Dispersion Characterization of Nanoclay in Molded Epoxy Disks by Combined Image Analysis and Wavelength Dispersive Spectrometry

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1 Introduction

Polymeric composites containing nanoscale constituents, such as nanotubes or nanoclays, are receiving considerable research interest due to the possibility of achieving superior thermomechanical properties. The properties of polymers as well as conventional composite materials are likely to be improved by the addition of nanoparticulates into the host matrix, even in minor amounts [1]. Among the nanosized particulates, nanoclay is used at various consumer products, owing to its low cost and accessibility. A series of pioneering research conducted at the Toyota Research Labs. Inc. [2–4] presented the advantages and utility of nanoclay reinforced composites. The originally organophobich gallery region of the clay layers was modified by Usuki et al. [2] by a cation exchange reaction. Through this reaction, the sodium ions between the layers were replaced with ammonium cations of \( \omega \)-amino acids, \( [\text{H}_2\text{N}^+(\text{CH}_2)_m\text{COOH}] \). The cation exchange reaction was carried out for different carbon numbers of \( \omega \)-amino acid, \( n \). The gallery spacing was measured with X-ray diffraction (XRD) and transmission electron microscopy (TEM) for each of the carbon numbers investigated. As the carbon number was increased from 2 to 18, the basal spacing between clay platelets was reported to increase 122%, from 1.27 nm to 2.82 nm [2]. This increase made intercalation of polymers between the platelets possible. Later, cation exchanged nanoclay (\( n=12 \)) was used as an additive in polymerizing \( \varepsilon \)-caprolactam, the monomer for nylon 6 [3]. Upon polymerization, XRD and TEM analyses revealed an additional 88% increase in the gallery spacing from the initial value of 1.7 nm. This additional increase was attributed to the swelling of \( \varepsilon \)-caprolactam during polymerization. Kojima et al. [4] tested various mechanical properties of intercalated nanocomposites. Despite a slight decrease in impact resistance, tensile and flexural properties improved by as much as 122% over the pristine nylon 6 with the addition of only 4.7 wt % nanoclay.

In addition to viscoelastic [5–7] and barrier [8] properties of nanoclay composites, researchers often focused on the potential improvement in thermomechanical properties [9–17]. An early study on polymeric nanoclay composites was conducted by Lan and Pinnavaia [9]. The authors prepared nanoclay from \( \text{Na}^+ \)-montmorillonite by an ion exchange reaction with alkylammonium chloride and bromide salts. The modified nanoclay was then mixed with EPON 828 epoxy resin at loadings ranging from 2 wt % to 23.2 wt %. XRD patterns indicated that nanoclay was fully exfoliated in the matrix. Consequently, 18- and 12-fold improvements in tensile strength and stiffness were reported, respectively, at the maximum loading of 23.2 wt %. However, the choice of poly(ether amide) as the curing agent resulted in subambient glass transition temperature for the epoxy matrix. Thus, the reported improvements in mechanical properties were with respect to the rubbery state properties. The improvements in thermomechanical properties were marginal for epoxy resin, which was glassy at room temperature [9].

Wang et al. [11], on the other hand, mixed three commercially

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available nanoclay types, Cloisite® 20A, Cloisite® 30A, and Nanomer® I.30TC, with various types of thermoplastic polymers. Having the evidence of increased spacing by XRD analysis, samples were subjected to mechanical tests. While the addition of nanoclay to polystyrene improved the elastic modulus by as much as 168%, the tensile and impact strengths were observed to deteriorate by as much as 39% and 87%, respectively. Abot et al. [12] observed a similar behavior for nanoclay reinforced epoxy. The modulus of the molded samples increased by 31%, whereas the tensile strength decreased by 28% for 20 wt % nanoclay loading. In addition, the glass transition temperature decreased as much as 28% over the range of nanoclay loadings.

The large variations observed in the improvements of thermomechanical properties are often attributed to inadequate dispersion of the nanoclay particles in the host matrix. Nevertheless, compared to postdispersion changes in mechanical and rheological properties, characterization of nanoclay dispersion at different length scales in the host matrix has not received adequate attention. Knowing that the mechanical properties of the polymers containing nanoclay are significantly influenced by the degree of dispersion, multiscale characterization of dispersion throughout the fabricated parts is particularly important.

