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Graphical Abstract



Research Highlights

► Development of new polyamide/organoclay nanocomposites was reported.

► Thermal performance of the nanocomposites was improved under inert and reactive atmospheres.

► Organoclay increased flame retardancy of nanocomposites.

Flammability and Thermal Properties of Novel Semi Aromatic Polyamide/Organoclay Nanocomposite

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Abstract:

The development of semi aromatic polyamide/organoclays nanocomposites (PANC) is reported in this communication. New polyamide (PA) was successfully synthesized through direct polycondensation reaction between bio-based diacid and aromatic diamine. PA exhibited strong UV-Vis absorption band at 412 nm. Its photoluminescence spectrum showed maximum band at 511 nm in the green region. The surface modification of montmorillonite was carried out through ion-exchange reaction using 1,4-bis[4aminophenoxy]butane (APB) as a modifier. Then PANCs containing 3 and 6 wt. % of the modified montmorillonite (MMT-APB) were prepared. Flammability and thermal properties of PA and the nanocomposites were studied by microscale combustion calorimeter (MCC), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA results in both air and nitrogen atmospheres indicated improving in thermal properties of PANCs compared to the neat PA. According to MCC analysis, a 31.6 % reduction in pHRR value has been achieved by introducing 6 wt. % of the organoclay in PA matrix.

Key words: Nanocomposite, Polyamide, Thermal Stability, Flammability, Organoclay

1. Introduction

Over the last decade, the polymer/layered silicate nanocomposites have received rising attention owing to their unique thermal, mechanical and gas barrier properties compared with those of neat polymer. While 30-40 wt. % microfillers are required for conventional composites, diverse properties of polymer can be significantly improved by incorporation of only minute amounts of clay (2–8 wt. %) in polymer matrices [1-4].

The typical selected clay for these types of nanocomposites is montmorillonite. The high aspect ratio of the platelets serves as interfacial volumes extender in nanocomposite and thus provides improved physico-chemical and mechanical properties [5]. However, incorporating of hydrophilic montmorillonite platelets into the hydrophobic polymer matrix has been a major challenge due to the incompatibility between polymer and montmorillonite. To overwhelm this deficiency, montmorillonite is organically modified by adequate modifiers such as quaternary ammonium or phosphonium salts [1, 6]. The blending of unmodified montmorillonite is limited to hydrophilic polymers such as polyethylene oxide and polyvinyl alcohol.

Polyamides are one of the most promising classes of engineering polymers. Due to their properties, such engineering polymers are potential matrices for nanocomposites. Semi-aromatic polyamides in particular, are of special interest because of their enhanced transparency, thermal stability, excellent barrier properties and solvent resistance [7-12]. Still, several applications of these polymers are only achieved through their nanocomposites. However, the limiting factors for processing and application of aromatic polyamides (aramids) (e. g. poor solubility in common organic solvents and extremely high transition temperatures) have been improved for semi-aromatic polyamides [13-18]. The polyamide/montmorillonite nanocomposites have recently raised so much attention as they offer tremendous applications in coatings, flame retardant agents and barrier and electronic materials and the advances toward their applications have been recently studied in details [19].

Incorporating of pyridine and its derivatives has been already reported to improve thermal stability of the polymeric matrices [20-23]. The rigid hetero-aromatic pyridine

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ring develops thermal and chemical stability of polymers while the polarizability of nitrogen atom can improve the solubility in organic solvents. Pyridine containing polymers easily undergo chemical modifications. Protonation or alkylation of the heterocyclic nitrogen atom, for instance, improves optical properties of polymers once used as luminescent (fluorescent) materials [24, 25].

The global reliance on petroleum-derived plastics along with growing environmental concerns has motivated developments in production and application of bio-based polymers [26]. Bio-based materials are fabricated using plant-derived substances as their main ingredients. These substances, as sustainable and eco-efficient products, can substitute the petrochemical-derived stocks. Their ingredients are normally a renewable resource and generally do not contain environmentally hazardous substances [27-30].

The present study deals with the synthesis of new semi aromatic polyamide (PA) and its subsequent nanocomposites with organically modified montmorillonite. Different properties of the developed nanocomposites are presented. Interesting findings on improvement of flame retardancy and thermal properties of the nanocomposites are discussed here.

