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Quantitative Measurement of Cellulosic Filler Dispersion in Thermoplastic Composites

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An image analysis technique was employed to quantitatively measure cellulosic filler dispersion in linear low density polyethylene (LLDPE) polymer for the assessment of a high intensity shear compounding process in manufacturing wood-fiber thermoplastic composites. Graphic images of samples obtained with a confocal microscope were analyzed by assigning different colors to the pixels which had different laser intensities depending on different reflecting behavior. A mixing index based on the variance ratio of sample mixture to that of ideal mixture was successfully applied for the quantification of cellulosic filler dispersion in LLDPE resin. The quantified filler dispersion was not directly related to the mechanical properties. However, the addition of dispersing agent improved filler dispersion and, in some cases, increased the strength and modulus of composites.

Keywords: Cellulosic filler dispersion; Image analysis; Dispersing agent; LLDPE

INTRODUCTION

As the use of thermoplastic polymer is increasing, considerable efforts have been made to find suitable low cost and reinforcing fillers. Among organic fillers, cellulosic materials were considered attractive alternates for reinforcing fillers in thermoplastics although mineral fillers such as talc, asbestos and mica have been used in the past. The use of cellulosic

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filler in thermoplastics is highly beneficial because of low cost, large availability, renewability, and high strength/weight efficiency. As a result, cellulosic filler incorporated thermoplastics have received much attention in extending thermoplastic resins such as polypropylene (PP), high density polyethylene (HDPE), polystyrene (PS) and polyvinylchloride (PVC) [1–4].

The use of reinforcing fillers enhances certain mechanical properties and reduces material cost. With the addition of filler, stiffness and strength of the composites, in general, are significantly improved. The development of cellulosic filler/thermoplastic composites is encouraged by the fact that they had several advantages over inorganic fillers [2]. These include; low hardness that minimizes abrasion of the equipment during processing, relatively low density, biodegradability, and low cost per unit volume basis. In particular, wood-fiber thermoplastic composites are fascinating for low cost/high volume applications. Potential applications of the composites are furniture components, door moldings, floor system for light-frame construction, and packaging pallets. A major current application is for the interior panels of automobiles.

Cellulosic fillers are being combined with thermoplastics in melt-blending processes. In this process, cellulosic fillers or wood-fibers are blended with the melted thermoplastics by shearing or kneading. Prior to the fabrication of composites, thermoplastic resin must be mixed with cellulosic fillers through a compounding process. It usually requires 1) a physical change in the components, 2) high shear forces to bring about the change, and 3) the polymer to be in the molten or rubbery state during mixing [5]. In particular, the dispersion of filler materials into thermoplastics, either to improve the mechanical properties of the polymer or to reduce the price per volume, is one of the most elementary situation in mixing process [6].

The purpose of mixing is to attain an acceptable degree of homogeneity or uniformity of composition and to some extent of the morphological structure of the mixture. A mixture is simply defined as a combination of two or more ingredients. We all have intuitive understanding of the difference between good mixing and bad mixing, but in practice it is quite difficult to quantify the measurement of mixing. Depending on the nature of the polymer form, the shaping process, and machinery used, there are two basic mixing functions; 'extensive or distributive mixing or blending', and 'intensive or dispersive mixing or compounding' [7].

Distributive mixing consists essentially of repeating the rearrangement of the minor component. Often this is termed as simple mixing. Dispersive mixing involves the more intimate dispersion of the additives into the matrix of the polymer.

Before assessing homogeneity of mixtures quantitatively, it is necessary to define the state of the mixtures. In other words, it is needed to answer what mixedness is and how a mixture is assessed. A complete characterization of the state of a mixture would require the specification of the size, shape, orientation, and spatial location of every particle of the minor component. However, in practice, such a complete characterization of the state of the mixture is not needed and simple methods often suffice. The state of the mixture can be characterized by gross uniformity, texture, and local structure [7]. The gross uniformity is a quantitative measure that characterizes the goodness of distribution of the minor component throughout the object or system analyzed. The perfect admixture might be defined as a state in which no variations in combination or morphology are observed at the relevant closedness or intensity of examination [8].

