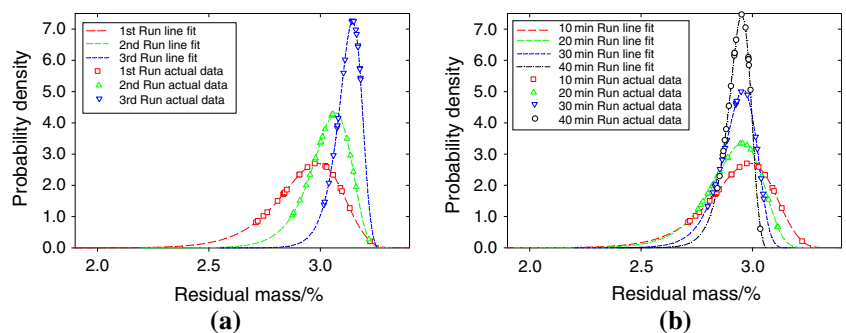


**Fig. 7** The bounds with 95% confidence for the Weibull distribution parameters (residual mass). **a** 1st blended, **b** 2nd blended, **c** 3rd blended, **d** 10 min blended, **e** 20 min blended, **f** 30 min blended, **g** 40 min blended

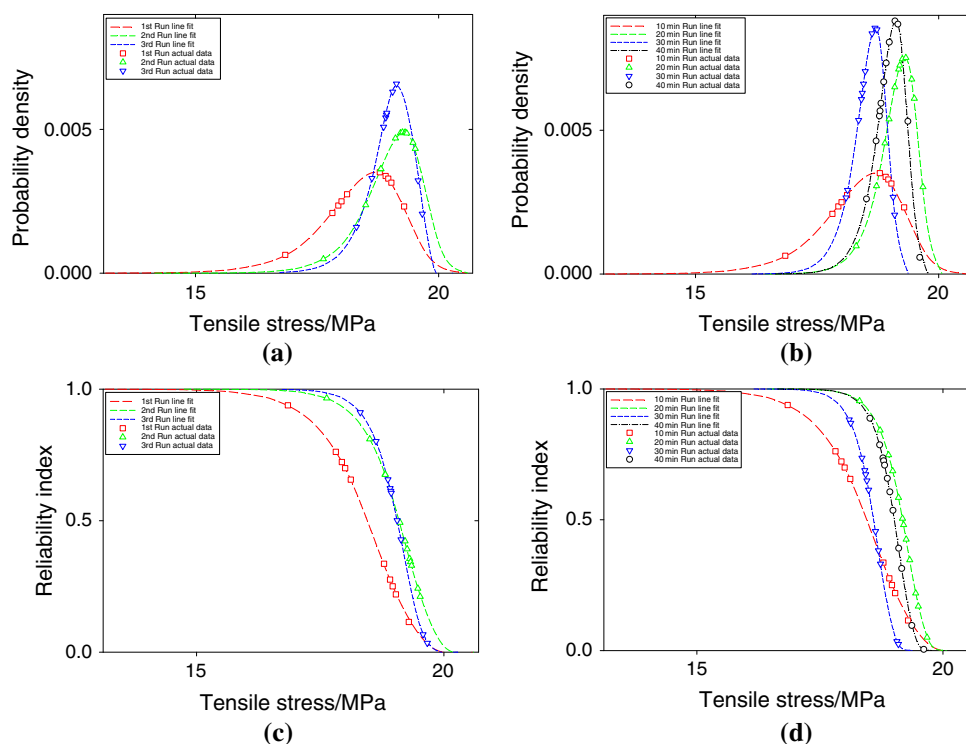


**Fig. 8** The bounds with 95% confidence for the Weibull distribution parameters (tensile stress). **a** 1st blended, **b** 2nd blended, **c** 3rd blended, **d** 10 min blended, **e** 20 min blended, **f** 30 min blended, **g** 40 min blended

**Fig. 9** Probability density of residual mass data with different process sequences **(a)** and blending times **(b)**



**Fig. 10** Probability density (a, b) and reliability (c, d) of tensile stress data with different process sequences (a, c) and blending times (b, d), respectively



vertical line that intersects with the curves. The values at the intersected points are the reliability index levels. The comparison between the increased process sequences and blending times indicates that the increased blending time with single batches exhibits good reliability distribution, which means more consistency in tensile strength. The probabilities of survival (reliability) plots are important to the structural designer because the allowable strength can be easily determined at any survival percentages.

## Conclusions

As the melt blending sequences and blending times are increased, the residual mass of the individual MCC-filled polypropylene composite samples showed less variation. This result suggests that dispersion of filler in the matrix polymer was improved. If the filler is dispersed thoroughly, the individual TG results should exhibit little variation and this is an ideal boundary condition. Based on this concept, a novel method for evaluating filler dispersion was developed using thermogravimetric analysis. The residual mass of cellulose nanofiber-filled PP composites increased as filler loading increased, and the result agrees with the rule of mixtures. This result suggests that the TG evaluation method is also feasible for cellulose nanofiber-filled thermoplastic composites. Improved filler dispersion leads to better uniform stress transfer in the composites and more consistent quality of the composite materials. From the

two-parameter Weibull distribution diagrams, it was found that there was no significant change in the mean tensile stress of the composites, however, when the process sequences and blending times increased, more consistent residual mass distributions and reliable tensile stress distributions are obtained because of improved filler dispersion. Based on these results, it can be concluded that reliabilities of mechanical performance of MCC-filled polypropylene composites were strongly influenced by filler dispersion.

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