Among the studies devoted to dispersion [18–20], Park and Jana [18] investigated epoxy aided dispersion of nanoclay in poly-methylmethacrylate (PMMA). The state of dispersion of nanoclay in PMMA was compared with that of a ternary system; PMMA, epoxy, and nanoclay. Wide angle X-ray diffractometry (WAXD) and TEM analyses indicated that a priori dispersion of nanoclay in epoxy matrix is more likely to produce exfoliated clay structures. Park and Jana [19] also approached the problem of exfoliation from a rheological viewpoint. They attributed the increase in gallery spacing, which eventually leads to exfoliation, to the elastic forces exerted by the epoxy chains as the cross-linking takes place. The authors concluded that the expansion in the gallery spacing takes place as long as the ratio of storage modulus to complex viscosity is kept above 2–4 s⁻¹.

The characterization of nanoclay dispersion, and thus, intercalation, and exfoliation has been often performed by two common methods. XRD has been preferred by the vast majority of researchers for quantitative analysis of intercalation and exfoliation [1–13,16–23]. This method involves diffraction of a well-quantified X-ray by the nanoclay platelets. Then, through Bragg’s law [24], the gallery spacing, if exists, can be determined as long as the diffraction angle and the wavelength of the incident X-ray are known. Although the XRD analysis provides accurate measurements of the gallery spacing in the order of Angstroms, it is prone to certain shortcomings. According to Kornmann et al. [23], for instance, gallery spacing distribution may lead to a broader intensity peak that is not clearly distinguishable. In addition, the dispersion quantification is most of the time performed on a small sample, which may not be representative of the whole composite as large spatial variations in dispersion might be present in the part. TEM, on the other hand, is suitable for qualitative analysis [3,4,7–11,16–19,22,23]. However, due to the high magnification of the TEM, the sample analyzed for dispersion is small and may not be representative of the whole part [25]. Especially, TEM would be a poor choice of characterization if tactoids of nanoclay are locally present in spite of exfoliation [23].

In this study, center-gated, nanoclay reinforced epoxy disks are fabricated and analyzed via an electron microprobe analyzer (EMPA) to characterize dispersion of nanoclay particles in epoxy matrix at different length scales. Scanning electron micrographs taken at various radial locations depict the presence of nanoclay clusters. Further analyses at different magnifications show that there is a continuum of cluster sizes ranging from several micrometers to nanometer level. Thus, larger nanoclay clusters are analyzed by performing digital image analysis on the images taken at 50X magnification, whereas smaller nanoclay clusters not visible at 50X images are quantified using wavelength dispersive spectrometry (WDS). The utility of this method was successfully demonstrated in an earlier study where dispersion of nanoclay in resin transfer molded composites containing 17 vol % glass fibers was analyzed [26]. In fact, using this method, much greater spatial coverage (i.e., along the molded part’s radii of several inches) was achieved, and thus process-induced morphological changes of nanoclay clusters in a molded composite were identified. In addition to dispersion of nanoclay, tensile and three-point bending tests are used to determine the effect of current state of dispersion on the mechanical properties. Results from dynamic mechanical analysis (DMA) are used to determine the change in glass transition temperature due to the presence of nanoclay.

2 Experimental Studies

2.1 Materials. Cloisite® 25A of Southern Clay Products Inc. is selected as the nanoclay type used in this study. This nanoclay is modified through cation exchange reaction by the supplier to increase the organophilicity of the gallery region, enabling polymer chains to intercalate between the layers. Nanoclay is dispersed in EPON 815C (Shell Chemicals) epoxy resin, which has a viscosity of approximately 0.74 Pa s (740 cP) at room temperature. Particular applications of this resin include primary and secondary structural parts fabricated via resin transfer molding. The addition of nanoclay, depending on the amount, may cause sharp increases in viscosity, which in turn reduces processability. Thus, owing to its low viscosity, EPON 815C is especially suitable for mixing with nanoclay. EPI-CURE 3282 is used as the curing agent for the cross-linking reaction. The gel time for this particular system is reported as approximately 20 min for 5:1 weight ratio of resin to curing agent. Considering that the mold filling in this study takes approximately 10 s, the molding is completed well before the cross-linking initiates.

2.2 Dispersibility Analysis. It is known that the dispersion of powders in liquid systems is spontaneous if the contact angle of the liquid on the powder is smaller than 90 deg [27]. In addition, the degree of spontaneity is higher if the contact angle is smaller, indicating more efficient dispersion. Prior to dispersion, the dispersibility of Cloisite® 25A in EPON 815C resin is assessed by analyzing the spreading of a drop of resin on a compacted nanoclay disk at 33°C. Compaction of the nanoclay is performed on an MTS 810 mechanical testing machine. The nanoclay powder is placed into a hollow cylinder, which has an inner diameter of 12.7 mm and a height of 25.4 mm. During compaction, a plunger is forced into the hollow cylinder by the movement of the cross head. The maximum pressure of compression is measured to be 20 MPa for the geometry of the compact. The actual pressure on nanoclay, however, may be an order of magnitude higher due to the limited area of contact between the particles as stated by Montes et al. [28].

