

Research Article

Compatibilizer Polarity Parameters as Tools for Predicting Organoclay Dispersion in Polyolefin Nanocomposites

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Nanocomposites give an innovative method to increase the mechanical, thermal, and barrier performance of polymers. However, properly dispersing the nanoparticles in the polymer matrix is often key in achieving high performance, especially in the case of hydrophilic nanoparticles and hydrophobic polymers. For that purpose, nanoparticles may be functionalized with organic groups to increase their affinity with the polymer matrix. Compatibilizing agents may also be included in the nanocomposite formulation. This paper aims at identifying parameters relative to the compatibilizer polarity that would allow predicting nanoparticle dispersion in the polymer nanocomposite. The analysis used published data on nanocomposite samples combining clay nanoparticles, polyolefins, and various compatibilizing agents. We studied the correlations between the nanoclay exfoliation ratio and five different parameters describing the compatibilizer hydrophilic-lipophilic balance: the acid value, the mole, and weight fraction of polar groups, the number of polymer chain units per polar group, and the number of moles of polar groups per mole of compatibilizer. The best correlation was observed with the number of polymer chain units per polar group in the compatibilizer. This parameter could be used as a tool to predict the dispersion of organoclay nanoparticles in polyolefins. Another important result of the study is that, among the compatibilizers investigated, those with a low acid value provided a better nanoclay exfoliation compared to those with a high acid value. This may indicate the existence of a maximum in the nanoclay exfoliation/compatibilizer polarity curve, which would open new perspectives for nanocomposite performance optimization.

1. Introduction

Polyolefin/nanoclay nanocomposites have raised a large attention because of the improvement obtained in mechanical, thermal, and barrier properties as well as dimensional stability [1–6]. A key element to get a good dispersion of the clay nanoparticles into the polymer matrix is the affinity between the polymer chains and the nanoclay platelets. Indeed, the nanoclay particles should be at least intercalated and ideally exfoliated to produce the desired performance improvement [1]. For that purpose, the nanoclay particles are generally organically modified by ionic exchange with organic cations such as those of an ammonium salt to improve their compatibility with the hydrophobic polymer matrix [7]. In addition, the process of dispersion may be facilitated by the use

of compatibilizers [8]. Compatibilizer molecules with surfactant ability can interact with the hydrophobic polymer and the hydrophilic nanoclay particles at the same time. The efficiency of the compatibilizer molecule depends on the type and polarity of the hydrophobic part of the molecule and the composition and dimension of the nonpolar lipophilic surfactant part. This hydrophilic/lipophilic balance may be measured and used to predict the surfactant capability of the compatibilizer.

The most commonly used compatibilizers are obtained by grafting polar groups on polymers and copolymers. Examples of these compatibilizers include maleic anhydride grafted on polyethylene (PE-g-MA) [9–27], on linear low density polyethylene (LLDPE-g-MA) [28–30], on polypropylene (PP-g-MA) [8, 10, 19, 31–55], and on styrene/ethylene-butylene/

styrene (SEBS-g-MA) [51, 56, 57]. Other polar groups grafted on polymers are itaconic acid [58–60], glycidyl methacrylate (GMA) [54], and acrylic acid (AA) [54, 61, 62]. A second type of compatibilizers is synthesized by polymer oxidation: oxidized polyethylene (OxPE) [22, 23, 25, 63–65], oxidized polypropylene (OxPP) [66, 67], and oxidized paraffins [68–73]. Some compatibilizers are also obtained by copolymerisation, for example ethylene-acrylic acid copolymers (EAA) [27, 61, 62, 74, 75] and ethylene-methacrylic acid copolymers (PE-PMM) [17, 27, 76–79].