2. Experimental

2.1. Materials

Oleic acid, 4-nitroacetophenone, 4-dimethylaminobenzaldehyde, ammonium acetate, N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), dimethylformamide (DMF), palladium charcoal, potassium permanganate (KMnO₄), hydrazine hydrate, pyridine, glacial acetic acid, ethanol, methanol and triphenyl phosphite (TPP) (all

purchased from Merck) and MMT-Na⁺ (Southern Clay Products, Inc.) were used without further purification. Commercially available calcium chloride (CaCl₂, Merck) was dried under vacuum at 150 °C for 6 h.

2.2. Monomer Synthesis

Synthesis of azelaic acid from oleic acid

Azelaic acid was synthesized through the oxidation of oleic acid's double bond using KMnO₄, following the procedure already reported in ref. [31] (Yield: 63 %).

4-(4-dimethylamino)phenyl)-2,6-bis (4-nitrophenyl)pyridine

In a 500 mL round-bottom flask, a mixture of 6.0 g (41 mmol) 4dimethylaminobenzaldehyde, 13.5 g (82 mmol) 4-nitroacetophenone, ammonium acetate (excess) and 150 mL glacial acetic acid was refluxed for 24 h. Upon cooling, the precipitated orange solid was collected by filtration and washed with ethanol. The yield of the crude product was 57%. Other specifications include m.p. 268-270 °C; FTIR (KBr): 3066 (s, br), 1591 (s), 1520 (s), 1440 (s), 1346 (s), 1208 (m), 1107 (s), 856 (s), 810 (s) and 731 (m) cm⁻¹. ¹H-NMR (DMSO-d₆, TMS) δ : 8.6 (4H), 8.4 (6H), 8.0 (d, 2H), 6.8 (d, 2H) and 2.9 (s, 6H) ppm.

4-(4-dimethylamino)phenyl)-2,6-bis(4-aminophenyl)pyridine

In a 250 ml round-bottom flask equipped with a reflux condenser and a dropping funnel, a suspension of the synthesized dinitro (5 g, 12 mmol) and palladium on carbon 10 % (0.1 g) in a mixture of ethanol (30 mL) and DMF (5 ml) was prepared. While heated to 80 $^{\circ}$ C and being stirred magnetically, a solution of hydrazine monohydrate 80 % (10 ml) in ethanol (15 ml) was added dropwise through the dropping funnel over 1 h. After 4 h, the mixture was filtered, yet too hot to remove Pd/C, and the solvent was

evaporated in vacuum to afford the orange solid product. Yield (%)=95; m.p. (°C) =118-120; FTIR (KBr): 3056 (m, br), 1593 (s), 1542 (s), 1512 (s), 1348 (s), 1276 (m), 1109 (m), 852 (m), 819 (s) and 690 (m) cm⁻¹. ¹H-NMR (DMSO-d₆, TMS) δ: 8.6 (d, 4H), 8.4 (m, 6H), 7.9 (d, 2H) and 6.8 (d, 2H) ppm.

1,4-bis(4-aminophenoxy)butane

1,4-bis(4-aminophenoxy)butane (APB) was synthesized according to the procedure reported in ref. [32].

2.3. Synthesis of semi aromatic polyamide (PA)

In a 50 mL round-bottom flask fitted with a stirring bar, 4-(4-dimethylamino)phenyl-2,6-bis(4-aminophenyl)pyridine (5.32 g, 14 mmol), azelaic acid (2.7 g, 14 mmol), calcium chloride (0.5 g, 4.5 mmol), triphenyl phosphite (8.7 mL, 28 mmol), pyridine (1 mL) and N-methyl-2-pyrrolidone (9 mL) were mixed and heated at 120 °C and refluxed in an oil bath for 10 h. Subsequently, the reaction mixture was poured into 200 mL methanol. The precipitated product was collected by filtration and rinsed thoroughly with hot methanol. Finally, the product was dried at 70 °C for 10 h inside a vacuum oven (Yield (%) =97).

