Processing of Transmission Electron Microscope Images for Quantification of the Layer Dispersion Degree in Polymer-Clay Nanocomposites

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Received 27 August 2008; accepted 25 March 2009
DOI 10.1002/app.30534
Published online 8 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Quantification of the layered silicates dispersion level is necessary to more accurately evaluate the performance in polymer/clay nanocomposites. In this article, a new approach is developed to quantify the degree of exfoliation, intercalation, and immiscibility of layered silicates in polymer matrix, based on bright-dark pixel measurement (BDPM) in transmission electron microscope (TEM) images. Several examples of exfoliated, intercalated, and immiscible composites with different polymer and clay systems were examined. The method is capable of estimating the percent contribution of all morphologies present in the image. Comparing with X-ray diffraction (XRD) evidences, it is indicated that as a rule of thumb, the exfoliated structure is dominant whenever the exfoliation percent calculated by BDPM methodology is over 65%, no matter what kind of clay or polymer matrix is used. The intercalated structure can be ascribed to the images with exfoliation level less than 65%, but with the intercalation degree over 28%. Application of this method can facilitate the modeling or correlation of various nanocomposite properties with respect to exfoliation degree. A quantified relation is also possible between XRD and TEM using this approach. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 531–542, 2009

Key words: dispersion; quantification; clay; nanocomposites; TEM

INTRODUCTION

In recent years, polymer/clay nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro- and macro-composites.[1]

Silicate layers in clay have a stacked platelet structure with each platelet having a thickness of approximately 1 nm and a size of a few 100 nanometers in the other two dimensions.[2] The crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery.[3]

The main characteristic of polymer/clay nanocomposites is the ability of the silicate layers to disperse into polymer matrix. Although the high aspect ratio (AR) of silicate layers is ideal for reinforcement, they are not easily dispersed in most polymers due to their preferred face-to-face stacking in agglomerated tactoids. Two different types of morphologies are therefore observed in true nanocomposites:

- Intercalation morphology, where insertion of polymer chains into the galleries occurs in a crystallographically regular fashion, and the distance between the layers just expand to a few nanometers.
- Exfoliation morphology, in which the individual silicate layers are separated in continuous polymer matrix by an average distance that depends on the layered silicate loading.[3]

In some cases, the produced composite has an immiscible structure where the layers remain in stacked forms (tactoid). In this kind of morphology, the silicate layers are flocculated due to hydroxylated edge-to-edge interactions.[1] Sometimes in preparation of polymer/clay nanocomposites, a combination of above three structures may coexist, where one is the dominant phase depending on dispersion degree of silicate layers into polymer matrix.

Currently, the following methods have been used to evaluate the clay dispersion in polymer/clay nanocomposites: (1) transmission electron microscopy (TEM), (2) X-ray diffraction (XRD), (3) scanning electron microscopy (SEM), (4) solid-state

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nuclear magnetic resonance (NMR),[4] (5) rheological techniques,[5] and (6) atomic force microscopy (AFM).[6]

Electron microscopy and XRD (particularly TEM and wide-angle X-ray diffraction (WAXD)) are the most conventional techniques in studying the structure of nanocomposites. Most of investigators, however, have applied these methods just for qualitative comparison of clay dispersion in nanocomposite samples. As the level of exfoliation degree of silicate layers in polymer matrix is vital for attaining the enhanced physical and mechanical properties, the quantification of clay dispersion are very useful in accurate examination of morphology in specimens. In addition, a quantified criterion is necessary for modeling and correlation of various properties of this kind of nanocomposites, in terms of exfoliation degree.

The XRD can quantify the dispersion degree, by monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers. However, little can be said about the spatial distribution of the silicate layers or any structural non-homogeneity in nanocomposites. According to Morgan and Gilman, this method may also fail to distinguish sometimes the exfoliated and immiscible morphologies.[7] Besides, some layered silicates initially do not exhibit well-defined basal reflections. Thus, the peak broadening and intensity decrease are very difficult to study systematically.[1]

Limited reports have been published so far, on quantitative techniques applied on electron microscopy images.[6,8–12] Basically, these studies that use different image processing techniques can be classified as the following methods:

1. Particle size measurement (PSM): In this method, the clay particle length (L_{clay}), the stack thickness (d_{clay}), and the correlation length (ζ_{clay}) between these stacks are measured. These parameters are used to estimate the AR of the stack, as well as the average number of individual layers in a clay clump. The higher the AR value, the lesser the number of layer platelets within the stack and thus higher dispersion degree.[8,9]
2. Particle density measurement (PDM): The principal of this method developed by Dennis et al.[10] and Fornes et al.[11] is to measure the clay particle density, i.e., the number of aggregated particles over a certain area, to compare the dispersion degree of different samples. An entity of a stack is counted as a single clay particle. Therefore, a higher density indicates larger degree of the clay exfoliation, and thus higher dispersion degree.
3. Linear intercept distance measurement (LIDM): Eckel et al.[12] placed an array of parallel lines over the TEM micrographs, and then divided the total length of the lines by the number of times the lines intersect the clay particles to obtain the linear intercept distance, i.e., the average clay particle spacing along the lines. As a stack of sheets is counted as an entity, smaller linear intercept distance indicates more number of particles along the lines and thus a better dispersion.
4. Free-path spacing measurement (FPSM): Luo and Koo[6] have also placed a gridline over the TEM micrograph and measured the free-path distance between the single clay sheets. They defined a probability of the free-path distance distribution in the range of 0.9–1.1μ ($D_{0.1}$), where μ is the mean spacing. It was found that the exfoliated composites had $D_{0.1}$ over 8%, while that of intercalated composites were between 4 and 8%. The morphology with dispersion parameter below 4% was suggested to be classified as immiscible structure.

In this work, we present a new simple method, named as bright-dark pixel measurement (BDPM), to quantify the layer dispersion degree in polymer/clay nanocomposites. A software package is prepared for processing of TEM images, from which the black and white pixels are counted in the image, and the level of exfoliation degree of layered silicate can be evaluated. The main advantage of this method, in addition to its simplicity, is that the percent of exfoliated, intercalated, and immiscible phases are determined individually in one microscopic image, no matter how much is the clay content in the sample and even for large number of layers in stacks.