Assessment of the state of admixture of a composition depends on the closedness of the examination. The 'scale of scrutiny' defined as the minimum size of the regions of segregation that would cause the mixture to be imperfect for the intended purpose was introduced by Danckwert [9]. It should include several particles of a component. So, it is clear that the more closely a mixture is scrutinized, i.e. the smaller the scale of scrutiny, the more likely it is to appear inhomogeneous or non-uniform. Furthermore, Tadmor and Gogos [7] pointed out that testing samples should be small enough compared to the scale at which those are being examined for uniformity and large enough compared to the size of the ultimate particle. The state of admixture depends not only on the scale of scrutiny but also on the sampling procedure [8].

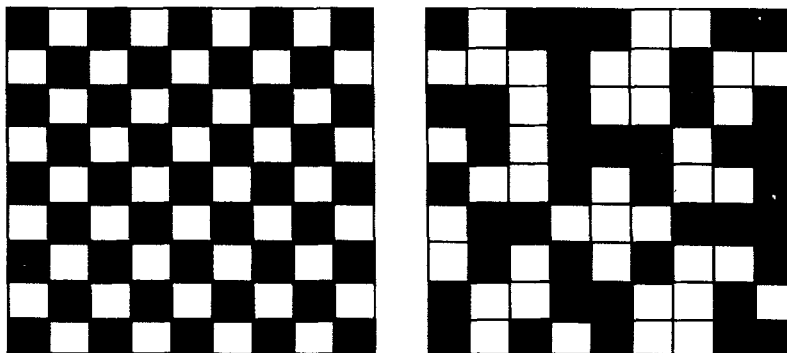
Dividing the two-component mixture into a number of portions and examining the portions separately introduces the possibility that their compositions will be found to differ from the overall composition. If the portions are large relative to the size of the elements of the composition, i.e. each portion contains a substantial number of these elements, the analytical results will reveal a distribution about a mean equivalent to the overall composition. A perfect uniformity is obtained when there is a uniform concentration of the minor component in all testing samples

taken from a specific system. Figure 1 (a) shows the perfect mixture, i.e. where every portion yields which will never be attained. The best that can usually be expected is a statistically random distribution (Fig. 1) (b), and a mixture with such a distribution may be regarded as an ideal or perfect mixture [8]. In general, accuracy of assessment of the state of admixture is improved by increasing the number and decreasing the size of samples.

A number of different approaches as to how to quantify the analyses of a number of samples taken from a mixture have been introduced, all essentially based on statistical and probability concepts. The aim of a statistical analysis of a mixture is usually to allocate a value to a 'degree of mixing' that will define numerically the state of admixture of a composition. In practice, an ideal mixture is defined as the completely random state.

Consider a mixture system of a minor component of uniform size in a major component, which can be solid or liquid. Statistically, a random mixture follows the binomial distribution function. If p is the volume fraction of minor component, and n is the number of particles taken from a binary mixture one at a time, and each was replaced before the next was taken, the probability, p , that the fraction of sample would be of k minor particles is given by:

$$p(k,n) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k} \quad (1)$$



(a) Perfect mixture

(b) Random mixture

FIGURE 1 The perfect (a) and random mixture (b) of a binary mixture.

The above equation shows that the distribution of the minor component in the samples depends both on the average concentration of the minor component, p and on the size of sample, n . The variance of the binomial distribution is given by:

$$\sigma^2 = \frac{p(1-p)}{n} \quad (2)$$

Numerous mixing indices were defined for evaluating the state of mixing [8]. These are indices that relate representative statistical parameters of the samples, such as the variance and mean to the corresponding parameters of the binomial distribution. Tucker and Suh [10] used the ratio of the variance for the sample mixture (s^2) to the variance of a random mixture (σ_r^2):

$$M = \frac{s^2}{\sigma_r^2} \quad (3)$$

which has the advantage that it provides a sensible numerical value for states of admixture that are more uniform than random. If the mixture is worse than random $M > 1$, if it is random $M = 1$, and if it is more uniform than random $M < 1$. For a uniform or perfect mixture, $M = 0$. This mixing index (M) was employed to evaluate the dispersion of cellulosic filler in thermoplastic composites compounded by the Gelimat mixer with LLDPE resin.