2.4. Surface modification of montmorillonite

The surface modification of montmorillonite was carried out by a cation exchange reaction between MMT-Na⁺ and the ammonium salt of APB to yield MMT-APB [33]. Briefly, 5 g MMT-Na⁺ montmorillonite was suspended in 700 mL distilled water at room temperature and stirred overnight. In another flask, 2 g APB was dissolved in 40 mL distilled water under magnetic stirring and the pH was adjusted to 3-4 using 1.0 M HCl aqueous solution. After stirring for 3 h, the second solution was added to the MMT

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suspension at a rate of approximately 15 mL min⁻¹ while vigorously stirring. The mixture was stirred overnight at room temperature. The dark violet precipitates were filtered using a Buchner funnel and washed at least four times to remove any excess ammonium ions. The product was dried in a vacuum oven at 60 °C for 24 h.

2.5. Synthesis of PA/organoclay nanocomposite

The nanocomposite was prepared by mixing the appropriate amounts of PA and MMT-APB. To achieve a uniform dispersion of montmorillonite platelets in the PA matrix, the mixture was vigorously agitated at 25 °C for 24 h. The nanocomposite was prepared in different concentrations of MMT-APB. The nanocomposites containing 3 and 6 wt. % MMT-APB (PANC 3 and PANC 6) were prepared by adding 0.97 g and 0.94 g PA into 50 mL flask containing 5 mL DMAc followed by the addition of 0.03 and 0.06 g MMT-APB, respectively. The reaction mixture was agitated overnight at 25 °C. The nanocomposites were obtained by pouring the hybrid solutions into petri dishes, followed by solvent evaporation under reduced pressure.

2.6. Characterization

Fourier transform infrared (FT-IR) data were recorded on Galaxy series FT-IR 5000 spectrophotometer (England). Vibration transition frequencies were reported in terms of wave number (cm⁻¹). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). For sample preparation, the powdered species were mixed with KBr and pressed in form of pellets and used for further characterization.

¹H NMR measurements were performed using a Bruker Avance III 500 spectrometer (Rheinstetten, Germany) operating at 500 MHz (¹H). DMSO-d6 was used as the solvent and the solvent signal was used for internal calibration (DMSOd6: δ (¹H)=2.5 ppm).

Molar mass (weight-average (M_w) and number-average (M_n) molecular weights) determination was performed by size exclusion chromatography (SEC) using Agilent Series 1100 (Agilent) system equipped with a pump, degasser and differential refractive index (RI) detector. Two Zorbax PSM Trimodal-S 250 mm x 6.2 mm columns (Rockland Tech, USA) were used. The measurements were performed using a mixed eluent N, N-dimethylacetamide (DMAc) with 2 vol% water and 3 g/L LiCl at a flow rate of 0.5 mLmin⁻¹. The molar mass was calculated after calibration with poly(2-vinylpyridine).

Solid state UV-Visible spectrum was recorded at room temperature in 190-790 nm spectral regions using a Cary 6000i UV-Visible/Near-infrared spectrophotometer (Varian).

Photoluminescence (PL) spectra were investigated using a Fluorolog 3 (Horiba JobinYvon, USA) fluorescence spectrophotometer.

The morphological analysis was carried out using transmission electron microscopy (TEM) on a LEO 912 microscope operated with an acceleration voltage of 120 kVat room temperature in bright field illumination mode.

Wide angle X-ray scattering (WAXS) was performed using 2-circle diffractometer XRD 3003 θ/θ (GE Inspection Technologies /Seifert-FPM, Freiberg, Germany) using Cu-K_a radiation (= 0.154 nm) generated at 30 mA and 40 kV in the range of $2\theta = 2^{\circ}$ - 12° with 0.05° as the step length.

The thermal stability of the samples was measured by thermogravimetric analysis (TGA, TA instruments Q 5000) in the range between room temperature and 700 °C at a heating rate of 10 °C/min in nitrogen atmosphere. The thermal properties of samples were

measured by differential scanning calorimetry (DSC, TA instrument Q1000) in the range between -80 °C and 230 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

Microscale combustion calorimeter (MCC-1, FTT) was used for the investigation of flammability of the samples [34, 35].