Basis of BDPM method for determination of dispersion degree

In the mechanism of TEM measurement, the specimen is illuminated by an electron beam. High resolution is possible because of the short wavelength of the electrons, and this requires operation in a vacuum since air scatters electrons. Thus, the TEM image contrast is due to electron scattering in specimen. Electrons scattered to large angles cannot pass through the objective aperture of instrument, and therefore do not contribute to the image in bright field. The most conventional contrast mechanism in the case of filled polymers is the mass-thickness contrast, where the image brightness depends on the local mass thickness (density × thickness). Darker regions in the bright-field image are regions of higher scattering.[13]

As in polymer/clay nanocomposites, the clay is denser than the polymer matrix (density of

montmorillonite is about 2 g/cc which is normally higher than that of virgin polymers[6]), the layered silicates scatter the electron beams to larger angles than the matrix does, and so appear darker. In the same manner, the stacks of silicate layers are denser than the exfoliated ones, hence result in a higher degree of scattering and form the darker part of image.

The BDPM method is based on the fact that any electron microscopic image consist a series of elemental pixels with different darkness. Ideally, when a high-resolution TEM image is prepared from a polymer/clay specimen with a uniform thickness, different phases with different darkness will result due to different densities. The greater the amount of aggregated layers in matrix, the higher is the darkness part in image. The exfoliated parts of silicate layers, however, do not significantly scatter the electron beam and seem bright. Therefore, the darker area in a microscopic image represents the intercalated or immiscible morphologies, depending on the intensity of darkness, whereas the brighter one is explanatory of exfoliated layered silicates.

Hence, according to our proposed method, the operational route to determine the contribution of exfoliation, intercalation, and immiscibility phases in a high-resolution microscopic image is as follows:

First, a gray spectrum coded with numbers between 0 and 64, is considered to define the bright-dark borderlines between phases. The scanned microscopic image is then analyzed using image-processing software. The borders or thresholds of relative darkness for any phase should now be defined by user according to resolution of corresponding image. Three different darkness codes (C_i) are determined that play the role of adjusting parameters in this method:

C_1: the borderline between the polymer matrix and exfoliated structure,

C_2: the borderline between the exfoliated and intercalated structures, and

C_3: the borderline between the intercalated and immiscible structures.

A typical darkness pattern for definition of these thresholds in the range of white to black colors is shown in Figure 1.

When any points in the image are defined as a part of polymer matrix, exfoliated, intercalated, or immiscible phases, then the number of pixels with color codes equal to or greater than C_1 is counted and named as n_t. This number is a relative measure of total clay content appeared in microscopic image. The number of pixels with color codes between C_1 and C_2 is a representative of exfoliation phase that is shown as n_{ex}. In the same manner, the number of pixels in image with color codes between C_2 and C_3, and those equal to or greater than C_3 are counted

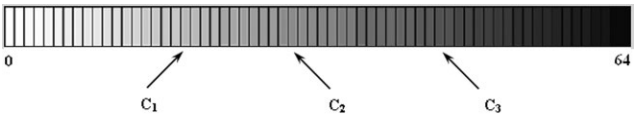


Figure 1 A typical darkness pattern for selection of exfoliated, intercalated, and immiscible thresholds in the range of white to black colors.

and attributed to intercalation (n_{ic}), and immiscible (n_{im}) phases, respectively. Finally, the percents of exfoliated, intercalated, and immiscible phases in the microscopic image of specimen are estimated by following relations, respectively:

$$\%\mathrm{Ex} = \left(\frac{n_{ex}}{n_t}\right) \times 100 \quad (1)$$

$$\%\mathrm{Ic} = \left(\frac{n_{ic}}{n_t}\right) \times 100 \quad (2)$$

$$\%\mathrm{Im} = \left(\frac{n_{im}}{n_t}\right) \times 100 \quad (3)$$

It is evident that the sum of n_{ex}, n_{ic}, and n_{im} is equal to n_t, or:

$$\%\mathrm{Ex} + \%\mathrm{Ic} + \%\mathrm{Im} = 100 \quad (4)$$

Briefly, the input data for this method are three color codes (thresholds) which are selected based on the bright and dark area on TEM micrograph. The outputs are then three processed images in which only the pixels corresponding to one of the exfoliated, intercalated, or immiscible phases are black colored, whereas the rest are white colored. This will clearly show the dispersion and population of each phase in the image. The percent values of each phase are also given. The phase with the highest percentage is may considered as the dominant phase in specimen.

RESULTS

In this section, the performance of BDPM methodology is evaluated in determination of dispersion degree of layered silicates in polymer/clay nanocomposites. The TEM micrographs of various systems with different polymer matrices are examined. Three different morphologies are extensively discussed and the results are compared with those obtained by other authors to evaluate the power of BDPM approach.

Exfoliated morphology

A typical microstructure of nanocomposite containing polyamide PA11 (or nylon 11) with 10 wt % Cloisite 30B® clay (organically modified mont-