So far, most of the studies on cellulosic fiber dispersion in thermoplastics have used light or scanning electron microscopy. [1, 11–12] The SEM observation can be of use for assessing mixture homogeneity in a qualitative way which might cause misleading. The weakness of these techniques is that it is difficult to quantitatively analyze the images. This is due to the fact that the image is an overlap of images from different layers throughout the depth of the sample.

This difficulty can be evaded using a confocal microscope. The key feature of the confocal imaging is that only what is in focus is analyzed. The images are not affected by light from areas outside the region of interest. The confocal microscope builds up its image by scanning a beam over the specimen surface. The illumination and detection are

confined to the same spot in the specimen at any one time so that position above and below the focal plane are excluded by virtue of an aperture. Thus, a confocal imaging system was used to obtain the mixing index which was the parameter to quantitatively measure the cellulosic filler dispersion based on mixture homogeneity.

The procedure of image analysis consists of obtaining a section, acquiring a digital image of the section, and analyzing the image. A digital image is a way of storing pictorial information in a computer. The picture is divided up into a large number of small areas, called pixels. For each pixel, the intensity of light is measured and recorded. The most common way to acquire a digital image is with a video camera. An alternative to the video camera is laser line scanning, which was employed in this study. In this technique, a low-power laser beam is focused on the surface of the section and intensity of the reflected light is measured by a photodiode. By scanning the beam over the section and taking periodic intensity readings of the reflected light, one builds up a digital image of the section. To analyze the mixture, the intensity at each pixel must be related to the composition of the mixture at that point. This can be done when different colors are being mixed together. The intensities are proportional to the compositions at each pixel. The image is analyzed by making each pixel either all dark or all light that is known as 'thresholding' operation [6].

There are wide varieties of mixing tasks and available mixing equipments, which also affect the mixing quality of products. For the compounding of cellulosic filler with thermoplastics, one of the promising processes is high intensive shear mixing using the Gelimat mixer, or K-mixer. The Gelimat mixer is being used for compounding of cellulosic fillers (e.g., wood-fiber or flour) with thermoplastics such as HDPE, PP and PS. The main advantages of the mixer are short residence time, low energy consumption and residual moisture flash off from partly dry fibers [12]. This process was reported to be effective for the compounding of recycled newsprint fibers with PP [13]. However, this evaluation was made by measuring the mechanical properties of the composites, not the fiber dispersion. There is a need to measure cellulosic filler dispersion for better understanding of compounding process in the Gelimat mixer. Thus, this study was carried out to quantitatively measure a cellulosic filler dispersion in linear low density polyethylene (LLDPE) resin.

MATERIALS

Sawdust was used as cellulosic filler for compounding with LLDPE resin and manufacture of the composites, and oven-dried to a moisture content of less than 10%. Long flakes in the sawdust were removed using a 5 mm screen. For the preparation of composites, a LLDPE (density, 0.926 g/cm³; melt flow index, 50g/10 min.) in powder form with no additives was provided by Esso Chemical Inc., Canada. The dispersing agent employed was Epolene C-16 (density; 0.934 g/cm³, approximate molecular weight; 4500, and acid no. 47), which can aid fiber dispersion in the matrix resin and was provided by Eastman Chemical Products Inc. The dispersing agent is a low molecular weight polyethylene with terminal anhydride end groups. Epolene C-16 was added to the composites during the compounding process in the Gelimat mixer (Werner and Pfleiderer Gelimat G-1), which is a high shear kinetic turbine mixer.

EXPERIMENTAL METHODS

A schematic diagram of the Gelimat mixer is given in Figure 2. The raw materials in the hopper is fed to the mixing chamber in which the materials are compounded by friction heat induced by the rotor-blade with various adjustable speeds (e.g., 3,300 rpm). The compounded material is discharged automatically at the pre-set temperature which is detected by optical fiber and controlled by an adjustable control unit.