The polarity of the hydrophobic part of compatibilizers is generally represented by its acid value (mg-KOH/g) or the weight percent of its polar component. These two values are weight-based and can be obtained from each other. The calculations involve the molecular weight of the polar groups and the number of polar functions in the polar groups capable of reacting with KOH. For compatibilizers with the same polar groups, the acid value and the weight percentage of polar groups are linked by a simple mathematical coefficient. However, these two values only provide a partial representation of the compatibilizer polarity. Indeed, the information about the molecular weight of the compatibilizer and its polymer chain units is needed to access a more realistic representation of its polarity and, in particular, its hydrophilic-lipophilic balance. Three other methods have been proposed in the literature to estimate the hydrophilic-lipophilic balance of compatibilizers. The first one is based on the calculation of the mole and weight fraction of polar groups [76]. The second one computes the number of polymer chain units (e.g., PP or PE) per polar group [80]. The third method suggests calculating the number of moles of polar groups per mole of compatibilizer [55]. It will be interesting to know which of these parameters better correlates with the compatibilizer nanoclay dispersion efficiency.

Two main types of techniques are available to evaluate the degree of dispersion of clay nanoparticles in polymer matrices, i.e., if they are intercalated and/or exfoliated: X-ray diffraction (XRD and wide angle XRD (WAXD)) and transmission electron microscopy (TEM). Our choice for this study is X-ray diffraction since it offers the possibilities to quantify the dispersion. In particular, it can be used to provide a measurement of the basal spacing d_{001} of the nanoclay particle after dispersion in the polymer matrix [13, 21]. These data can give an estimate of the degree of intercalation of the nanoclay in the polymer matrix. In addition, X-ray diffraction also allows estimating the extent of nanoclay exfoliation using the area under the d_{001} peak [9, 46]. Based on the degree of intercalation and exfoliation, it is thus possible to assess the nanoclay dispersion capacity of the compatibilizer.

In this study, correlations between different parameters characterizing the compatibilizer polarity—the acid value, mole and weight fraction of polar groups, number of polymer chain units per polar groups, and number of moles of polar groups per mole of compatibilizer—and the quality of the nanoclay dispersion in the polyolefin matrix are analysed for a series of data from the scientific literature. The nanoclay dispersion quality is expressed in terms of degree of intercalation and exfoliation provided by X-ray diffraction

data (XRD or WAXD). The ultimate objective is to identify the compatibilizer polarity parameters that could be used as tools for predicting and optimizing organoclay dispersion in polyolefin nanocomposites.

2. Experimental Approach

Over 100 papers dealing with the utilisation of compatibilizers for dispersing organoclay in polyolefin nanocomposites were analysed. Among them, 20 papers provide X-ray diffraction results (XRD or WAXD) and all the information required about the compatibilizer (acid value and molecular weight). The nanoclay dispersion also depends on the type of clay and organic modification. Only two types of nanoclay were taken into consideration: octadecylamine-modified montmorillonite (OCT) and dimethyl dihydrogenated tallow ammonium modified montmorillonite (DMDHTA). The compatibilizer/clay ratio also affects very strongly the degree of intercalation and exfoliation of the clay nanoparticles. For this reason, one compatibilizer/clay ratio was selected for the study: 3/1 (wt./wt.). The extrusion temperature was also considered during the data selection: it is situated between 165–210°C depending on the type of nanoclay and polymer. In the end, results for 17 nanocomposite samples obtained from eight papers were used for the analysis.

Table 1 presents the characteristics of the nanocomposite samples included in the analysis. The compatibilizers are characterized by the molecular weight and acid value. The compatibilizer molecular weight values were directly obtained from the corresponding papers. The acid values listed in Table 1 were either also available in the corresponding papers or have been calculated based on the polar group content provided in the papers according to the following equation:

$$AV = \frac{PGC \cdot NAG \cdot Mw_{KOH} \cdot 1000}{100 \cdot Mw_{pg}}, \quad (1)$$

where AV is the acid value in mg KOH/g; PGC is the polar group content expressed in wt%; NAG is the number of polar groups in the compatibilizer monomer unit; Mw_{KOH} is the molecular weight of KOH; and Mw_{pg} is the molecular weight of the polar groups.

For the matrix, the type of polymer and the extrusion temperature are reported in Table 1. The organoclays are characterized by the type of clay and organic modification as well as by the initial basal spacing d_{001} . Finally, data reported for the nanocomposite samples are the organoclay/polymer ratio and the organoclay basal spacing in the composite.