Dispersibility experiment is carried out by placing a drop of epoxy resin on a disk-shaped compacted nanoclay that has a diameter of 12.7 mm and a thickness of approximately 3.9 mm. A drop of EPON 815C resin is placed on the compacted nanoclay surface and its spreading is monitored via a charge coupled device (CCD) camera equipped with a high magnification lens (VZM 450i, Edmund Industrial Optics). The snap shots of the resin drop are captured from the recorded movie file and used to determine the penetration of the resin into the compact and temporal evolution of the contact angle on the nanoclay surface. Contact angle is determined by θ/2 method, which assumes that the resin drop is a part of a perfect spherical shape. The errors introduced by this assumption are corrected by using the procedure suggested by Yang and Lin [29]. Several snap shots illustrating the spreading of epoxy resin on compacted nanoclay surface are depicted in Fig. 1.

The mechanical breakdown of powder clusters during dispersion is more likely if the host liquid can rapidly impregnate the cluster. Hence, the decrease of drop volume associated with the resin penetration into the nanoclay compact is calculated by digi-
followed by 1 h degassing at room temperature started, nanoclay is gradually added. The mixing time of 15 min is measured with a Brookfield DVII+viscometer as 0.86 Pa s. Room temperature viscosity of the nanoclay/resin mixture is measured immediately after the completion of 15 min mixing period, the vacuum as it would result in accelerated evaporation of solvents.

2.3 Mixing of Nanoclay in Epoxy Resin. Cloisite® 25A nanoclay is dispersed into E-PON 815C epoxy resin by means of mechanical mixing using a constant-speed vertical mixer. Similar mechanical mixing procedures have been utilized for preparing nanoclay/polymer composites [5,9]. As the mixing of the resin started, nanoclay is gradually added. The mixing time of 15 min is followed by 1 h degassing at room temperature (approximately 21°C). During degassing, the resin batch was not subjected to vacuum as it would result in accelerated evaporation of solvents. Immediately after the completion of 15 min mixing period, the room temperature viscosity of the nanoclay/resin mixture is measured with a Brookfield DVII+viscometer as 0.86 Pa s (860 cP). At the end of degassing, visual observation did not indicate precipitation of nanoclay or the presence of nanoclay tactoids.

Majority of the studies in the literature report improvements in some polymer properties for nanoclay contents up to 5 wt.%. As the nanoclay content is increased further, significant reduction in properties such as strength is frequently observed. In addition, viscosity of polymers increases substantially at higher nanoclay loadings, thus lowering its processibility. This increase in viscosity would adversely affect liquid molding processes, such as resin transfer molding. In a recent study by Hamidi et al. [31], the viscosity of nanoclay/epoxy system, similar to the current study is investigated. Hamidi et al. observed almost 50% increase in viscosity as the nanoclay content exceeds 2 wt.%. Therefore, the final nanoclay content of the fabricated disks is adjusted in this study to be 2 wt. %.

2.4 Molding and Sample Preparation. Samples to be used in the dispersion quantification and thermomechanical analyses are fabricated by a custom made experimental molding setup. The details of the molding setup are described in detail elsewhere [31–33] and depicted here in Fig. 2.

A total of six disk-shaped parts with a diameter of 152.4 mm and an average thickness of 5 mm are molded. Three of these disks do not contain nanoclay and the remaining three contain Cloisite® 25A nanoclay, which will be referred to as pristine polymer and nanocomposite throughout the article, respectively. As a result of stoichiometric ratio of 5:1 of resin to curing agent by weight, the final nanoclay content of the nanocomposite disks are calculated as 1.7 wt. %. It should be noted that before fabrication, the resin used for pristine polymer is mixed and degassed under the same conditions as the resin used for nanocomposite fabrication. This assured that any difference measured in the properties of pristine polymer and nanocomposite is only due to the presence of nanoclay.