Sawdust particles were first pre-coated with a dispersing agent, Epolene C-16 wax (5% relative weight of sawdust) in the mixer for 1.5 minutes. The matrix resin was compounded in the turbine mixer (running at the tip speed of 3,300 rpm), and automatically discharged at the pre-set temperature of 190 °C. The hot melt mess was cooled and subsequently granulated and then injection molded. The compounded and granulated products from the Gelimat mixer were injection-molded using an Engel ES-28 machine equipped with a standard ASTM test specimen mold. The molded test specimens were conditioned at room temperature for two days prior to testing. The mechanical properties were measured according to ASTM standard procedures: tensile properties (D 638); flexural properties (D 790). All properties were measured using the computerized testing machine. All properties were

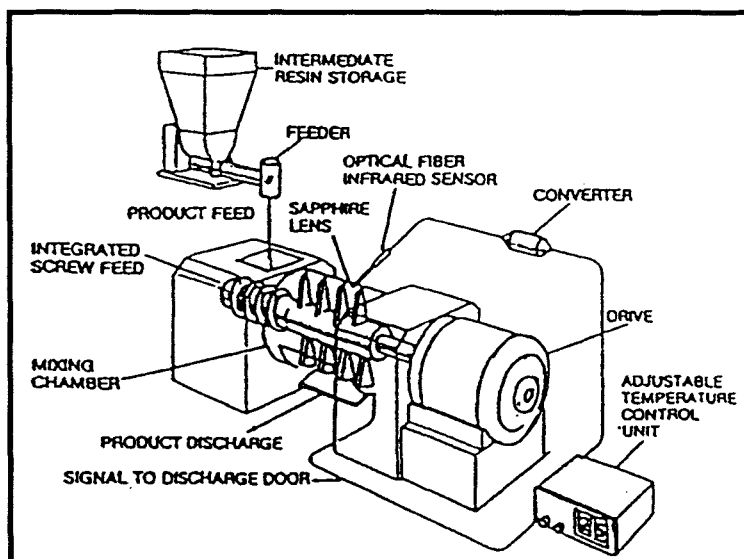


FIGURE 2 A schematic diagram of the Gelimat mixer.

measured at room temperature with six replications; the mean values are presented.

IMAGE ANALYSIS

The compounds discharged from the mixer was used for the preparation of specimens. A number of small blocks of the compounds were used to cut a 20 μm thick section with a sliding microtome. These thin sections were stained with safranin to identify lignocellulosic components in specimens and then mounted on slide glass. The prepared specimens were used for quantitative assessment of the filler dispersion by Confocal Imaging System (MRC-600) installed at the Ontario Laser and Light-wave Research Centre (LLRC) in the University of Toronto. The image analysis system used consisted of a color video camera, microcomputer with color monitor, and image analysis software.

Images obtained by scanning specimen surface with laser were captured by video camera, stored on the computer's hard drive and analysed

using the image analysis software. The analysis was performed on the formulations of the Gelimat mixing. Since the sample was opaque, a reflective mode which can cause different reflecting behaviors of laser depending on materials was chosen for the study. The objective lens used had a 5 X magnification which corresponds to a numerical aperture of 0.12. With this numerical aperture of the lense, the depth of focus falls to the 4 mm² level which can cover relatively large sawdust particles in the analysis area.

Two colors observed in the confocal photographs were obtained by assigning these colors to the pixels which have different laser intensities depending on different reflecting behavior. The whole laser intensities were ranged from 0 to 255. Figure 3 shows confocal micrographs (a) before and (b) after the color assignment to pixels. Sawdust particles, being more reflective, appear as the bright region under the microscope before color assignment were assigned to red color that had laser intensities ranged from 20 to 255. The matrix polymer was assigned to blue color that has laser intensities ranged from 0 to 19. The relative contrast of the two phases was determined by the gain level, black level and the aperture size of the confocal microscope. The aperture size controls the total amount of light reaching the detector and would remain fixed throughout the experiments.