In addition to the acid value, four other parameters characterizing the compatibilizer polarity were calculated for each compatibilizer: the mole and weight fraction of polar groups (according to [76]), the number of polymer chain units (PP or PE) per polar group (according to [80]), and the number of moles of polar groups per mole of compatibilizer (according to [55]).

The calculation of the weight fraction of polar groups used the compatibilizer acid value according to the following equation:

TABLE 1: Characteristics of the polyolefin-montmorillonite nanocomposite samples included in the analysis.

Sample number	Compatibilizer		Polymer		Organoclay		Nanocomposite		References	
	Type (Trade name, Supplier)	Acid value (mg KOH/g)	Molar weight (MW)	Type	Extrusion temperature (°C)	Type (Trade name)	Clay basal spacing d_{001} (nm)	Organoclay/polymer ratio (wt./wt.)		Clay basal spacing d_{001} (nm)
1	PP-g-MA (PB3200, Crompton)	11	120 000	PP	165	OCT (nanomer I.30 P)	2.36	80/15	2.89	[47]
2	PP-g-MA (PB3000, Crompton)	14	61 000	PP	165	OCT (nanomer I.30 P)	2.36	80/15	2.99	[47]
3	PP-g-MA (PB3150, Crompton)	6	330 000	PP	165	OCT (nanomer I.30 P)	2.36	80/15	2.67	[47]
4	PP-g-MA (PP-MA-1010, Sanyo)	52	30 000	PP-MA-1010 ^a	190	OCT (own synthesis)	2.20	75/25	5.88	[48]
5	PP-g-MA (PP-MA-1010, Sanyo)	52	30 000	PP-MA-1010 ^a	200	OCT (own synthesis)	2.10	75/25	6.30	[49]
6	PP-g-MA (PP-MA-1001, Sanyo)	26	40 000	PP-MA-1001 ^a	190	OCT (own synthesis)	2.20	75/25	7.37	[48]
7	PP-g-MA (CA100, Arkema Orevac)	11	88 000	PP	180–200	DMDHTA (Cloisite 20A)	2.51	80/15	3.11	[50]
8	PP-g-MA (Polybond 3200, Crompton)	11	95 804	PP	190–210	DMDHTA (Cloisite 20A)	2.42	84/12	3.49	[54]
9	SEBS-g-MA (Kraton FG 1901X, Shell)	20	97 700	PP	200	DMDHTA (Cloisite 15A)	3.34	85/15	3.71	[57]
10	LLDPE-g-MA (18302 N, Arkema Orevac)	9	125 000	LLDPE	200	DMDHTA (Cloisite 20A)	2.59	92/6	No d_{c001} pic	[30]
11	LLDPE-g-MA (Bondyram 4001, Polyram)	9	69 000	LLDPE	200	DMDHTA (Cloisite 20A)	2.59	92/6	4.42	[30]
12	LLDPE-g-MA (Bondyram 4001A, Polyram)	9	200 000	LLDPE	200	DMDHTA (Cloisite 20A)	2.59	92/6	4.34	[30]
13	PP-g-AA (polybond 1002, Crompton)	46	162 504	PP	190–210	DMDHTA (Cloisite 20A)	2.42	84/12	3.20	[54]
14	PP-g-GMA (PP-g-GMA, own synthesis)	7	190 409	PP	190–210	DMDHTA (Cloisite 20A)	2.42	84/12	3.65	[54]
15	OxPE (AC 316, Honeywell)	16	12 928	LLDPE	160–180	DMDHTA (Cloisite 20A)	2.28	85/15	3.16	[23]
16	OxPE (AC 330, Honeywell)	30	8 850	LLDPE	160–180	DMDHTA (Cloisite 20A)	2.28	85/15	3.43	[23]
17	OxPE (AC 395, Honeywell)	42	8 400	LLDPE	160–180	DMDHTA (Cloisite 20A)	2.28	85/15	3.22	[23]