Molding operation is performed at a constant flow rate of 5.32 cm³/s. For the given volumetric flow rate, filling of mold cavity for each disk takes approximately 10 s. During filling of center-gated disks, three-dimensional, nonuniform stress states will develop. Using the volume flow rate and the mixture viscosity of 0.86 Pa s, shear and radial stresses [34] on nanoclay clusters are expected to be as high as 136.5 Pa and 68.2 Pa, respectively. Once the mold filling is completed, the exit gates are clamped and the resin flow is continued for an additional second in order to apply postfill packing pressure. Packing is shown to yield composite parts with less voids and improved performance by Oliveto et al. [35]. Upon completion of molding, the molds are left for curing at ambient temperature for 7 days. At the end of initial curing period, the disks are demolded and postcured in a convective oven at 70°C for 24 h. A milling machine and a template are used for cutting various samples for tension, three-point bending, and glass transition temperature testing. The spatial distribution and designation of the samples on the molded disks are depicted in Fig. 3.

2.5 Quantification of Dispersion. Preliminary analysis of the microstructure of the nanocomposite is carried out using Jeol JSM-880 high resolution scanning electron microscope (SEM). The scanning electron micrographs indicated that the nanoclay was present in the form of clusters of various sizes. Further investigation of the microstructure at various magnifications revealed a continuum of cluster sizes starting from as much as 30 μm in diameter down to nanometer scale. A sample image of the nanocomposite taken at 2500× magnification is shown in Fig. 4, on which nanoclay clusters of various dimensions are pointed out.

To characterize the dispersion of nanoclay in a composite part, one needs to consider the dispersion of nanoclays at all relevant length scales. As pointed out earlier, the current XRD and TEM methods usually lack spatial coverage for thorough dispersion characterization of a nanocomposite. Adequate spatial cover-
Fig. 3 Spatial distribution of samples cut from each disk. Dispersion analysis is performed on the through-the-thickness plane cut along the O-O section. Parts labeled 1 and 5 are for tensile testing and 2a, 2c, 4a, and 4c are for three-point bending tests.

Fig. 4 Clay clusters of various sizes are visible in SEM image taken at 2500× magnification.

Fig. 5 SEM images are thresholded to discriminate the nanoclay from the matrix background. The depicted image is obtained after thresholding an SEM image captured at 50× magnification.

Dispersion analysis at both micron and submicron levels and also to provide adequate spatial coverage for the whole nanocomposite, we analyzed nanoclay clusters using both image and compositional analyses by an EMPA at multiple radial locations.

Quantification of dispersion is carried out by a Cameca SX50 EMPA. This particular EMPA, in addition to its imaging capability by SEM, provides detailed compositional analysis via five wavelength dispersive spectrometers and a KEVEX Delta-class energy dispersive X-ray analyzer. Using the wavelength dispersive spectrometers with properly chosen diffraction crystals, compositional analyses of elements with atomic numbers 5 and above can be precisely performed. The automation of the equipment is provided by a PC-based SAMx system for both WDS and image gathering.

Dispersion of nanoclay in the molded epoxy disks is quantified on Sample 3 located along the center of the molded nanocomposite disk, as shown in Fig. 3. In order to analyze the distribution of nanoclay in the radial direction, the sample is cut into half along its width and length (i.e., Section O-O in Fig. 3). One of the quarter pieces of Sample 3 is then embedded into the sample holder of the EMPA, such that its through-the-thickness cross section is exposed for analysis. Characterization of dispersion is achieved by analyzing the nanoclay clusters in two categories. Nanoclay clusters visible at 50× magnification are characterized by digital image analysis. At the utilized resolution of 1024 × 1024, the smallest cluster that can be resolved at 50× magnification is the size of a pixel, which is 1.5 μm. This category of nanoclay clusters will be referred to as microscale clusters. The remaining nanoclay, i.e., the nanoclay clusters smaller than 1.5 μm, is quantified using compositional analysis via WDS. In the remainder of the article, this category of nanoclay clusters are going to be referred to as nanoscale clusters.

Images of the cross section along the centerline are captured at 50× magnification into 1024×1024 arrays at steps of 4 mm along the disk radius. These images are captured in the backscattered electron mode at 20 kV accelerating voltage and 5 nA beam current. Images along the radius are subjected to modal image analysis to determine the nanoclay volume fraction and other relevant parameters. This is realized by converting the originally 8-bit gray scale images to binary images and performing object analyses by UTHSCSA IMAGE TOOL® software. This procedure is performed five times on each image in order to reduce the uncertainties associated with the thresholding process. A sample post-modal analysis image, indicating the nanoclay clusters is given in Fig. 5, taken at r = 11.2 mm, contains 1842 nanoclay clusters with an average area of 43 μm², representing 3.17% area fraction.

