

Effect of organic modifiers on dispersion of organoclay in polymer nanocomposites to improve mechanical properties



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ABSTRACT

The hydrophilic/hydrophobic organoclays with varying quaternary ammonium substituents (QAS) were successfully synthesized and used as filler in unsaturated polyester (UPE) resin-organoclay nanocomposites to enhance mechanical properties. The organoclay-BQASMMT₁₈ (octadecyldimethylbenzylammonium bromide modified montmorillonite) with only 3 wt% in the UPE enhanced tensile strength, tensile modulus, flexural strength and elongation at break by the order of 4.6, 2.4, 2 and 2.4, respectively compared to the pristine UPE. The tensile strength and hardness of the UPE-organoclay nanocomposites were increased with increase in organoclay content in the nanocomposites. However, the tensile and flexural strength decreased with increased loading of BQASMMT₁₈ from 3% to 5 wt% due to less dispersibility of organoclay in nanocomposites. Moreover, dispersibility of hydrophobic organoclays in UPE nanocomposite is higher with respect of hydrophilic and pristine clay.

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1. Introduction

Nanocomposites are the hybrid materials containing the matrices such as ceramic, metal, and polymeric materials ingraining the nanomaterials [1,2]. Among them, polymers have relatively poor mechanical, thermal, and electrical properties when used in pristine form. However, lightweight, easy fabrication, exceptional processability, durability and relatively low costs of polymer matrices make them materials of choice in recent years [2,3]. Polymer nanocomposites with nanomaterials as fillers have been reported to exhibit enhancement of mechanical [4], thermal [5], flame-retardant [6] and barrier properties [7] without significant loss of transparency, toughness or impact strength [8]. Such filler loaded polymer nanocomposites are widely applicable in technology fields such as aerospace, construction, offshore applications, waterlines, and automotive industries [9,10].

Clays have stimulated much research interest as filler materials in composites due to their unusual mechanical, electrical, optical,

and magnetic properties [6,11,12]. Additionally, with their large surface area [13], high cation exchange capacity [14], possibility of easy modification [15,16], unique structural properties and nanometer sized platelets with very small cross-sectional area makes them attractive candidates as filler additives [16–18]. The first study on montmorillonite clay (MMT) based polymer nanocomposite was made by Okada et al. on polycaprolactam [19]. However, higher phase separation and agglomeration of organoclay in polymer nanocomposite was reported due to higher interaction of clay platelets in many polymer nanocomposites [20,21].

To avoid possible agglomerations and to produce structured polymer nanocomposite, modification of the MMT by organic surfactants has been widely practiced compared to other modification techniques [22]. The MMT with higher ion exchange capacity is generally converted to organoclay by exchanging the exchangeable inorganic cations such as Na⁺ and K⁺ with bulky organic ion based surface active agents [23,24]. Quaternary ammonium salts (QAS) are commonly used as surface active agents compared to the siloxane and phosphonium ion based surface active agents, due to their versatile functionalization, easy mode of modification and cost effectiveness [14,15]. The QAS with linear long carbon chain tends to arrange randomly in the basal space of the clay and resulted in increasing the basal spacing between the clay layers

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[14,15,25]. Similarly, benzyl substitution on the one end of long chain QAS was found to increase the basal spacing due to their steric complexity in vicinity to the charge moiety [14]. With the increase in basal spacing, monomers and polymers with different polarities can enter the inter layers of clay platelets and cause further separation, in other words exfoliation, which resulted into the polymer nanocomposite material with enhanced mechanical and thermal properties [2,22].

Unsaturated polyester (UPE) resin is one of the widely used thermosetting polymer because of their low cost, easy processing, excellent corrosion resistance and good thermal and electrical properties [24,26]. Mechanical properties, such as stiffness and strength of UPE have been enhanced by incorporating organoclay in UPE polymer matrix [27,28]. One of the first report with UPE-organoclay nanocomposite for the significant improvement in mechanical properties was reported by Kornmann et al. [29] wherein, the mechanical properties enhanced two times by dispersing 1.5 vol% clay in UPE-organoclay nanocomposite, which is highest among similar findings recently [28,30–32]. In addition, layer expansion and dispersity of other silicate filler such as sand, silica and aluminosilicate is not as high as organoclay in enhancing the mechanical properties of UPE nanocomposite with similar loading [21,33,34].