^aNo additional polymer; only includes compatibilizer and nanoclay.

$$\text{Weight fraction of polar groups} = \frac{AV \cdot Mw_{pg}}{NAG \cdot Mw_{KOH} \cdot 1000} \quad (2)$$

The determination of the mole fraction of polar groups involved traditional chemical calculations based on the compatibilizer acid value and the molecular weight of the polymer units in the compatibilizer chain. The number of polymer chain units per polar group was computed from the acid value according to the following equation:

$$\begin{aligned} \text{Number of polymer chain units per polar group} \\ = \frac{Mw_{KOH} \cdot 1000}{AV \cdot Mw_{polymer}} \end{aligned} \quad (3)$$

where $Mw_{polymer}$ is the molecular weight of PP or PE units in the compatibilizer chain.

Finally, the number of moles of polar groups per mole of compatibilizer is also obtained from the acid value and includes the molecular weight of compatibilizer Mw_c :

$$\frac{\text{mol}_{pg}}{\text{mol}_{comp}} = \frac{AV \cdot Mw_c}{NAG \cdot Mw_{KOH} \cdot 1000} \quad (4)$$

In some rare instances, not enough information was available to compute some of these parameters as indicated by notes to Table 1.

The degree of intercalation and exfoliation of the nanoclay was estimated using the X-ray diffraction data found in the papers. The basal spacing d_{001} of the clay nanoparticles in their original condition and after dispersion in the polymer matrix was used to compute the information about the degree of nanoclay intercalation. It is represented by the difference between the position of $d_{001|initial}$, the initial organoclay basal spacing, and the position of $d_{001|composite}$, the organoclay basal spacing in the composite.

In the case of the degree of nanoclay exfoliation, since the shape of the d_{001} peak is very similar for the different samples, the peak height was used for the calculation instead of the peak surface area. The degree of exfoliation of the nanoclay was computed according to the following equation:

$$\% \text{ exfoliation} = \left(1 - \frac{H(d_{001|composite})}{H(d_{001|initial})} \right) \cdot 100, \quad (5)$$

where $H(d_{001|initial})$ is the height of the d_{001} peak for the nanoclay in their original condition and $H(d_{001|composite})$ is the height of the d_{001} peak in the nanocomposite.

3. Results

A comparison of data for the organoclay basal spacing in the initial condition and in the nanocomposite, $d_{001|initial}$ and $d_{001|composite}$ in Table 1, shows that intercalated structures are present in almost all nanocomposites. However, it would be difficult to estimate the exact ratio of intercalated structures since there is no direct relation between the intercalation ratio and the basal spacing shift. It can be noted that one nanocomposite sample was possibly completely exfoliated

(sample 10) since no organoclay basal spacing $d_{001|composite}$ peak was observed in the corresponding XRD/WAXD spectrum.

Table 2 provides the compatibilizer acid values (in mg KOH/g) for the different nanocomposite samples. It also gives the result of the calculation of the other parameters used to describe the polarity of the compatibilizer: mole and weight fraction of the polar groups, number of polymer chain units per polar group, and ratio of number of moles of polar groups per mole of compatibilizer. Finally, the results in terms of degree of exfoliation for each nanocomposite sample are presented. The values of degree of exfoliation vary from 58 to 100%.

Figures 1–5 show the variation of the nanoclay exfoliation ratio as a function of, respectively, the acid value, the mole and the weight fraction of polar groups, the number of polymer chain units per polar group, and the ratio of the number of moles of polar groups per mole of compatibilizer.

Figure 1 shows that the acid value is relatively well correlated with the exfoliation ratio ($R^2 = 0.5558$). There appears to be a negative relationship between the nanoclay exfoliation ratio and the acid value of the compatibilizer. This may indicate that, for compatibilizers with an acid value situated between 6 mg·KOH/g and 52 mg·KOH/g, those with lower acid values provide a better nanoclay dispersion than those with a high acid value.