WDS is preferred for compositional analysis of nanoscale clusters due to its accuracy. Prior to WDS analysis, nanoclay powder is analyzed for its composition via energy dispersive X-ray analysis (EDXA) in order to determine the major elements building up the particular nanoclay type used in this study. From the EDX spectrum, the major elements are determined as silicon, aluminum, magnesium, and iron, as shown in Fig. 6. These elements are targeted by WDS along the cross section of the part at discrete points that are 500 μm apart. After several trial experiments, WDS analyses are performed at 5 nA beam current with a spot diameter of 20 μm to avoid extensive beam damage that would cause inaccurate results. A pristine polymer sample is also analyzed for its composition at ten random points to be used as the background corrections.

2.6 Thermomechanical Testing. In addition to dispersion analysis, various thermomechanical tests are performed in order to elucidate on the state of exfoliation. Although the strength of the epoxy is likely to degrade due to the presence of larger clusters, if part of the nanoclay is exfoliated, the adverse effects of larger
clusters would be alleviated. Therefore, if the strength of the nanocomposite is comparable or higher than that of the pristine epoxy, one can conclude that exfoliated nanoclay clusters are present at levels sufficient to induce enhancements in macroscale properties.

Samples 1 and 5 (Fig. 3) of all six disks are reserved for tensile testing. The tensile force on the sample is increased from 0 kN to 8.90 kN over 120 s, and the ultimate tensile strength (UTS) and stiffness (E) are determined according to ASTM D3039/D3039M-00 standard.

Three-point bending test is performed on a total of 12 samples that are designated as 2a, 2c, 4a, and 4c of all three disks. The samples are strained at the center at a rate of 1.0 mm/min. Flexural strength and stiffness are reported according to ASTM D790-03 standard.

Samples for glass transition temperature measurements are obtained by sectioning Specimen 3 of one of the disks for both pristine polymer and nanocomposite into two 50.8 mm long samples. The measurements are performed by an RDAIII rheometer (Rheometric Scientific, Inc.) according to ASTM E1640-99 standard. The samples are subjected to oscillatory shear under torsion at a frequency of 1 Hz while the temperature is ramped from 24°C to 121°C at a rate of 1°C/min. As stated by the ASTM standard, the glass transition temperature can be measured by the sharp drop registered by the storage modulus or the peaks observed in loss modulus and loss tangent. Furthermore, it is indicated that glass transition temperature calculated by tangent delta method is generally higher than the one obtained by loss modulus method. Storage modulus method, on the other hand, indicates that glass transition temperature calculated by tangent delta method is generally higher than the one obtained by loss modulus method. Storage modulus method, on the other hand, yields the lowest glass transition temperature. In the current study, the glass transition temperatures of the pristine polymer and nanocomposite samples are calculated by two of these methods. The first one involves determining the temperature at which the onset of storage modulus reduction occurs and the second one is the temperature at which loss modulus registers a peak. Results from both analyses are reported individually.

3 Results and Discussions

3.1 Wetting of Nanoclay. Dispersion is the first step leading to intercalated and exfoliated nanoclay structures and eventually the improvement in performance of polymer matrix composites. The dispersibility of Cloisite® 25A in epoxy is analyzed by establishing the relation between the work of dispersion and the spreading of epoxy on compacts of the particular nanoclay type. The work of dispersion, $W_d$, is defined as [27]

$$W_d = -6\gamma_{LV}\cos\theta$$

where $\gamma_{LV}$ is the surface tension of epoxy resin and $\theta$ is the contact angle between the nanoclay compact and epoxy resin. The dispersion is said to be spontaneous when the work of dispersion is negative (i.e., the work is done by the system). This condition, according to Eq. (1), can only be satisfied when the contact angle is smaller than 90 deg. In addition, the magnitude of work of dispersion, thus the degree of spontaneity of dispersion increases as the contact angle gets smaller. Consequently, one can conclude that the dispersion is more effective for contact angles approaching zero.

The dynamic contact angle of the resin on Cloisite® 25A is determined from the drop spreading experiments described earlier. The temporal evolution of the contact angle is shown in Fig. 7. The contact angle of resin on the nanoclay compact is observed to start from 109.3 deg and approach to its final static value of 42.8 deg in approximately 20 s. Note that 20 s is adequate for the sessile drop to reach its stable state where the static contact angle can be measured.