Ideally, it is sought to obtain desirable properties at minimum concentrations of the organoclay additives (1 to 5 vol%) as compared with conventional phase separated filler materials in a polymer nanocomposite (20–30 vol%) making the organoclays as preferential materials for filler applications [21]. However, till now, full exfoliation of organoclay in UPE has remained a difficult task to achieve. That is probably due to the organoclay in the UPE matrix is still in the form of multilayered stacks, with expanded galleries, rather than individual clay platelets.

Hence, in the present work an attempt has been made to improve the mechanical properties (such as tensile, flexural and impact strength) of UPE-organoclay nanocomposite. The preparation and characterization of UPE-organoclay nanocomposite using clays with varying lipophilicity have been investigated. The distribution of pristine and organoclay platelets in UPE matrix is investigated by scanning electron microscopy. The correlation of hydrophobicity/lipophilicity of clay to its degree of exfoliation and its subsequent effect on mechanical properties of UPE-organoclay nanocomposite is not reported so far to the best of our knowledge.

2. Experimental section

2.1. Materials

The resin used to prepare nanocomposites was general purpose Polyester resin, PATPOL 32-01, obtained from Patel Polymers, Ahmedabad, Gujarat, India. The typical properties of UPE resin having viscosity 400–500 cPs at 25° C and specific gravity 1.075 at 25° C. Methyl ethyl ketone peroxide (MEKP) was used as catalyst and cobalt octoate as promoter for curing process, and these were provided by Patel Polymers, Ahmedabad, Gujarat, India. MMT was obtained from Jani clays, Ahmedabad, Gujarat, India; which is refined bentonite clay with CEC 120 meq/100 g. The organoclays LQASMMT n and BQASMMT n , (where $n = 14, 16$ and 18 carbon chain length and L and B denotes linear/aliphatic and benzyl/aromatic nature of substituents respectively) were prepared at our laboratories as per our previous report [14].

2.2. Synthesis and characterization of organoclays

Organoclays were prepared by following an ion-exchange process reported with a detailed synthesis and characterization

method in our previously published work [14]. In brief, the Stoke's law of sedimentation was performed on MMT lumps to obtain pure MMT (P-MMT) and P-MMT was added in an aqueous 0.01 M QAS solution to reacted for 45 min at 70° C under drop-wise addition followed through pH adjustment to 3–4 by HCl under continuous stirring condition for 30 min. The product was then washed by centrifugation and dried overnight at 80–90° C in oven and passed to 200 mesh sieve. The organoclays were prepared by an ion-exchange process with the use of LQAS n and BQAS n were named as LQASMMT n and BQASMMT n , respectively (where $n = 14, 16$ and 18 carbon chain length). The loading of the QAS was confirmed by the analytical techniques [14]. A schematic representation shown in Fig. 4 is perceived illustration of the organoclay preparation via surfactant loading.

2.3. Synthesis of nanocomposites

UPE-organoclay nanocomposites were prepared by using melt intercalation method. In this investigation, organoclay was swollen in UPE resin. Different amounts *viz.*, 0, 1, 3 and 5% W/W of organoclay (organo-MMT), P-MMT were mixed with the UPE resin by means of a mechanical stirrer for 3 h at room temperature to obtain a homogeneous mixture, followed by degassing and vacuum to avoid oxidation of UPE resin. MEKP (methyl ethyl ketone peroxide) and cobalt octoate were added as a curing agent and hardener, respectively, for UPE resin, at a ratio of 100:1.4:1.4 by weight at slow stirring. The liquid mixture was then cast in a preheated, cleaned and releasing agent smeared molds (Teflon), followed by curing at room temperature for 24 h. To ensure complete curing, the nanocomposite with and without organoclays were post cured at 80° C for 4 h. The post cured nanocomposite were left in the oven and allowed to cool gradually to ambient temperature before removal from the molds. The cured UPE-organoclay nanocomposite were machined into different dimensions as per the standard specifications for running mechanical property characterization tests by different methods. The nanocomposite prepared by organo-MMT such as LQAS n , BQAS n and P-MMT clay were named as *m*LQMUPE, *m*BQMUPE and *m*MUPE respectively, where *m* corresponds to percentage weight of clay in nanocomposite (ranging from 0 to 5% (W/W)).