The gain level is used to amplify the pixel intensity; the black level, on the other hand, assigns the out of focus region to be blue. These parameters ensure the best contrast between the red and blue region to be obtained. It was assumed that the average volume fraction of the sawdust particles examined fixed at 30% in the overall mixture. Consequently, the gain level and the black level for analysis area at each location were adjusted such that the red and blue regions were set to a 30 to 70 ratio. The volume fraction of sawdust was determined from the number of red pixels versus the number of blue pixels in areas selected randomly throughout the sample. At each location, the sample variance was obtained and divided by ideal variance to get a variance ratio (i.e. mixing index) for the comparison. The analyses were repeated with fifteen locations in the sample and the average values are presented.



FIGURE 3 Confocal micrographs of samples (a) before and (b) after color assignment.

RESULTS AND DISCUSSION

The first step in quantitatively assessing the homogeneity of mixture is to define the state of mixture. The variance for the ideal random mixture was calculated according to the variance of binomial distribution expressed as $\sigma^2 = p(1-p)/n$, where p is the volume fraction of sawdust, and n is the number of wood particles in the mixture taken within each sample analysis area. The number of particle, n , in an analysis area was calculated using the Hatch-Choate transformation equation [15]. For this calculation, it is assumed that the surface mean diameter (d_s) is equal to the projected area diameter (d_a). Then the transformation equation was used to get the projected area diameter. The n was obtained dividing the analysis area by the projected area of one particle. The following is the procedures and a sample calculation of the variance for ideal random mixture.

The particle size of feed sawdust was obtained by dry sieving 30 g of sample for 15 minutes using Ro-Tap Shaker. Sieve data were obtained by weighing the appropriate sieve trays before and after sieving. Then, the data were plotted on a log-normal probability paper to get the particle size distribution. Figure 4 shows the result of the particle size distribution. As shown, the distribution curve was quite a straight line that can be obtained the log-normal distribution law. Therefore, the Hatch-Choate equation was used to transform geometric median diameter by weight (d_{gm}) to surface mean diameter (d_s) by an equation¹⁵;

$$\log d_s = \log d_{gm} - 4.605 \log^2 \sigma_j \quad (4)$$

For the feed sawdust used, the geometric diameter by weight is 700 μm , and the standard deviation (σ_j) is 2 based on log-normal law which is expressed as $\sigma_j = \sqrt{x_{84}/x_{16}}$. Solving Eq. (4) gives the surface mean diameter of 267.8 μm . Then, it is assumed that the surface mean diameter is equal to the projected area diameter. The use of projected area diameter gives the projected area (A_p) of sawdust particles (i.e., $A_p = \pi/4 d_s^2 = 56322.8 \mu\text{m}^2$).

For an analysis area of 4014489.6 μm^2 (i.e., about 4.01 mm^2), the number of particles is equal to the analysis area divided by the projected area of sawdust particles, which is 71.3 for this case. Since the volume fraction of sawdust (30% by weight) is 0.22, the number of sawdust