Quantum Chemical Calculation

The density functional theory (DFT) with a three-parameter Becke-style hybrid functional (B₃LYP) was adopted for the calculations of the electronic structures of the PA [36]. The structure was optimized using the PA segment unit with terminal hydrogen. The $6-311^{++}G(d,p)$ basis set was utilized for the geometry optimizations [37, 38]. All calculations were performed using the Gaussian-03 D.02 [39] program package.

3. Results and discussions

3.1. Synthesis of the monomers

Oleic acid, being the precursor for the synthesis of azelaic acid, is a monounsaturated 18-carbon fatty acid mostly found in animal fats and vegetable oils. The oxidation of unsaturated oleic acid in presence of potassium permanganate yields azaleic acid.

Chichibabin method was used for preparation of dinitro compound containing pyridine group (Scheme 1) [40, 41]. In particular, the condensation of 4dimethylaminobenzaldehyde along with 4-nitroacetophenone in presence of ammonium acetate afforded the dinitro compound in one step. This product was subsequently reduced using hydrazine monohydrate and as a catalyst palladium on charcoal (10%) was used.



Scheme 1. Synthesis route of the diamine

3.2. Synthesis of PA

The PA was synthesized via direct polycondensation reaction of an equimolar mixture of azelaic acid with the aromatic diamine (Scheme 2).



Scheme 2. Schematic representation of the synthesis of PA

In order to investigate the electronic structure of PA and the repeated position of groups, computational calculations at $B_3LYP/6-311++G(d,p)$ level were used. Fig. 1 demonstrates the optimized molecular structure of PA.



Figure 1. Theoretical optimized spatial structure for ground state of PA

The ¹H-NMR spectrum of PA is displayed in Fig. 2. The appearance of N-H protons at 10.1 ppm is indicative of the amide groups in the main chain. The CH_3 proton is evident at 3.0 ppm while the resonance of aromatic protons occurs in the range of 6.9-8.3 ppm and CH_2 protons of the CH_2 group appear in the range of 1.8-2.3 ppm.



Figure 2. ¹H NMR spectrum of PA in DMSO-d₆

The SEC measurement of the synthesized PA exhibited number-average molecular weight (M_n) and weight-average molecular weight (M_w) of *ca*. 22800 and 48100 g/mol, respectively, according to poly(vinyl pyridine) (PVP) standard. The polydispersity index is 2.1.

Optical properties of PA

The optical properties of PA were investigated by UV-Vis and photoluminescence techniques. As shown in Fig. 3, PA exhibits strong UV-Vis absorption bands at 350–440 nm with a maximum absorption (λ_{max}) at 412 nm, assignable to π - π * transition resulting from the conjugation between the aromatic rings and nitrogen atoms. Photoluminescence spectrum of PA film shows a strong fluorescence at around 511 nm in green region.



Figure 3. UV-Vis and PL spectra of PA in the solid film

3.3. Preparation of PANC

Novel bio-based PANCs containing 3 and 6 wt. % MMT-APB (PANC 3 and PANC 6, respectively) were successfully prepared in dry DMAc media through a solution intercalation technique. The interaction of MMT-APB in polymer matrices can improve physical properties and morphology of the resulting nanocomposite.

3.4. Characterization of nanocomposite

FTIR study

Fig. 4 shows FTIR spectra of the neat PA and its nanocomposites. The FTIR spectrum of PA shows a peak at 3410 cm⁻¹ which has been assigned to the NH groups. In the spectrum of the nanocomposites, the presence of a peak at 1040 cm⁻¹ corresponding to the Si–O bonding and peaks at 400–600 cm⁻¹ corresponding to Al–O and Mg–O bondings indicated the incorporation of organoclay in the PA matrix. It can be concluded that the PANCs have characteristic pick not only for neat PA bands, but also for organoclay.



Figure 4. FTIR spectra of PA and PANCs

Nanocomposite structure

XRD technique is widely used to investigate the dispersion degree of montmorillonite in matrices. Intercalated and/or exfoliated polymer/montmorillonite nanocomposites can be classified based on displacing of the peak in terms of the gallery height of the montmorillonite.