The penetration of the resin drop into the nanoclay compact is an indication of the effectiveness of the dispersibility, since the mechanical breakdown of powder tactoids accelerate as they are penetrated by the liquid. To assess the total volume of resin penetration into the nanoclay compact, the percentage volume loss is determined by digital image analysis and shown in Fig. 7. It is observed that 16% of the initial volume of the resin drop has penetrated into the nanoclay compact in 20 s.

3.2 Dispersion of Microscale Clusters. Dispersion of microscale clusters is quantified by performing digital image analysis on the SEM images captured 4 mm apart along the radius of the composite. These images are transformed into binary images and the nanoclay contents are calculated. In addition to phase fraction analyses, the morphology of the clusters is analyzed. Radial distribution of clay content is shown in Fig. 8 together with 95% confidence interval error bars.

The images are taken at a total of 11 locations, starting from $r=3.2$ mm. As shown in Fig. 8, nanoclay content is not varying significantly along the radius except for a small reduction after the inlet gate. The highest microscale nanoclay content is observed closest to the inlet (i.e., $r=3.2$ mm) at 2.0%. When data from all 11 images along the radius are combined, the average contribution of microscale clusters is determined as 1.5% by volume. It should be noted that the volume fraction calculated here is, in fact, the area fraction of the clusters identified in each image. It is expected that the area fraction values obtained from the processed images would correlate well with the actual volume fraction of nanoclay at that location, as spatial distribution of clusters remains, unstructured in the tangential direction (i.e., perpendicular to the image
plane) due to the axisymmetry of the disk. The volume fraction results are not converted to weight fraction, since the effective density of nanoclay is unknown for the current degree of compaction of the clusters.

Although the volume fraction of nanoclay at microscale seems to remain around 1.5% along most of the disk radius, the size distribution of these nanoclay clusters may change radially. During filling of the disk-shaped cavity, clusters experience both shearing forces due to the small gap width and compressive forces due to the radially decelerating flow [36]. These viscous forces may facilitate cluster breakdown, thus yielding much smaller clusters in the radial direction. To investigate this possibility, the number of nanoclay clusters is obtained for the same set of images taken along the radius. The results reveal a significant increase in the number of clusters along the radius, as shown in Fig. 9. The increase in the nanoclay cluster density is as much as 170% from an initial value of 567.2 clusters/mm² near the inlet (i.e., \( r = 3.2 \) mm) to 1562.2 clusters/mm² near the outer edge of the disk at \( r = 43.2 \) mm. Knowing that the volume fraction of nanoclay is almost uniform at around 1.5%, the increase in the number of clusters in the radial direction indicates that the clusters become finer at the outer edges of the disk. The breakdown of nanoclay clusters into finer sizes during the filling of a thin-gap-width cavity has not been reported before. This breakdown phenomenon yields a spatially nonhomogeneous microstructure in molded nanocomposites.

The breakdown of the nanoclay clusters into smaller sizes can further be demonstrated by analyzing the percentage contribution of finer particles (i.e., <3 μm²) to the total number of clusters at various points along the radius. Figure 10 shows the percentage contribution of finer particles as a function of radial distance measured from the center of the disk. The results indicate that the relative percentage of finer particles is continuously increasing along the radius. From near the inlet at \( r = 3.2 \) mm to the outer edge of the disk at \( r = 31.2 \) mm, the percentage of finer particles increase by 72% from an initial value of 13.5% to 23.2%.

These results confirm that along the flow direction, nanoclay clusters are preferentially transported and/or broken down into smaller particles due to the viscous stresses mentioned earlier. A more thorough analysis of this variation can be performed by investigating the percentage change of the contribution of different cluster sizes with respect to the cluster size distribution at the inlet. For this reason, the microscale nanoclay clusters are divided into four groups based on their areas, \( A \). These four cluster area groups are (i) \( A < 3 \) μm², (ii) \( 3 \) μm² \( \leq A < 20 \) μm², (iii) \( 20 \) μm² \( \leq A < 50 \) μm², and (iv) \( A \geq 50 \) μm². The relative percentage of the four different cluster size groups at each radial location is calculated. To illustrate the reduction of nanoclay cluster size, percentage contribution of each cluster size at a particular radial location is divided by percentage contribution of that cluster size at the inlet (i.e., \( r = 3.2 \) mm). For example, clusters with \( A < 3 \) μm² make up 13.5% of the total clusters at the inlet, whereas same size clusters make up 14.5%, 20.4%, and 23.2% of the total clusters at \( r = 15.2 \) mm, 23.2 mm, and 31.2 mm, respectively. Thus, at these three radial locations, the percentage contribution ratios of these small clusters are 7.6%, 51.3%, and 72.1%. The percentage contribution ratios are calculated for all four cluster area groups at the three radial locations, as shown in Fig. 11. One can observe that the percentage contribution ratio of all cluster area groups are decreasing in the radial direction except for clusters with \( A < 3 \) μm². Thus, compared to inlet, small clusters are making up greater portion of the cluster size distribution as the radial position increases. The results depicted in Figs. 9–11 clearly indicate that although the volume content of nanoclay remains almost uniform in the radial direction, the sizes of clusters are considerably reduced. The extent of the reduction in size seems to correlate well with the disk radius. Two factors may be contributing to this spatially nonuniform size distribution. First, more mobile small clusters may move faster than the large ones along the flow direction during filling of the mold cavity and accumulate at the outer edges of the disk. However, small cluster sizes and the highly viscous nature of the resin yield creeping flow with negligible inertia effects. Hence, the local flow is totally dominated by viscous forces and all clusters will move with the flow. The second and more likely scenario is the breakdown of nanoclay clus-