2.4. Instrumentation and techniques

Thermogravimetric analysis (TGA) was carried out with a Mettler thermal analyzer, TA4000. The specimen was heated from the ambient temperature to 700° C under nitrogen flow (100 cm³/min). For measuring the mechanical properties, the nanocomposites were prepared under hydraulic presses, having a maximum working pressure of 260 kg/cm², with a Teflon holder of 20 mm diameter. UTM (LLOYD LR10K PLUS) machine was used to measure tensile and flexural strength by ASTM-D638 at a speed of 5 mm/min, while the test specimens were rectangular in shape with a dimensions of 120 × 15 × 3 mm³. Minimum five samples were tested at room temperature for each measurements and the average values were reported. Hardness was measured as per ASTM D224 using a Blue Steel digital durometer (Shore D tester). Impact strength of the nanocomposites was measured on impact tester made by central institute of plastics engineering and technology (CIPET), Ahmedabad, India as per ASTM D256 with a striking velocity was 3.46 m/sec. The notched samples for the Izod impact strength were prepared using special notch cutting tool. The average of five readings was reported. The morphology of the organoclay was analyzed by TEM analyzer model JEOL, JEM 2100. Scanning electron microscope (SEM) images for surface morphology were obtained with a JEOL JSM-6500F microscope.

3. Results and discussion

On the basis of our elaborated previous work on preparation and characterization of various organoclays, an understanding of the structure property relationship between QAS and MMT has been developed. The properties of the organoclays have been varied by changing size of chain length and type of other QAS substituents [14]. There are two important parameters which determine the compatibility of these organoclays with polymer matrix, one being the *d*-spacing (inter layer spacing in organoclays) and the other being hydrophobicity [35]. Our previously reported data on *d*-spacing measured using XRD (see Table 1) is provided to support TEM studies carried out in current work. Table 1 suggest the loading of QAS remains same, meanwhile *d*-spacing and hydrophobicity (contact angle) were increased with increasing chain length and benzyl substituents (see Fig. 1).

Transmission electron microscopy (TEM) of P-MMT and organo-MMT has been shown in Fig. 2. The TEM is used to visualize and ascertain the arrangement pattern of platelets before and after modification of clay. The results obtained were correlated well with *d*-spacing of the organoclay obtained by XRD (see Table 1). In general, platelets are attached tightly in pristine clay due to presence of static interaction between clay platelets. However, static interaction is believed to be decreased after introducing QAS moieties in the organoclay and resulted in increased *d*-spacing and deagglomerated platelets in TEM images.

In Fig. 2, the micrographs A, B, and C represent the arrangements of the clay platelets in P-MMT, LQASMMT₁₈ and BQASMMT₁₈, respectively. Whereas the micrographs D, E and F represent the magnifying view of A, B and C respectively. In Fig. 2A and D, the clay platelets seems aggregated due to stronger surface charge interaction in it and very low basal spacing (*d*-spacing), which doesn't allow to peel off the clay platelets. As described earlier, the intercalation of QAS into basal planes of clay increase the *d*-spacing and interlayer spacing, which resulted in to increase exfoliation, shown in Fig. 2B and C. Fig. 2C and F shows the complete exfoliation of clay platelets due to intercalation of BQASMMT₁₈ while Fig. 2B and E shows less exfoliation of clay platelets modified by the intercalation of LQASMMT₁₈. Since the size of benzyl substituted QAS (BQAS), give rise to increase in basal space and decrease the charge interactions compared with the aliphatic substituted QAS (LQAS). The platelets segregation in organoclays is higher for the case of BQASMMT₁₈, which can be clearly seen in Fig. 2C and F, this can be attributed to less static interaction between platelets due to increased *d*-spacing.

3.1. Characterization of polymer-clay nanocomposites

The UPE-organoclay nanocomposites, prepared from pristine and organoclays were characterized thoroughly. As the melt compounding of UPE resin and organoclays is the viable method to prepare nanocomposites, for which it is necessary for organoclay to

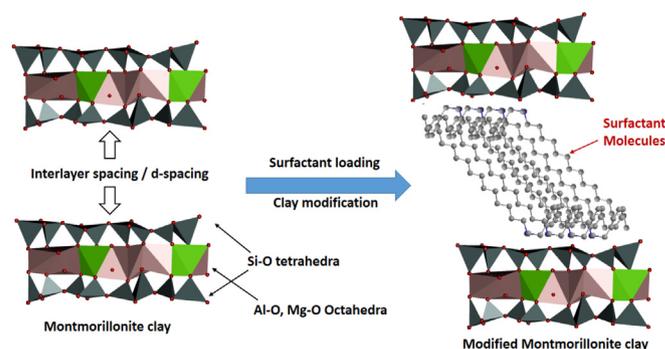


Fig. 1. Schematic representation of clay modification with various Quaternary Ammonium Surfactants (QAS). The increase in inter layer spacing (*d*-spacing) is depicted due to intercalation of surfactant molecules in clay layers [14].

withstand the high processing temperature, to find the presence of the organoclay in the nanocomposites by measuring the ignition loss of polymer-clay nanocomposites through thermogravimetric analysis.