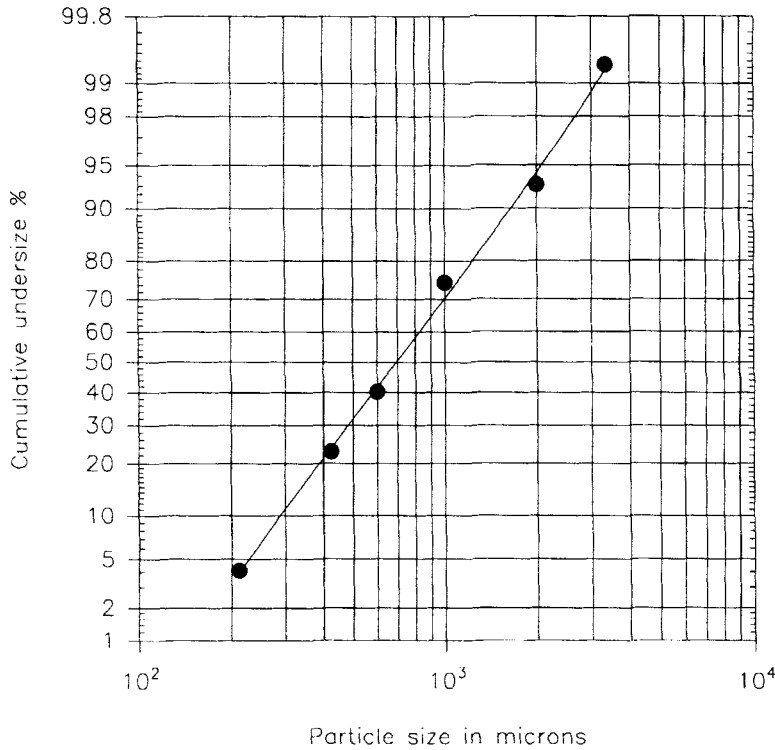


FIGURE 4 The particle size distribution of sawdust in log-normal paper.

particles is equal to 71.3×0.22 , i.e., 15.7. The variance of an ideal random mixture is calculated using the binomial function (i.e., Eq. (3); $\sigma^2 = p(1-p)/n = 0.22(1-0.22)/15.7 = 0.0109$ where p is the volume fraction of sawdust in composites. The sawdust volume fraction (V_p) was calculated using the densities of sawdust (ρ_p) and LLDPE (ρ_m) as 1.4 g/cm³ and 0.926 g/cm³, respectively, and was given by weight basis:

$$V_p = \frac{W_p/\rho_p}{W_p/\rho_p + (1 - W_p)/\rho_m} \quad (5)$$

The variance of other analysis areas can be obtained by the same way used.

The experimental mixtures were first tested for randomness by comparing the sample variances evaluated at fifteen locations on the sample

surface with the variance of an ideal random mixture. Figure 5 shows the variance ratio of both random and sample as a function of analysis area. The variance ratio decreased with increasing the analysis area under the microscope and then stabilized above the analysis area of 4 mm^2 . Moreover, this result suggest that the variance of experimental mixture obeys the binomial distribution above the analysis area of 4 mm^2 . Therefore, the analysis area for sawdust particles was fixed as 4 mm^2 . The analysis area should be large enough to cover particles under examination. Certainly, the size of analysis area depends on material being examined. For example, an analysis area was chosen as 1.07 mm^2 for submicron size ceramic particles, which gave a satisfactory assessment of filler homogeneity [16]. Based on the Eq. (3), the variance ratio

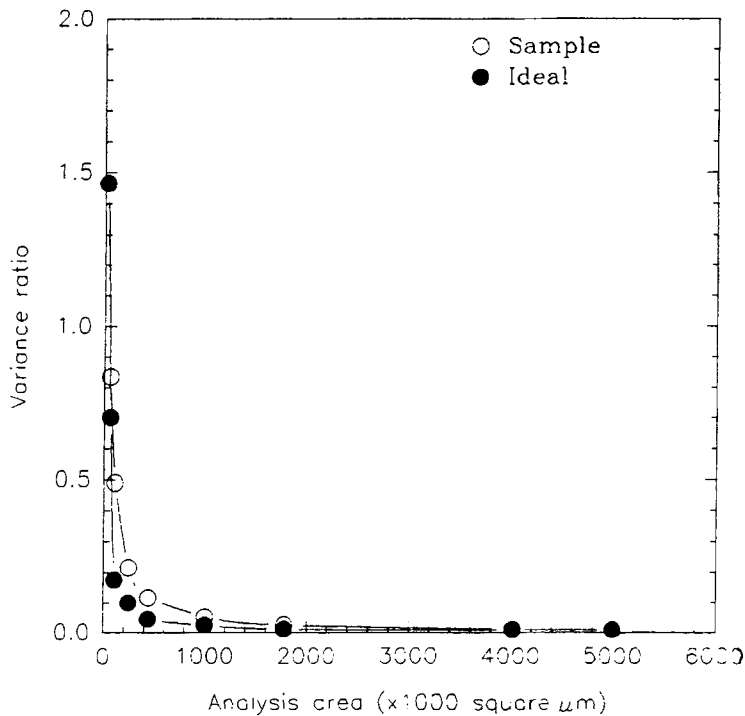


FIGURE 5 Variance ratio of actual and ideal mixture versus analysis area adjusted by zoom factor.

of the sample variance (S^2) to the random variance (σ_r^2) was used as a mixing index (M) for comparison.