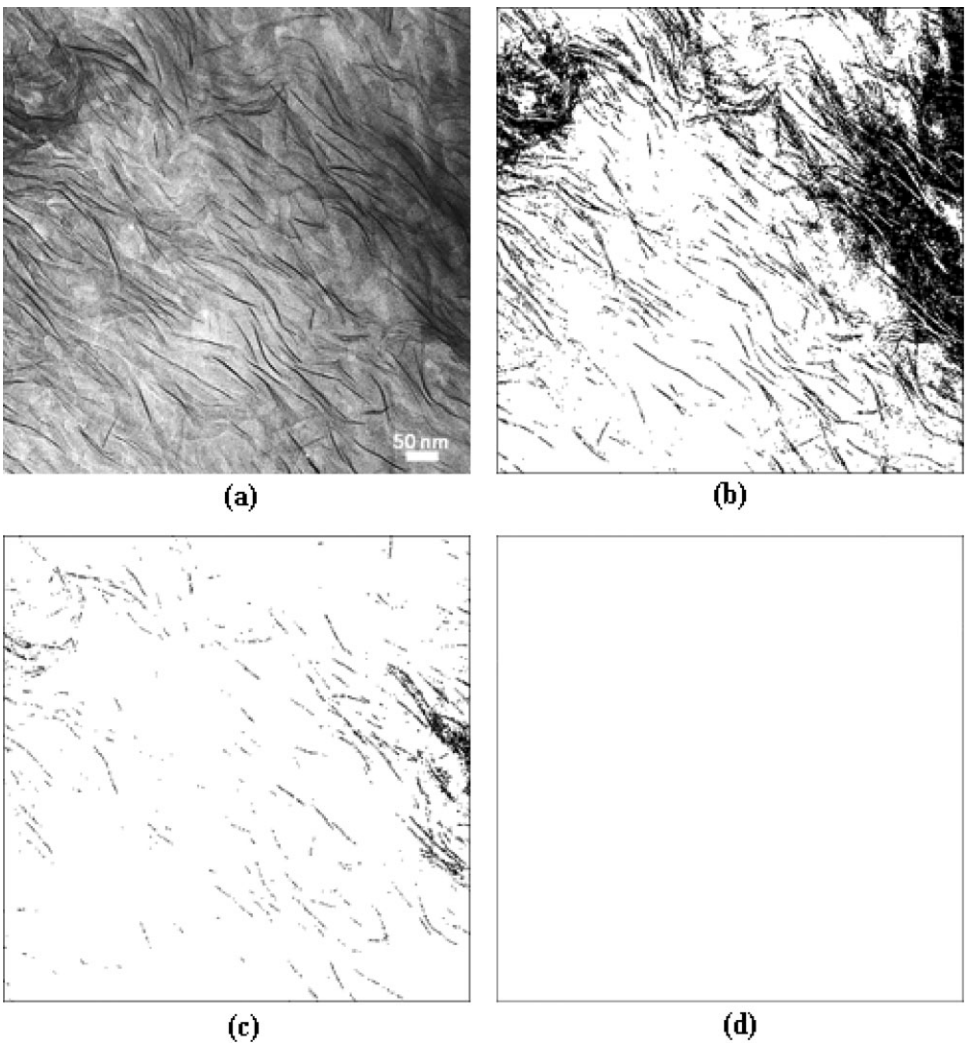
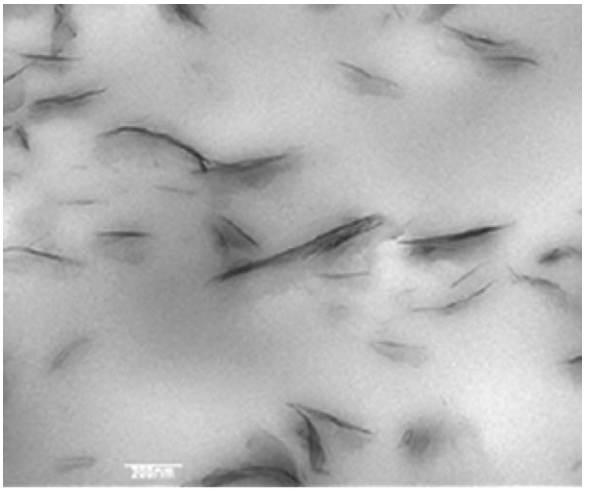


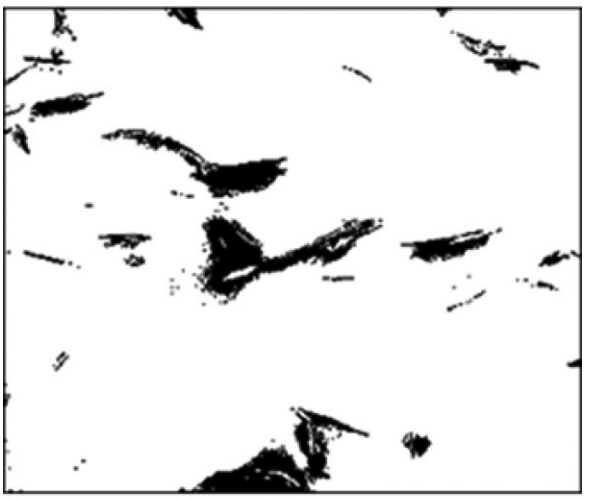
Figure 2 (a) The TEM micrograph of nanocomposite (PA11 with 10 wt % clay) reported as exfoliated morphology,[6] and the processed images produced by BDPM approach: Exfoliated part (black points in (b)), intercalated part (black points in (c)), and immiscible part (nothing in (d)).

morillonite), is reported as exfoliated morphology by Luo and Koo as shown in Figure 2(a).[6] Generally, the original clay clumps are broken up and the clay platelets are dispersed all over the entire area. The processing of this image with BDPM methodology results in three different images for three morphologies [Fig. 2(b–d)]. The area with exfoliated clay is distinguished from other parts by black points, as shown in Figure 2(b). Similarly, the black points, shown in Figure 2(c) represent the intercalated structure, and the white areas are related to remaining parts (polymer matrix + exfoliated part + immiscible part). The quantitative measurements, obtained from BDPM method indicates 93.7% exfoliated, and 6.3% intercalated structures. The BDPM method does not indicate any immiscible morphology for this system as a clear image is generated corresponding to this structure [Fig. 2(d)]. The dominant phase is the exfoliated one, and this result is in accordance to that obtained by FPSM method.[6]

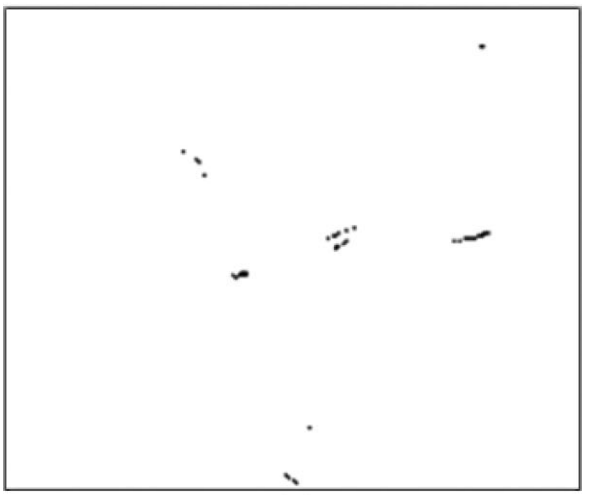
The next example is related to the work of Nguyen and Baird who have developed a process to help the exfoliation and dispersion of Cloisite 20A® nanoclay into polypropylene (PP) matrix with the aid of supercritical CO_2.[14] As shown in Figure 3(a), a efficient dispersion is observed in nanocomposite samples with 6.6 wt % clay due to the use of a twin-screw extrusion, supercritical CO_2, and maleic anhydride compatibilizer. This TEM observation is confirmed in the referenced article, as no peak has been appeared in WAXD pattern. The analysis of the TEM image by BDPM approach proves quantitatively the dominant exfoliated morphology in this nanocomposite, as shown in Figure 3(b). The processed intercalated morphology of this sample is also given in Figure 3(c). The percent contributions of



(a)



(b)



(c)

Figure 3 (a) The TEM micrograph of nanocomposite (PP with 6.6 wt % clay) reported as exfoliated morphology,[14] and the processed image produced by BDPM approach: Exfoliated part (black points in (b)), and intercalated part (black points in (c)).

exfoliation and intercalation morphologies are 91.0%, 9.0%, respectively.