The compatibilizer mole and weight fraction of polar groups were calculated for 14 of the 17 nanocomposite samples. For the three remaining samples with OxPE-type compatibilizers, no information was available about the type and ratio of polar groups. Downward trends can be observed in Figures 2 and 3 for the variation of the nanoclay exfoliation ratio with, respectively, the compatibilizer mole and weight fraction, similar to what was observed for the exfoliation ratio/acid value relation. Therefore, for studied compatibilizers with an acid value situated between 6 mg·KOH/g and 52 mg·KOH/g, lower values of the mole and weight fraction of polar groups in the compatibilizer lead to an improved nanoclay dispersion. Similar or slightly higher values of the coefficient of determination R^2 were obtained here compared to the exfoliation ratio/acid value relationship.

A better correlation was observed for the number of polymer chain units per polar group ($R^2 = 0.742$ in Figure 4). It shows that, within the studied range of values, compatibilizers with a higher number of polymer chain units per polar group lead to a better nanoclay dispersion in polyolefin matrices.

Figure 5 presents the exfoliation ratio as a function of the number of moles of polar groups per mole of compatibilizer. No correlation is observed between this compatibilizer polarity parameter and the exfoliation ratio.

4. Discussion

The basic parameter describing the compatibilizer polarity is its acid value. From this parameter, other parameters taking into account additional characteristics of the compatibilizer can be computed. The number of polymer chain units per

TABLE 2: Parameters describing the compatibilizer polarity and characterizing the quality of the nanoclay dispersion.

Sample number	Compatibilizer type (Trade name)	Acid value (mg KOH/g)	Molar fraction of polar groups	Weight fraction of polar groups	Number of polymer chain units per polar group	Mole of polar groups per mole of compatibilizer (mol _{pg} /mol _{comp})	Degree of exfoliation (%)
1	PP-g-MA	11	0.0041	0.0096	121	11.76	78
2	PP-g-MA	14	0.0053	0.0122	95	7.61	72
3	PP-g-MA	6	0.0023	0.0052	222	17.64	79
4	PP-g-MA	52	0.0200	0.0454	26	13.90	58
5	PP-g-MA	52	0.0200	0.0454	26	13.90	57
6	PP-g-MA	26	0.0099	0.0227	51	9.27	72
7	PP-g-MA	11	0.0041	0.0096	121	8.63	74
8	PP-g-MA	11	0.0041	0.0096	121	9.39	75
9	SEBS-g-MA	20	— ^b	0.0176	— ^b	17.41	92
10	LLDPE-g-MA	9	0.0023	0.0079	222	10.02	100
11	LLDPE-g-MA	9	0.0023	0.0079	222	5.53	83
12	LLDPE-g-MA	9	0.0023	0.0079	222	16.04	86
13	PP-g-AA	46	0.0177	0.0402	29	66.61	64
14	PP-g-GMA	7	0.0053	0.0177	190	23.75	89
15	OxPE	16	— ^a	— ^a	125	3.69	75
16	OxPE	30	— ^a	— ^a	67	4.73	60
17	OxPE	42	— ^a	— ^a	48	6.29	74

^aCould not be calculated because the nature and ratio of polar groups are not known. ^bCould not be calculated because the ratio of polymer units in the copolymer chain is not known.

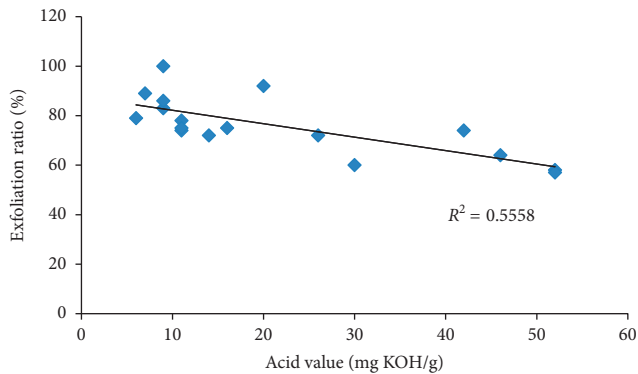


FIGURE 1: Nanoclay exfoliation ratio as a function of the compatibilizer acid value.