A diffraction peak around $2\theta = 8.9^{\circ}$ corresponds to *d*-spacing of 9.9 A° for the layered silicates in MMT-Na⁺ (Fig. 5). For MMT-APB, a strong peak at $2\theta = 6.6^{\circ}$ resulted from diffraction of the crystal planes of layered silicates indicates that layered silicates have been intercalated by APB molecules to a *d*-spacing of 13.4 A°. This is consistent with the idea that *d*-spacing of the layered silicates in MMT-APB increase due to the size of swelling agent. According to Bragg's law, a shift in 20 value from higher to lower level is indicative of an increase in d spacing [29]. The XRD patterns of PANC 3 and PANC 6 display peaks at $2\theta = 4.2^{\circ}$ and 4.1° , respectively. This might result from partial exfoliation or intercalation with d-spacing of 21.03 and 21.5 A°. The intensity of peaks increased in PANC 6 due to the extensive agglomeration of MMT-APB [42].



Figure 5. XRD pattern of MMT-Na⁺, MMT-APB, PA, PANC 3 and PANC 6

TEM investigation was carried out in order to observe the morphological structure of the PANCs (Fig. 6). The TEM micrograph of PANC 3 (Fig. 6a) enlightens both areas with intercalation and areas with exfoliation morphologies. PANC 6 also showed a non homogeneous distribution in orientation and size (Fig. 6b). Moreover, a higher level of aggregation was observed with increasing the quantity of MMT-APB. The observed aggregation of the nanolayers could be attributed to strong van der Waals interactions of nanolayers especially at higher concentrations. The formation of hydrogen bonds between the nanolayers and the PA matrix does not suffice to counterbalance the strong van der Waals interactions between nano-layers at higher concentrations.



Figure 6. TEM images of PANC 3 (a) and PANC 6 (b)

Thermal properties of nanocomposites

The thermal degradation of PA and the corresponding nanocomposites with different MMT-APB loadings were studied under different environments by TGA. The consequent weight loss versus operating temperature under nitrogen and air environments are plotted as shown in Fig. 7 and 8, respectively.

According to the TGA investigations, the effect of the selected atmosphere on degradation of the PA and PANCs is significant. As observed from Fig. 7 and 8, the nanocomposite undergoes single-stage decomposition in the nitrogen atmosphere and double-stage decomposition in the air atmosphere. Under air, the first stage of degradation reaction is observed between 325 °C and 400 °C for PA and between 300 °C and 500 °C for PANCs. This initial reaction step was close to the one observed under nitrogen (between 350 °C and 500 °C). The second stage of the decomposition under air appeared between 400 °C and 600 °C for PA and between 500 °C and 700 °C for PANCs.

Since it is not observed under nitrogen, this step might be oxidative in nature. It is also notable that PA and PANCs treated in air exhibited faster degradation compared to the corresponding samples treated in nitrogen.

Detailed TGA data, i. e. 5% ($T_{initial}$) and 10% (T_{10}) weight loss temperatures and char yield for PA and PANCs, in nitrogen and air environments are summarized in Table 1. The observed decomposition temperatures $T_{initial}$ and T_{10} in air atmosphere are almost the same as compared with the data in nitrogen atmosphere; this suggests that the presence of oxygen does not influence the thermal stability of the nanocomposites. Also, PA and nanocomposites retain lower residue in air compared to the nitrogen atmosphere. This could stem from the thermal oxidative degradation of the polymer chain in the presence of oxygen; i. e. the presence of oxygen had caused a higher degree of cleavage of amide groups at high temperature.

PA and the nanocomposites showed slight weight loss below 200 °C in both environments which could be due to removal of moisture or monomer remains. After adding MMT-APB, both the nanocomposites were more thermally stable than neat PA, showing significant increase in $T_{initial}$ and T_{10} . This enhancement in the thermal stability could be associated to the presence of montmorillonite nanolayers with high thermal stability and the great barrier properties that maximize the heat insulation. However, as can be seen in Table 1, $T_{initial}$ and T_{10} decreased for PANC 3 with addition of MMT-APB in air atmosphere. It might be due to the presence of oxygen and oxidation effect of MMT-APB.