Intercalated morphology

To evaluate the capability of BDPM method for recognizing the intercalated morphology, a typical TEM micrograph, prepared in our recent work is illustrated as shown in Figure 4(a). This image is obtained for thermoplastic starch/clay nanocomposite with 6 wt % CMMT (MMT activated with citric acid).[15] Using the BDPM approach, the exfoliated, intercalated, and immiscible structures are separately marked with black points in Figures 4(b–d), respectively. The percentages of individual morphologies are 61.0% exfoliated, 38.0% intercalated, and 1.0% immiscible structures.

These results are in good agreement with XRD pattern. Figure 5(a) shows the XRD patterns obtained for the nanocomposite.[15] The intercalation of silicate layers in the sample with 6 wt % clay has led to a single diffraction peak around 3.7°. This peak corresponds to 2.4 nm spacing for the layered silicate distance, showing intercalation morphology for this sample.

As another illustration for intercalated structure, a TEM micrograph of TPS/CMMT nanocomposite with 10 wt % clay is also examined.[15] [Fig. 6(a)]. The quantitative values, obtained via the BDPM method are 30.6% for exfoliated, 65.0% for intercalated, and 4.4% for immiscible structures [Fig. 6(b–d)]. These results are confirmed with XRD patterns as the peak around the angle $2\theta = 5.98°$ of the CMMT ($d_0 = 1.48$ nm) has shifted to around 4.5° ($d_0 = 1.96$ nm), leading to an intercalated structure for the TPS/CMMT nanocomposite [Fig. 5(b)].

Immiscible morphology

For immiscible structure with large tactoids, the selected example is cyanate ester PT15 matrix with 5 wt % 30B clay, as shown in Figure 7.[6] The authors (Luo and Koo) have found an immiscible structure in this composite according to FPSM method. Figure 7(b,c), indicates the processed images obtained via the BDPM methodology. The quantitative measurement gives 25.9% intercalated and 74.1% immiscible structures. No significant exfoliated dispersion is detected in the TEM image of this composite (not shown).

The second example is related to the microstructure of NOVALAC-based cyanate ester loaded with 10 wt % MEL-MMT (MMT with melamine ammonium salt modifier), as shown in Figure 8(a).[7] The presence of immiscible large stacks leads to a wide angle scattering of electrons, and so appearance of dark pixels in TEM image. Estimation of dark area by BDPM method indicates about 95% immiscible

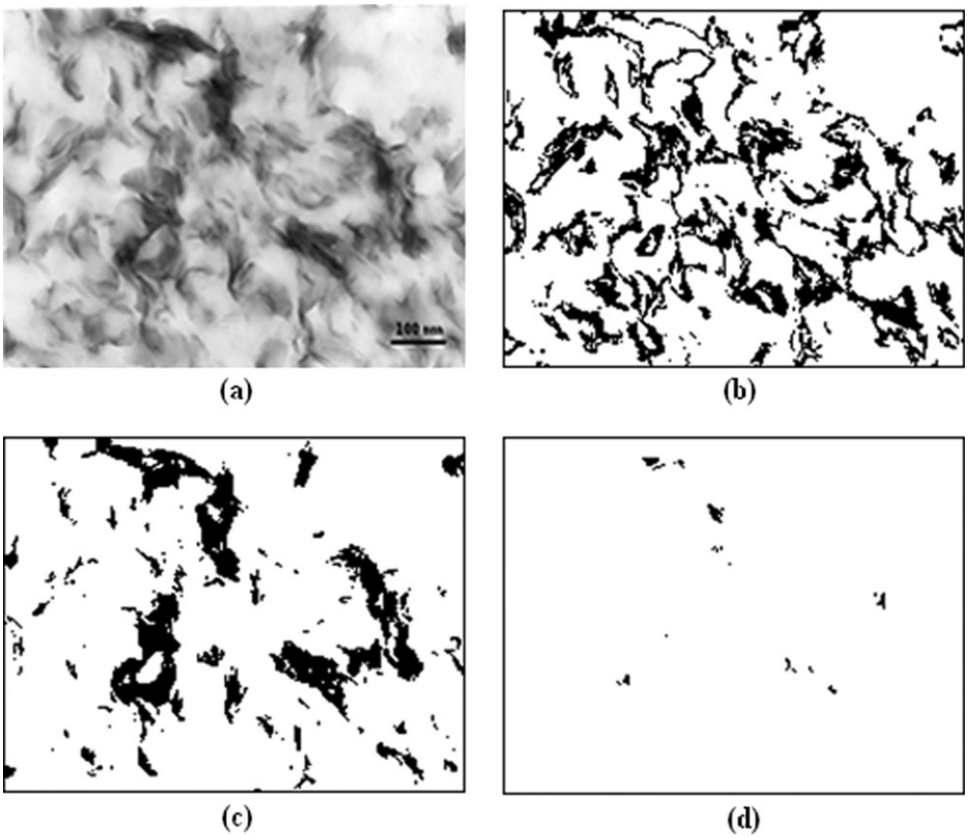


Figure 4 (a) The TEM micrograph of nanocomposite (TPS and 6 wt % CMMT), as intercalated morphology,[15] and the processed images produced by BDPM approach: Exfoliated part (black points in (b)), intercalated part (black points in (c)), and immiscible part (black points in (d)).

structure. The exfoliated and intercalated structures were negligible, and are not shown in Figure 8. Indeed, the immiscible systems should be described as microcomposites rather than as immiscible nanocomposites.