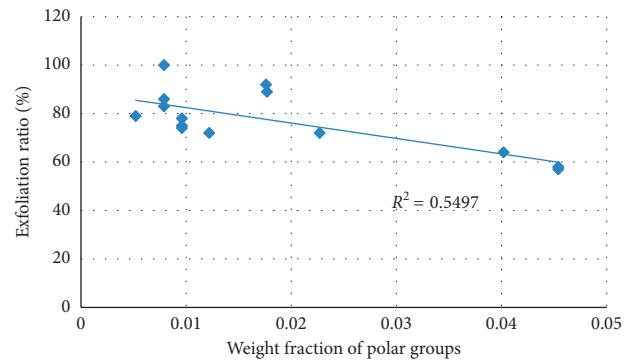


FIGURE 3: Nanoclay exfoliation ratio as a function of the weight fraction of polar groups in the compatibilizer.

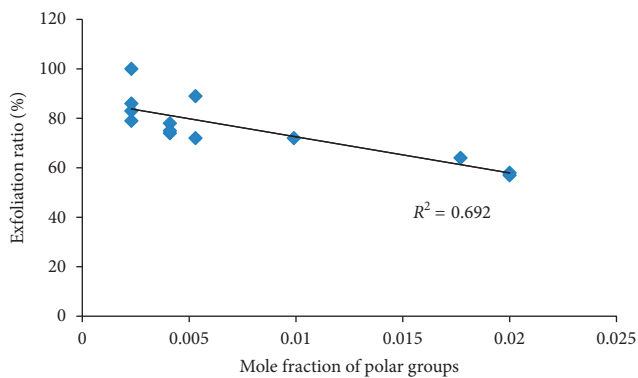


FIGURE 2: Nanoclay exfoliation ratio as a function of the mole fraction of polar groups in the compatibilizer.

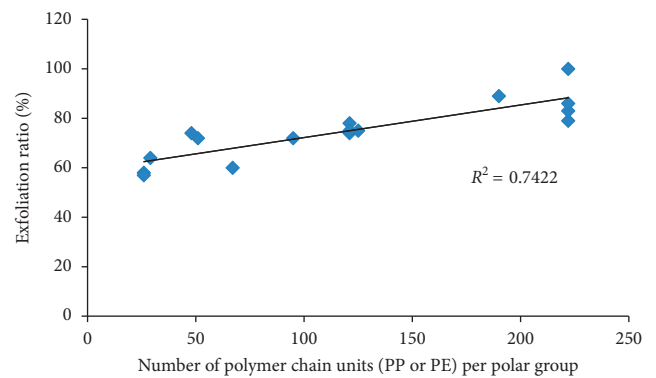


FIGURE 4: Nanoclay exfoliation ratio as a function of the number of polymer chain units per polar group in the compatibilizer.

polar group includes the molecular weight of polymer units in the compatibilizer chain. The number of moles of polar groups per mole of compatibilizer includes the molecular

weight of compatibilizer. Two other parameters were investigated: the weight fraction, which uses the molecular weight of the compatibilizer and the molecular weight of the

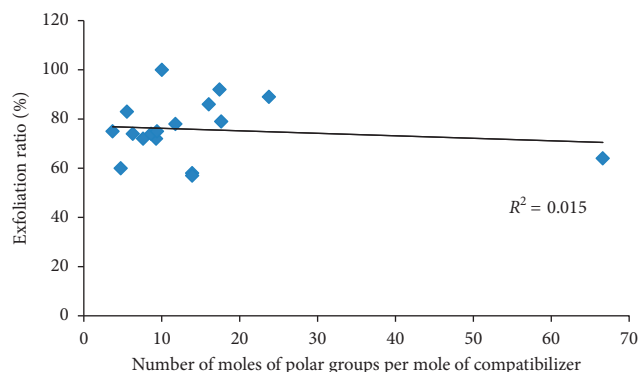


FIGURE 5: Nanoclay exfoliation ratio as a function of the number of moles of polar groups per mole of compatibilizer.

polar groups, and the mole fraction, for which the calculation also includes the molecular weight of the polymer units in the compatibilizer chain.