![Fig. 8 Radial distribution of nanoclay clusters dispersed in microscale](image_url)

![Fig. 9 Change in number of nanoclay clusters along the radius of the nanocomposite disk](image_url)

![Fig. 10 Percentage contribution of nanoclay clusters smaller than 3 μm² along the radius. Results indicate that the outer edges of the disk contain a higher percentage of finer clusters.](image_url)
ners due to the shear and compressive stresses induced as a result of flow kinematics. It is well known that the small cavity thickness yields high shear stresses, which are dominant over the planar stresses. The circular disk geometry, on the other hand, yields decelerating flow in the radial direction and develops compressive forces on particles suspended in the flow. It is possible that this combined stress state affected the cluster transport during filling and induced some level of cluster breakdown along the disk radius.

It should be noted that calculating weight fraction of nanoclay clusters larger than 1.5 μm by only using scanning electron micrographs is not possible. The nanoclay clusters observed by scanning electron microscopy have effective densities different than that of nanoclay platelets. Due to the submicron scale air entrapments and partial intercalation by the epoxy polymer, the effective densities of the larger nanoclay clusters are expected to vary, which makes accurate conversion from volume or area fraction to weight fraction not possible.

3.3 Dispersion of Nanoscale Clusters. Dispersion of nanoclay structures smaller than 1.5 μm is analyzed by WDS at locations 500 μm apart along the radius. A total of 82 locations are analyzed between \( r = 3.2 \) mm and \( r = 43.7 \) mm. After background corrections using the pristine polymer sample, the nanoclay distribution along the radius, in terms of weight percentage, is given in Fig. 12. As it was the case for the dispersion in microscale, weight percentage of nanoscale clusters did not indicate any clear dependency on the radial position. An average of 0.4 wt % of the nanoclay is found to be dispersed to particle dimensions smaller than 1.5 μm. The points that are targeted with the microbeam are carefully chosen to avoid microscale nanoclay clusters that have been captured by the image analysis. However, a finite material volume is used in WDS analysis, which is formed by the penetration of the microbeam approximately 5 μm below the surface of the targeted point. Therefore, subsurface nanoclay clusters that are larger than 1.5 μm but invisible at the scanning electron micrographs may contribute to the nanoclay content determined by WDS. In fact, the spikes that reach up to 2 wt % in Fig. 12 can possibly be locations with a cluster present a few microns beneath the sample surface.

For the given beam current and X-ray counting times, 3-σ minimum detection limit (3-σ MDL) for the targeted elements is determined. For magnesium, aluminum, silicon, and iron, the MDLs are calculated as 0.02%, 0.02%, 0.03%, and 0.04%, respectively. Evidently, throughout the WDS analyses, the peak to background intensity ratio and counting times were adequate for the determination of the microbeam approximately 5 μm below the surface of the targeted point. Therefore, subsurface nanoclay clusters that are larger than 1.5 μm but invisible at the scanning electron micrographs may contribute to the nanoclay content determined by WDS. In fact, the spikes that reach up to 2 wt % in Fig. 12 can possibly be locations with a cluster present a few microns beneath the sample surface.