The XRD patterns of this sample in solid and powder forms are shown in Figure 9. Although the immiscible structure was evident in TEM photograph, no diffraction peak is observed for specimen in solid state. However, the peak in XRD pattern of composite in

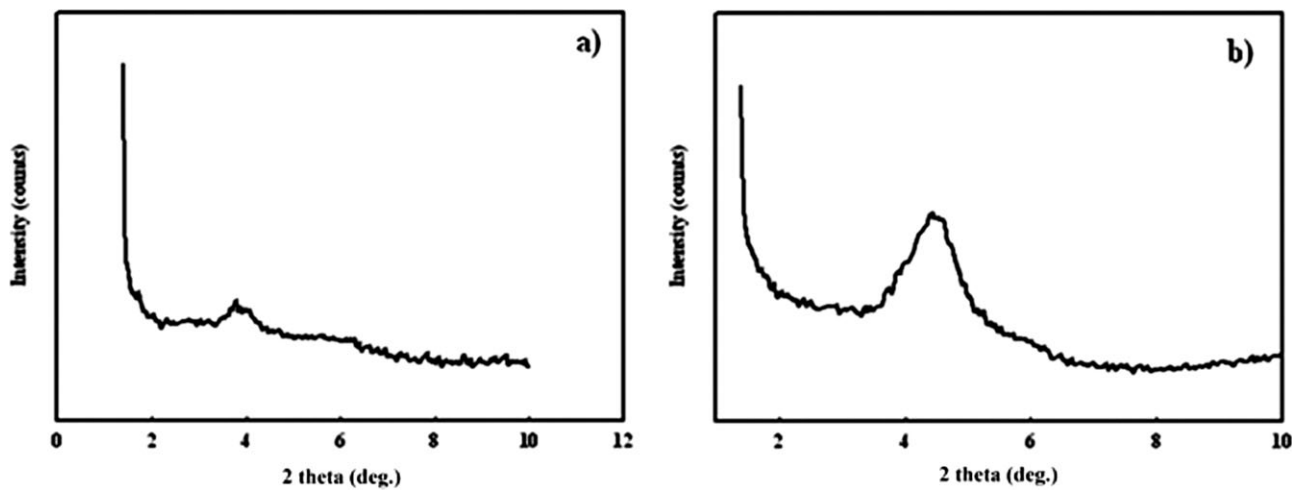


Figure 5 XRD patterns for TPS/CMMT nanocomposite with (a) 6 wt % and (b) 10 wt % clay content.[15]

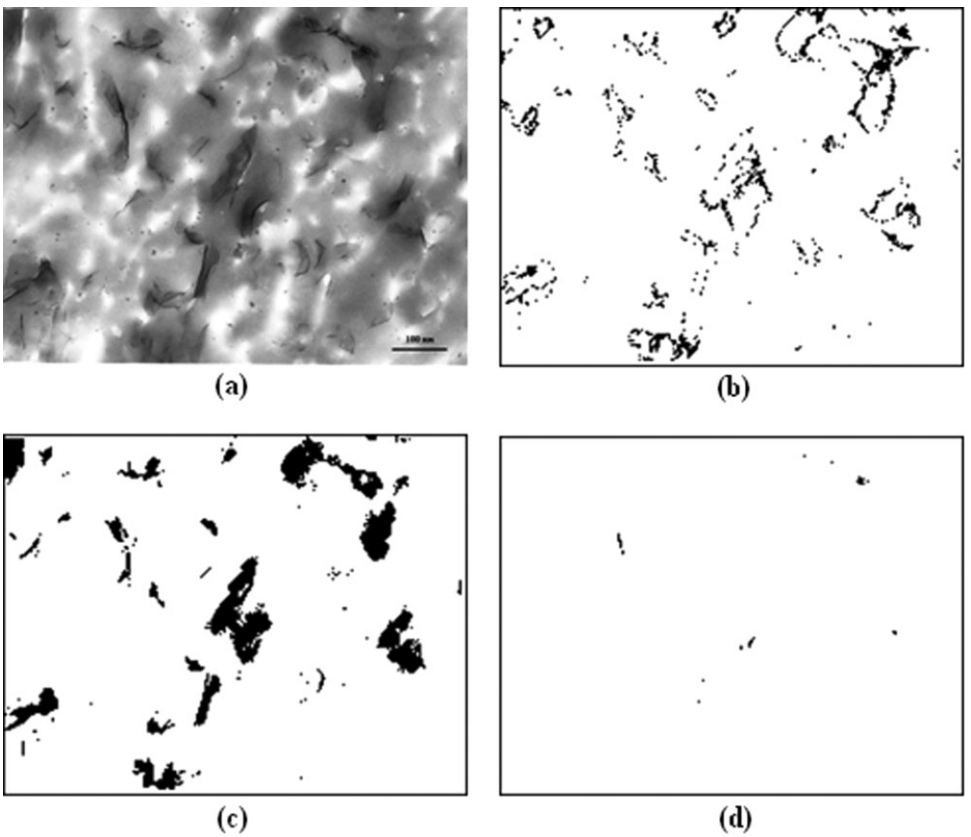


Figure 6 (a) The TEM micrograph of nanocomposite (TPS and 10 wt % CMMT), as intercalated morphology,[15] and the processed images produced by BDPM approach: exfoliated part (black points in (b)), intercalated part (black points in (c)), and immiscible part (d).

powder form, at the same angle as that of modified clay, proves the immiscible morphology. This indicates the dependency of the XRD results to the state of sample examined. This type of phenomena is attributed to a preferred orientation of crystallites in solid samples that may be removed when the sample is converted to powder form. Therefore, the XRD sometimes fails in recognizing the exfoliated structure from immiscible one for different states of materials.[7] The TEM evidence is also necessary for a certain suggestion.

DISCUSSION

Dispersion criteria in BDPM method

The capability of BDPM method in recognizing the exfoliated, intercalated, and immiscible morphologies has been evaluated for even some more polymer/clay hybrids as shown in Table I. The types of polymer matrix and clay, as well as the author assessment on the morphology of synthesized nanocomposite are given in this Table. Beside the observation on the quality of TEM photograph, the absence of peak in corresponded XRD pattern has also been considered as a confirmation for exfoliation mode of morphology.