Thermogravimetric analysis of pristine UPE resin block and UPE-clay nanocomposites having 3% (W/W) of P-MMT and organo-MMT, are shown in Fig. 3. It is evident from the thermal analysis that all the organoclays composites and pristine clay composite decomposed almost in the same temperature range, indicating the similar thermal stabilities of all the clay nanocomposites. However, the main difference was found in the weight after decomposition. The weight of pristine UPE nanocomposite after decomposition was 7.43%, however, for the case of MUPE, LQMUPE₁₈ and BQMUPE₁₈ were 4.05%, 3.65% and 3.81%, respectively. The difference in the residue weights after decomposition is due to the decomposition of present clays in the UPE and identical loading of clay in nanocomposite. Which only suggest the presence of clay materials in the UPE nanocomposites with a uniform amounts.

3.2. Mechanical properties of clay nanocomposite

Mechanical properties of polymer nanocomposites generally depend on factors such as nature and content of the filler. The extent of interaction of the filler with polymer matrix and the uniformity of dispersion of the filler within the matrix [2,5]. It would be interesting to measure two parameters namely surface hardness (Shore D hardness) and impact strength (measure of toughness) for the nanocomposites to evaluate the effect of fillers. The surface hardness is a property measured in lateral direction, whereas the modulus is measured longitudinal direction to the filler loading [36]. The measured values of Shore D hardness are illustrated in Fig. 4, where, the surface hardness values of UPE nanocomposite, UPE-organoclay nanocomposite such as MUPE, LQMUPE₁₈ and BQMUPE₁₈ are in the range of 60–65 Shore D. It also can be observed that, the incorporation of P-MMT into UPE-clay

Table 1
QAS loading, *d*-spacing and contact angle of clays.

Sample	Amount of QAS loaded (mmol/g)	<i>d</i> -spacing (Å)	Contact angle (°)
P-MMT ^a	—	12.8	76
BQASMMT ₁₈	0.74	24.2	127
BQASMMT ₁₆ ^a	0.68	23.6	118
BQASMMT ₁₄ ^a	0.74	23.1	98
LQASMMT ₁₈	0.72	19.6	77
LQASMMT ₁₆ ^a	0.70	18.9	72
LQASMMT ₁₄ ^a	0.75	17.4	69

^a As per our previous report [14].

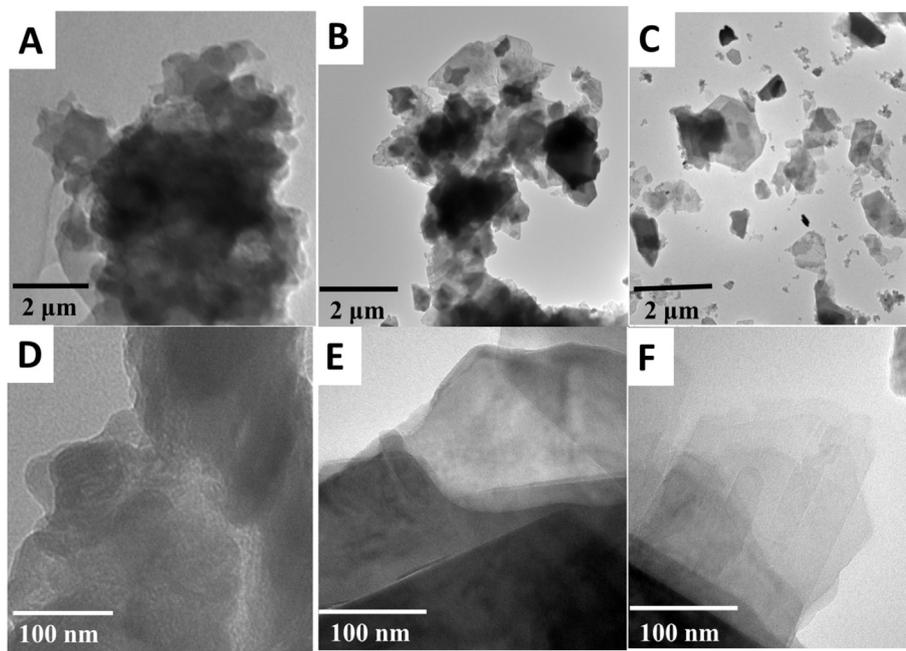


Fig. 2. Transmission electron microscopy of organoclays: transmission electron microscopy images of platelets of A. P-MMT, B. LQASMMT₁₈ and C. BQASMMT₁₈. D, E, and F represents magnification of images represented in A, B and C respectively.