As mentioned earlier, the mixture is worse than random if the mixing index is higher than 1 while the mixture is random if the mixing index is less than 1. If the mixing index is equal to 1, the mixture is random. The variance ratios of all samples are greater than those of random mixtures. In other words, the dispersion of sample is worse than random. The mixing indices of sample mixtures prepared by compounding without and with dispersing agent were obtained. The variance ratio for samples without dispersing agent was 1.55 which was greater than 1. On the other hand, treated samples with dispersing agent gave a variance ratio of 0.97 which is less than 1. The result indicated that treated mixtures with dispersing agent are better, and non-treated mixture are worse than random, respectively. This might be attributed to the action of dispersing agent during compounding process. That is to say, the dispersing agent can facilitate the filler dispersion during compounding by wetting the surface of sawdust particles. Another physical phenomena is the fact that sawdust particles are broken down into small sizes in the Gelimat mixer compounds.

Figures 6 and 7 show the mechanical properties of composites prepared by the compounding in the Gelimat mixer. Tensile and flexural strengths of the composites are shown in Figure 6. Sawdust filled composites show higher flexural strength than that of pure LLDPE polymer. This is due to sawdust particles acting as a reinforcing filler in LLDPE. The figure also shows that flexural strength is larger than tensile strength. This larger flexural strength might be attributed to the orientation of sawdust particles in the skin of injection molded samples. It is known that the fibers in the skin of sample are tending to have orientation parallel to mold flow direction during injection molding process [2]. Furthermore, wood-fiber orientation in PP resin was observed by light microscope [17]. The flexural strength further increased with the addition of dispersing agent during compounding in the mixer. This might be due to two possible reasons; i) better dispersion of sawdust particles in matrix resin as indicated by the mixing index, and ii) improved the interfacial adhesion between wood particles and matrix resin.

However, the tensile strength of composites slightly decreased when sawdust was added without dispersing agent whereas it showed small

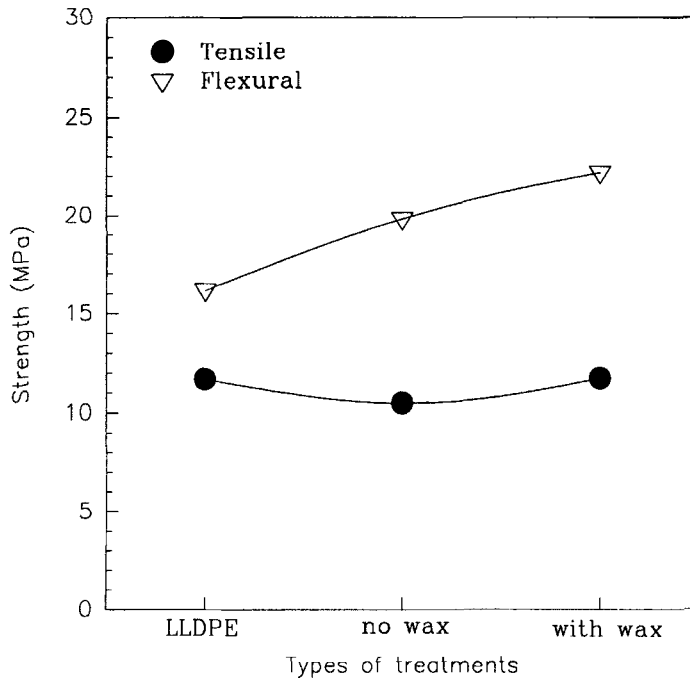


FIGURE 6 Tensile and flexural strength of the composites compounded by the Gelimat mixer without and with wax treatments.

increase with the use of dispersing agent in the compounding process. Slight decrease in tensile strength might be due to increased inhomogeneity by sawdust addition into LLDPE resin. Another probable reason might be the lack of adhesion between sawdust particles and LLDPE resin. In other words, the dispersing agent facilitates the filler dispersion only, not the interfacial adhesion which has significant influence to tensile strength of short fiber reinforced composites [18].