It is a difficult task in all quantitative techniques including the BDPM method to propose general dispersion criteria in nanocomposites due to sensitivity of the performance of these methods to the resolution and magnification of TEM images. However, as a rule of thumb, we can find some ranges for which the dominant morphology can be guessed.

As it is implied from Table I as well as the examples explained in this article, the exfoliated structure is the dominant morphology whenever the exfoliation percent calculated by BDPM methodology is over 65%, no matter what kind of clay or polymer matrix is used.

According to data obtained by BDPM method, when the contribution of exfoliation structure is less than 65%, and the percent contribution of intercalation structure exceeds 28%; then the peak replacement to smaller angles is observed in XRD patterns, and thus an intercalated morphology is reported.

We can also consider an immiscible morphology predominant for samples with a peak in XRD pattern at the same angles as that of clay used. A significant contribution percent for immiscible phase is

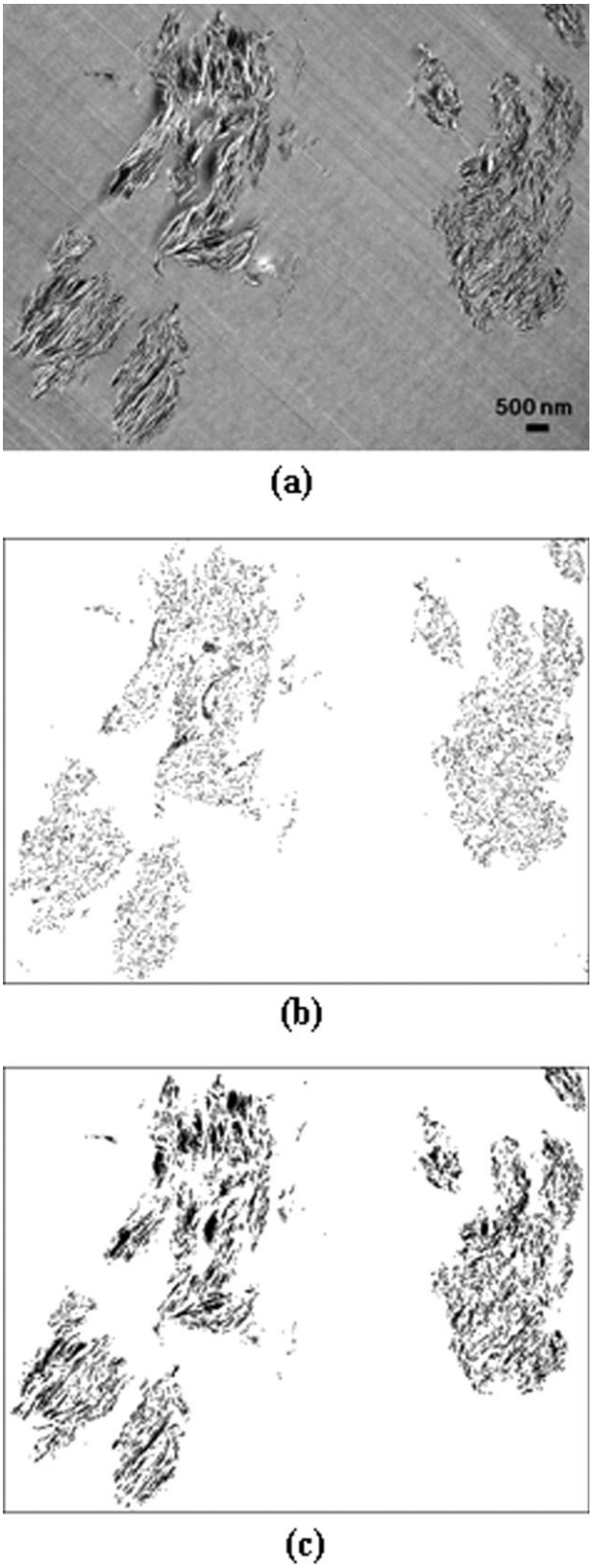


Figure 7 The TEM micrograph of composite (PT15 with 5 wt % 30B),[6] reported as immiscible morphology (a), and the processed images produced by BDPM approach: Intercalated part (black points in (b)), and immiscible tactoids (black points in (c)).

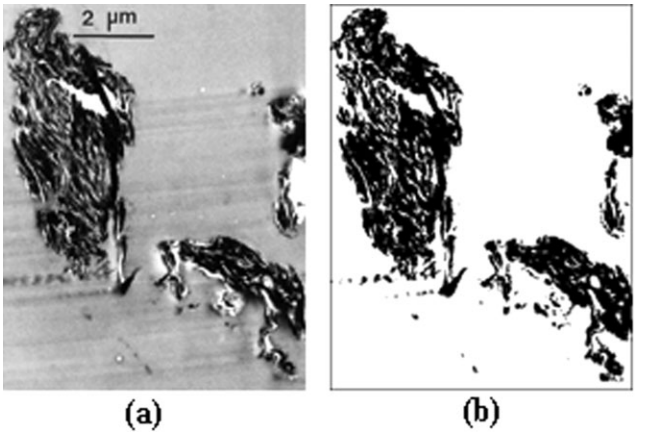


Figure 8 (a) The TEM micrograph of composite (Novalac-based cyanate ester with 10 wt % MEL-MMT), reported as immiscible morphology,[7] and the processed images produced by BDPM approach: immiscible tactoids (black points in (b)).

obtained in BDPM method as observed for example in the work reported by Morgan and Gilman (Fig. 8).[7]

Correlations involved in dispersion degree using BDPM methodology

One of the interesting features of BDPM method is its potential to correlate the quantified dispersion degree in TEM processed images with other