The best correlation for the nanoclay exfoliation ratio was observed with the number of polymer chain units per polar group in the compatibilizer. It best expresses the optimal balance between the hydrophilic groups connecting with the nanoclay particles and the lipophilic groups attracted to the matrix polymer chains to maximize the level of exfoliation of the nanoclay in the polymer matrices. This parameter could easily be used as a tool to perform a first selection of best candidate compatibilizers for nanoclay dispersion in polyolefin matrices.

The coefficient of determination decreased slightly when the mole fraction of polar groups in the compatibilizer was considered. A further decrease in the quality of the correlation was observed with the acid value and the weight fraction of polar groups. There was no correlation with the number of moles of polar groups per mole of compatibilizer. It is interesting to note that taking into account the molecular weight of compatibilizer seems to have a detrimental effect on the quality of the correlation with the nanoclay exfoliation ratio. The coefficient of correlation R^2 was at 0.7422 when the acid value was only combined with the molecular weight of polymer units in the compatibilizer chain. This coefficient decreased to 0.692 when both the molecular weight of polymer units in the compatibilizer chain and the molecular weight of compatibilizer and to 0.015 when only the molecular weight of compatibilizer was combined to the acid value. More investigations are needed to better understand the phenomena behind these observations.

The surprise of this analysis has been the downward relation between the nanoclay exfoliation ratio and the compatibilizer polarity. All at once the acid value, the mole fraction of polar groups, the weight fraction of polar groups, and the number of polar chain units per polar group point towards a better nanoclay exfoliation obtained with low polarity compatibilizers. This result can only be explained if one considers that the compatibilizer effect on nanoclay exfoliation is the outcome of two opposing phenomena. On one hand, the compatibilizer should have a good affinity with the nanoclay particles, i.e., a large number of polar

groups; however, this will diminish its affinity for the polymer matrix. On the other hand, the compatibilizer should also have a good affinity with the polymer matrix, i.e., a large number of nonpolar groups. Additional data points corresponding to very low polarity compatibilizers, i.e., with an acid value less than 6 mg-KOH/g, are necessary to complete the analysis regarding this hypothesis. However, if confirmed, this could indicate that the optimal choice of compatibilizer has not been reached with the set of published data analysed: the choice of a compatibilizer with a better fitted polarity may lead to an increased nanoclay dispersion, resulting in improvements in mechanical and barrier performance properties for instance.

5. Conclusions

A large interest for polyolefin/nanoclay nanocomposites has been observed because of potential gains in mechanical, thermal, and barrier performance as well as dimensional stability at a limited cost. The first step in achieving these gains is a good dispersion of the nanoparticles in the polymer matrices. This study has provided tools to predict/optimize organoclay dispersion in polyolefin nanocomposites through the analysis of the correlation of various expressions of the compatibilizer polarity with the nanoclay exfoliation ratio.

The best correlation was observed with the number of polymer chain units per polar group in the compatibilizer. This parameter, which is computed based on the compatibilizer acid value and the molecular mass of polymer units in the compatibilizer chain, can be used to predict the dispersion of organoclay nanoparticles in aliphatic polymers such as polypropylene and polyethylene.

Acceptable levels of correlation were also obtained with three other polarity parameters: the acid value, and the mole, and weight fraction of polar groups. In some instances, the lower quality of the correlation observed with the nanoclay exfoliation ratio seemed to be linked to the inclusion of the molecular weight of compatibilizer into the calculation of the parameter used to describe the compatibilizer polarity.

Finally, the most important and at the same time the most controversial conclusion of this study is that, for compatibilizers with an acid value situated between 6 and 52 mg-KOH/g, those with a low acid value provided a better nanoclay exfoliation compared to those with a high acid value. The addition of nanoclay dispersion data for compatibilizers with acid values lower than 6 mg-KOH/g would be necessary to better understand this phenomenon.

Data Availability

The data used in the paper were obtained from the literature. The source of these data is also provided in the paper with references to the corresponding published papers.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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