Tensile and flexural moduli of composites are shown in Figure 7. The addition of sawdust provided reinforcement with matrix polymer, leading to increased stiffness of composites. As in strength properties, flexural modulus also showed larger value than that of tensile modulus. This might be ascribed to the orientation of sawdust particles in the skin of injection molded samples. The stiffness in flexural and tensile tests further increased with the addition of dispersing agent. As mentioned

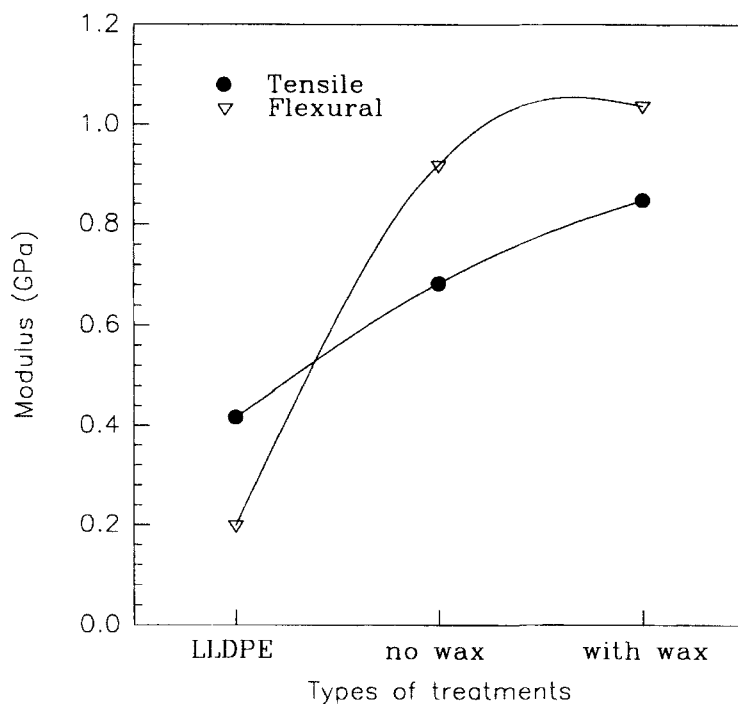


FIGURE 7 Tensile and flexural modulus of the composites compounded by the Gelimat mixer without and with dispersing agent.

earlier, the filler dispersion was improved with dispersing agent. Thus, this increased filler dispersion possibly influences the modulus of composite.

The results in this study indicated that mechanical properties of the composite are not directly related to the filler dispersion but rather combinations with other factors such as interfacial adhesion, fiber aspect ratio, etc. In fact, it was already reported that the aspect ratio of wood-fibers greatly reduced during compounding in the Gelimat mixer [19]. Nevertheless, when the dispersing agent was added, the filler dispersion was improved and the strength and modulus of composites were increased. However, overall properties of sawdust LLDPE composites were fairly low compared to those of HDPE-, or PP- based composites. In this study, a LLDPE with high melt flow index was used just for the quantification of cellulosic filler dispersion. In consideration

of the practical application of wood-fiber/thermoplastic composites, it is expected to work on HDPE or PP resin filled with wood-fibers in the future.

CONCLUSIONS

Cellulosic filler dispersion was successfully quantified with an aid of imaging analysis technique with the aid of confocal microscope. The variance ratio of the sample mixture to ideal mixture was used as mixing index for comparison. Based on the comparison of mixing index of various mixtures, the filler dispersion in matrix resin was found to be better than random for the Gelimat mixer compounding aided with dispersing agent. The filler dispersion was worse without the addition of a dispersing agent. The mechanical properties (strength and modulus) of sawdust/LLDPE composites compounded by the mixer were not directly related to filler dispersion. When added dispersing agent, filler dispersion was improved, and hence those properties were increased. Overall properties were relatively low compared with HDPE- or PP-based composites.

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