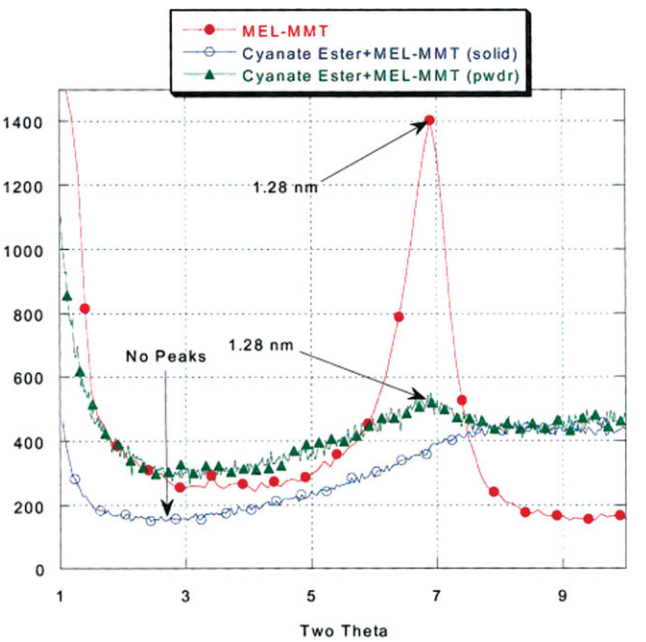


Figure 9 XRD patterns (in solid and powder forms) for Novalac-based cyanate ester composites with 10 wt % MEL-MMT.[7] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Dispersion Degree Based on BDPM Method for Some More Polymer/Clay Nanocomposites in Literature

Ref.	Matrix	Clay type (loading level (wt %))	*d*-spacing in XRD pattern/ pure clay (nm)	Author assessment about morphology	Dispersion degree based on BDPM method (%)		
					Ex.	Ic.	Im.
16	Starch	MMT (5)	1.8/1.12	Intercalated	31.4	61.8	6.81
17	Epoxy resin	APS/GPS-MMT[a] (5)	6.2/2.9	Intercalated	22.1	77.9	0.0
18	PP-*g*-MA	Organophylic clay (7.5)	2.85/2.67	Ordered intercalated	17.0	68.2	14.8
19	Polyester	Cloisite 25A (6)	1.84/1.57	Intercalated	26.8	65.9	7.3
20	PMMA	Modified clay[b] (3)	Two peaks in 1.40 & 2.85/3.1	Intercalated with a few exfoliated	29.2	56.7	14.1
18	PP-*g*-MA	Organophylic clay (4)	2.94/2.67	Disordered intercalated	46.3	44.7	9.0
10	Polyamide 6	Cloisite 15A (3.1)	3.62/3.15	Intercalated	49.5	41.2	9.3
10	Polyamide 6	Cloisite 15A (3.1)	3.77/3.15	Intercalated	56.0	39.5	4.5
10	Polyamide 6	Cloisite 15A (3.1)	3.8/3.15	Intercalated	58.3	39.0	2.7
21	Starch	MMT (2)	2.00/1.22	Exfoliated	60.2	35.8	4.0
22	Starch/PVA blend	MMT (2.5)	1.73/0.98	Agglomeration of the platelets	51.3	35.2	13.5
11	Low MW Nylon 6	Organoclay[c] (1.5)	2.01/1.85	Mixed structure	52.3	33.6	14.1
23	PP	OMMT[d] (4)	3.39/1.96	Partially exfoliated (some of the clays layers are still stacked)	62.4	28.7	8.9
11	High MW Nylon 6	Organoclay[c] (1.5)	No peak/1.85	Well exfoliated	93.2	6.8	0.0
17	Epoxy resin	Organoclay[e] (5)	No peak/5.9	Highly exfoliated	73.3	26.7	0.0
17	Epoxy resin	Organoclay[f] (5)	No peak/3.3	Exfoliated with a few very small stacks	68.6	31.4	0.0
24	PE	CPC-MMT[g] (2.4)	No peak/1.98	Exfoliated	72.1	27.9	0.0
14	PP	Cloisite 20A (6.6)	No peak/1.2, 2.5	Exfoliated with little aggregates	68.9	28.8	2.3
18	PP-*g*-MA	C18-MMT (2)	No peak/2.67	Nearly exfoliated	67.3	25.6	7.1
22	Starch/PVA blend	MMT (2.5)	No peak/0.98	Exfoliated (many single platelets and small tactoids)	65.1	31.4	3.5

[a] Layered silicates through sole gel reaction of cationic triethoxysilane propylamine formyl ethyl trimethyl ammonium iodide (APS) and 3-glycidoxypropyl trimethoxysilane (GPS) (APS/GPS = 1/1).
[b] The clay (montmorillonite, MMT), functionalized with a zwitterionic surfactant, octadecyl dimethyl betaine (C18DMB).
[c] $(HE)_2M_1R_1$ based MMT.
[d] MMT modified by octadecylammonium chloride.
[e] Clay modified by APS and GPS (see footnote a), APS/GPS = 1/4.
[f] Clay modified by APS and GPS (see footnote a), APS/GPS = 1/2.
[g] Montmorillonite (clay), pretreated with cetyl pyridinium chloride (CPC) at a molar ratio of 1 : 1

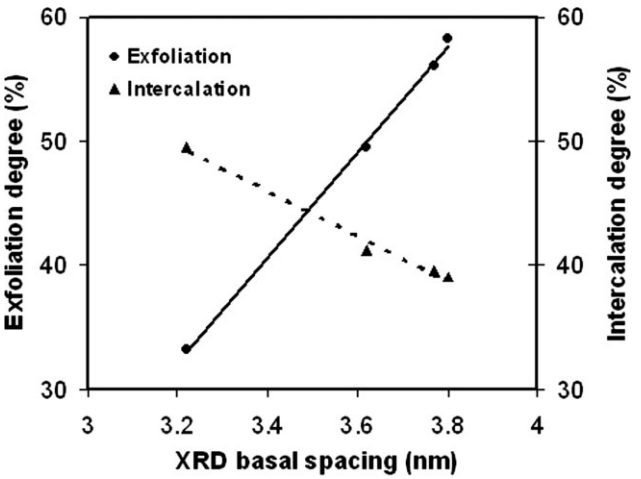


Figure 10 Variation of exfoliation and intercalation percents with *d*-spacing (nm) in XRD pattern of PA6/Cloisite 15A nanocomposites. The TEM images as well as XRD basal spacing are obtained from Dennis et al.[10]

properties including the interlayer basal spacing in XRD patterns. This needs a particular attention of course, that is some similar samples (identical in polymer matrix and clay type), but with different dispersion degree, should be used in correlation. The same TEM instrumentation and measurement conditions (identical in resolution and magnification) are also necessary for this purpose.