The glass transition temperature of PA and the nanocomposites were investigated by DSC technique and the resulting data are summarized in Table 1. The incorporation of

aliphatic and side chain units into the polymer back-bone results in the formation of PA with low glass transition temperature (T_g) (143 °C). The TGA analysis in Table 1 illustrates a systematic increase in T_g value of nanocomposite showing interaction between two phases. In fact, the incorporation of silicate layers reduced the segmental motion of polymer chains and shifted the baseline of DSC curve towards higher temperature.



Figure 7. TGA analysis for PA and PANCs in N₂ atmosphere



Figure 8. TGA analysis for PA and PANCs in air atmosphere

Table 1. Summarized TGA analysis data for PA and PANCs

	Thermal properties in air			Thermal properties in N ₂				
Samples	$T_{initial}(°C)^a$	$T_{10}(°C)^{b}$	Char yield ^c	$T_{initial}(^{\circ}C)$	$T_{10}(^{\circ}C)$	Char yield	$T_g^{\ d}$	
PA	287	365	29.7	243	323	61.7	143	
PANC 3	241	348	30.8	275	374	64.0	145	
PANC 6	283	397	31.7	264	381	67.1	152	

^a Temperature at which 5% weight loss

^b Temperature at which 10% weight loss

^c Weight percentage of material left after TGA analysis at a maximum temperature of 800°C

^g glass transition temperature was recorded by DSC at a heating rate of 10 °Cmin⁻¹ in N₂

Flame retardant properties

In order to study the flammability of PA and nanocomposites, microscale combustion calorimeter (MCC) was used and the heat release rate (HRR) versus temperature were

plotted (Fig. 9). The measured parameters for all samples including heat release rate (HRR) (calculated from the oxygen depletion measurement) and total heat release (THR) (obtained by integrating the HRR curve) are shown in Table 2. It was observed that PA has a peak HRR (pHRR) value of 111 W/g and THR value of 13.7 KJ.g⁻¹. PA showed low pHRR value and high char yield amount due to high aromatic content and presence of pyridine groups (see Table 1). The char residue formation in PA and its nanocomposites brings in good flame retardancy properties. However, as observed in Fig. 8, the HRR curve pattern for PA is significantly different from that of PANCs. In particular, once compared to PA, pHRR and THR values decrease by introducing 3 wt. % MMT-APB. Further increase in loading MMT-APB up to 6 wt. % will cause decrease of pHRR and THR to lower values (76 W/g and 10.9 KJ.g⁻¹, respectively).

The relative decrease of pHRR and THR values of PANC 3 and PANC 6 compared to PA, suggests that MMT-APB has a high efficiency on improving the flame retardancy. Also, the shape of HRR/temperature curves seem slightly more smooth in case of PANCs compared to PA, which means the decomposition of PA have been affected by introducing MMT-APB into the polymer backbone.



Figure 9. Temperature-dependent HRR analysis for PA and PANCs obtained by microscale combustion calorimetry (MCC)

Table 2. MCC ar	nalysis data		
Samples	PA	PANC 3	PANC 6
pHRR (W/g)	111	86	76
THR (KJ.g ⁻¹)	13.7	13.6	10.9
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pHRR=peak heat release rate; THR=total heat release

4. Conclusions

New PA nanocomposite was fabricated by solution intercalation method. The polyamide was synthesized with desired molecular weight by polycondensation reaction between heterocyclic diamine and bio-based azelaic acid. The introduction of bulky, electron-donating trialkylamine, pyridine and aliphatic groups disrupted the copolanarity

of aromatic units in polymer chain and hence increased the flexibility. As this could also cause an increase in inter-chain spacing (free volume), enhanced solubility and improved glass transition temperature of PA are expected as well. TGA analysis in air and nitrogen atmosphere showed that the PA leaves a high amount of char residue. In comparison to PA, organoclay incorporated PA exhibited enhanced thermal stability and char yields. The improved thermal properties of PA nanocomposites were mainly attributed to the physical and heat barrier effect of MMT-APB. The MCC analysis suggests that the presence of organoclays imposes a good effect on the flame retardancy of PA by decreasing pHRR and THR values of nanocomposites. The concentration of MMT-APB plays a significant role on the flame retardancy of PA nanocomposites. An enhanced fire resistance was observed once the concentration of organoclay was reduplicated.

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