3.4 Thermomechanical Testing. After the state of nanoclay dispersion is determined, improvements in thermomechanical properties over the pristine polymer are analyzed. In most cases, improvements of the strength values are an indication of the existence of exfoliated nanoclay platelets within the matrix. Unlike the majority of the studies on nanoclay/epoxy composites, we observed improvements in both tensile strength and stiffness. As shown in Fig. 13, 9.5% and 4.5% improvements in UTS and stiffness are observed in nanocomposite samples compared to pristine polymer. Note that only 0.4 wt % of the nanoclay is dispersed into particles smaller than 1.5 μm, whereas the rest is found in forms of clusters larger than 1.5 μm. The improvement in tensile strength is most likely provided by the dispersion at the nanoscale rather than the microscale. The error bars shown in Fig. 13 are 95% confidence intervals obtained from a total of six samples.

The results of three-point bending tests are shown in Fig. 14. Unlike tensile results, improvement is observed only in flexural stiffness. As the flexural stiffness improved by 6.6% over the pristine polymer, the flexural strength deteriorated by 7.2%. The error bars in Fig. 14 depict 95% confidence interval obtained from a total of 12 samples. It should be noted that the samples for flexure tests are located closer to the inlet gate compared to the samples used for tensile tests, as illustrated in Fig. 3. Hence, the average nanoclay cluster size is expected to be larger in the flexure samples, which might be the reason for the strength reduction in these samples. Such process-induced spatial variation of proper-
ties is not uncommon in molded composites. For example, process-induced reduction of mechanical properties near the inlet gate of glass/epoxy disks has been reported by Olivero et al. [35].

Glass transition temperature is an indication of chain mobility and molecular integrity of polymer composites. At the glass transition temperature, the transformation from glassy to rubbery state is indicated by a sudden drop in the storage modulus, $G'$, of the material. In addition, the loss modulus, $G''$, and the loss tangent register a peak when the material is going through glass transition. The changes in storage and loss moduli as a function of temperature for the pristine polymer and the nanocomposite are illustrated in Fig. 15. At temperatures lower than 50°C, the storage modulus of the polymer and nanocomposite are very similar. However, at higher temperatures, as the glass transition takes place, storage modulus of the nanocomposite is observed to be significantly higher than the polymer. The shift in both moduli curves to higher temperatures with the introduction of nanoclay indicates improvement in the glass transition temperature. The results derived from Fig. 15 are summarized in Fig. 16. As mentioned by the ASTM standard, glass transition temperatures determined using the peak loss modulus method are observed to be consistently higher than glass transition temperatures determined by storage modulus method. With the current state of dispersion, the glass transition temperature determined by storage modulus displayed a 4% increase from 64.2°C to 66.9°C. This increase becomes 4.5%, from 66.5°C to 69.6°C, when the peak of loss modulus is used.

![Fig. 14 Effect of nanoclay reinforcement on the flexural properties](image1)

![Fig. 15 Evolution of storage and loss moduli for pristine polymer and nanocomposite as a function of temperature](image2)

![Fig. 16 Glass transition temperature of pristine polymer and nanocomposite calculated by two different approaches](image3)

The improvements in the thermomechanical properties, although marginal, may indicate the presence of exfoliated nanoclay platelets.

4 Conclusions

Dispersion state of nanoclay in molded epoxy disks is investigated. Dispersion state is quantified at two different length scales using a combination of SEM and WDS. The scanning electron micrographs are preferred to analyze nanoclay clusters that are larger than 1.5 μm (microscale dispersion), whereas WDS is used to quantify the nanoclay dispersed into structures smaller than 1.5 μm (nanoscale dispersion). This approach also enabled us to investigate the size distribution of nanoclay clusters radially within the molded part and revealed spatial nonhomogeneities in the microstructure.

Significant variation is not observed in the nanoclay content along the radius of the molded disk at both micro- and nanoscales. However, a thorough investigation of the microstructure revealed a considerable increase in the number of clusters along the radius. The number of clusters is increased by 142%, indicating smaller cluster sizes toward the outer edges of the molded disk. For instance, clusters smaller than 3 μm² increased from 13.5% of the total clusters at the center to 23.2% at r = 31.2 mm. This nonuniform size distribution is attributed to flow induced breakdown of nanoclay clusters due to the high viscous stresses generated during mold filling. WDS showed that the amount of nanoclay dispersed at nanoscale is 0.4 wt %, which is 23.5% of the overall 1.7 wt % nanoclay initially loaded.

The presence of nanoclay at 1.7 wt % slightly affected the thermomechanical properties. Tensile strength, stiffness, and flexural strength increased by 9.5%, 4.5%, and 6.6%, respectively, whereas flexural strength is found to degrade by 7.2%. The nanoclay also increased the glass transition temperature of the polymer by as much as 4.5%.

References