As an illustration, variation of exfoliation and intercalation percents, calculated via BDPM method, with *d*-spacing in XRD pattern of polyamide 6/ Cloisite® 15A nanocomposites, is indicated in Figure 10. The TEM photographs and XRD basal spacing are obtained from Dennis et al.[10] The samples are just different in the process conditions leading to different dispersion degree of clay into the matrix. When the distance between silicate layers are increased, the exfoliation degree in TEM image is also increased, as expected. It is implied from Figure 10, that at least for this system the exfoliation and intercalation percents change linearly with *d*-spacing (nm) of nanocomposites.

Under a controlled condition, the percent contribution of each structure in the TEM image is also very useful parameter in modeling or correlation of various physical properties of nanocomposites with their exfoliation degree. As an illustration, consider the TEM micrographs of epoxy filled with synthetic α-zirconium phosphate (ZrP) nanoplatelets (2% by volume), which have been reported by Sun et al.[25] The researchers have prepared three samples with distinctively different levels of exfoliation, then have measured their oxygen permeability and have prepared TEM micrographs at the same resolution and magnification. They have discussed just qualitatively the effect of dispersion levels on permeability. Here, we have analyzed the TEM images by BDPM method. Figure 11 indicates quantitatively the reduction of permeability (or improvement of barrier property) with increasing the exfoliation percent in nanocomposites.

Comparison of BDPM method to previous methods

Luo and Koo have compared extensively the more recent FPSM method with PSM, PDM, and LIDM methods.[6] Briefly, the PSM method can not distinguish between various exfoliated structures as the AR will be constant for all of the single platelets. Application of this method is therefore limited to intercalated or immiscible systems with large evident tactoids.

The PDM is applicable to exfoliated, intercalated, or immiscible system. It is, however, dependent on the clay content because the density is related to the clay loading. This method does not also count the internal spacing between the clay particles. Thus, the density counting would produce the same results for systems with the same number of particles but with different dispersion.

The LIDM and FPSM methods are basically similar as both of them use array of parallel lines to intercept the clay particles for the distance measurement. The LIDM measures the spacing between stacks, and FPSM measures the free-path spacing between the single layer sheets. Also, the LIDM depends to the loading, whereas the FPSM does not. The FPSM is mainly designed for exfoliated and intercalated microstructures with small size tactoids. However, for a system containing larger tactoids, this method works difficultly because it is hard to count the spacing within the large tactoids.

Actually, the main similarity of BDPM method to all other quantitative methods is that the TEM image should be processed in all approaches to measure the amount of individual layers as well as stacks.

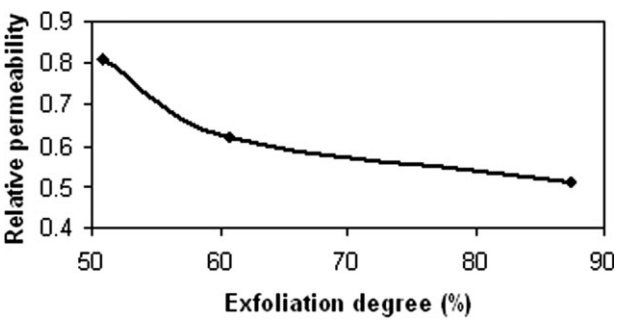


Figure 11 Variation of relative permeability with exfoliation percent in epoxy/ZrP nanocomposites. The permeability data are obtained from Sun et al.[25].

Some errors will be expected anyway in all quantitative methods, particularly if the resolution of the TEM micrograph is of low quality. Despite very simple base and logic behind the BDPM shortcut method, however, its failure does not exceed the other competing methods.

As it was mentioned before, in many TEM images of nanocomposites, different morphologies may be appeared simultaneously in a sample. Normally, the dominant phase is considered by authors to report the dispersion degree of filler into the polymer matrix. The unique advantage of BDPM method is its capability to estimate the percentages of exfoliated, intercalated, and immiscible structures of layered silicate in polymer matrix, individually in a TEM micrograph. The FPSM method suggests merely a region instead of some values for exfoliated as well as intercalated structures. As it was said, in that method the structure is considered as exfoliated, intercalated, or immiscible if the dispersion parameter ($D_{0.1}$) is over 8%, between 4 and 8%, or below 4%, respectively. Various degrees of intercalations for example are characterized with a same criterion.

The BDPM method takes also the advantage of independency to clay content, whereas the FPSM method limits to the samples with small number of stacks. In addition, the application of BDPM method can be extended even to polymeric nanocomposites with nano-fillers other than silicate layers. This is due to the fact that this method does not stand on the dimensional or geometrical measurements, as other methods do.

Finally, we believe two shortcomings of our proposed method. The first one is its higher dependency to the thickness of sample, as the electron scattering and therefore darkness in the image can be resulted due to greater thickness of specimen in addition to higher density of materials in sample. This means that a specific attention is necessary in sample preparation during TEM analysis. Beside, using the BDPM method, the percent contributions of morphologies may vary in some degrees depending on the color codes selected by user. The sophistication in recognition of exfoliated, intercalated, and immiscible structures is therefore vital in this case. Determination of the dominant phase is not, however, dependent on the accuracy of color code selection, excluding in borderlines. The aim of our future work is to reduce the sensitivity of BDPM method to these error factors.

CONCLUSIONS

A new method for quantification of dispersion degree of silicate layers in polymer/clay nanocomposites is presented based on the BDPM in TEM images. Several examples with different morphologies were examined from literature survey with different polymer matrix and silicate layers. The results show the reasonable power of BDPM method in estimation of percent contribution of exfoliated, intercalated, and immiscible structures individually in TEM images. This is the unique advantage of this methodology that can be used specifically in modeling or correlation of physical and mechanical properties of polymer/clay nanocomposites in terms of dispersion degree. A correlation between XRD basal spacing and dispersion degree in TEM image is also possible with this method.

Comparing the result of BDPM method with those obtained with XRD and other evidences, it was found that as a rule of thumb the exfoliated morphology would be dominant if the exfoliation percent in the TEM micrograph is over 65%. The intercalated structure can be ascribed to the images with exfoliation less that 65%, but the intercalation over 28%.

The other advantage of this method is its independency to clay content. Even, the method can be extended to evaluate the dispersion of other types of nano-fillers in the matrix.

The authors would like to appreciate Mr. H. Izaki and Mr. M. Pourmehr for their contributions in developing the computer program in this work.

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