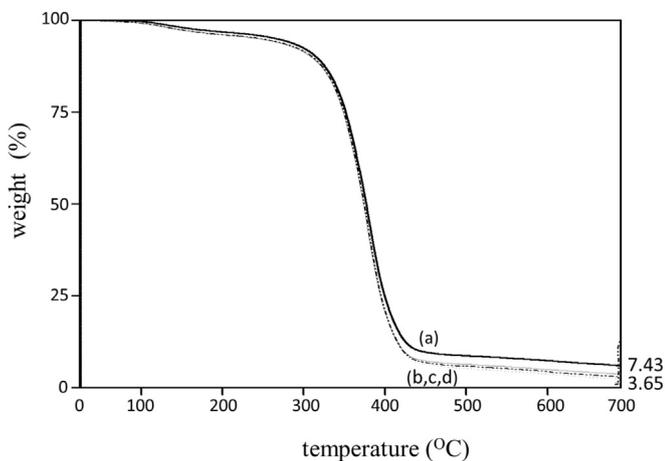


Fig. 3. Thermal analysis of composites: thermogravimetric analysis showing decomposition of (a); UPE polymer block, (b), (c) & (d) polymer nanocomposites of 3MUPE, 3LQMUPE₁₈ and 3BQMUPE₁₈.

nanocomposite (MUPE) show insignificant improvement in surface hardness. Whereas, the values for BQMUPE₁₈ are significantly higher while that of LQMUPE₁₈ are marginally higher when compared to hardness values of MUPE. This is indicative of better interaction and uniform dispersibility of BQAS₁₈ treated organoclay platelets leading to effective exfoliation in the base matrix [14,15]. The intercalated/exfoliated clay platelets effectively restrict indentation and increase the hardness of the nanocomposites [17]. It is worth noting that the increasing the content of clay additive in UPE resin gradually from 1% to 5% show proportional increase in Shore D hardness for the nanocomposites.

The impact strength evaluation is carried out to study the toughness of polymer nanocomposites. The impact strength of UPE nanocomposite is influenced by the filler such as P-MMT and organoclays with LQAS₁₈ and BQAS₁₈ modifier, which has been

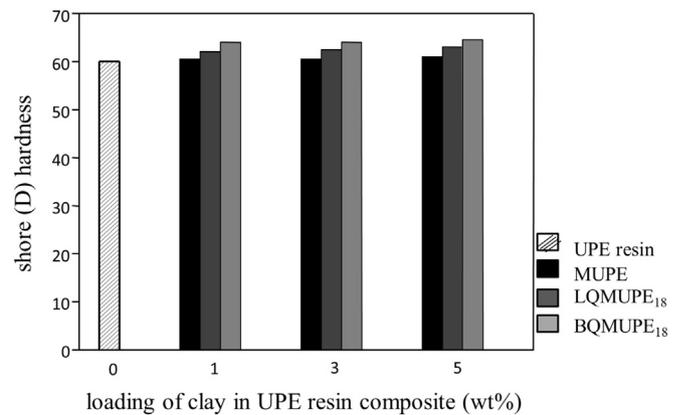


Fig. 4. Hardness comparison: comparison Shore D hardness of pristine UPE resin block and polymer nanocomposites of MUPE, LQMUPE₁₈ and BQMUPE₁₈.

shown in Fig. 5. The impact strength of the pristine UPE resin block (5.8 J/cm²) is higher than modifying clay UPE resin composite (2–2.8 J/cm²). From Fig. 5, it was noticed that a noticeable decrease in impact strength of the nanocomposites as an increase in filler content up to 3 wt% and further increase in filler content slightly reduces the impact strength. The reason for the decrease in impact strength was stiffness in materials due to the presence of clay particles. As the filler loading increase in nanocomposite, they tend to make agglomerate and resulted in stress active point. These stress points make nanocomposite to break easily and decrease the impact strength.

Meanwhile, tensile modulus, tensile strength and percentage elongation at break of UPE nanocomposites with and without clay with their loading amount represented in Figs. 5 and 6. Pristine UPE resin block has higher tensile modulus due to their having uniform surface. With increasing filler loading, the tensile modulus is found to be decreasing, this is because of the clay platelets altering the polymer matrix and thus disturbing the geometry of the polymer

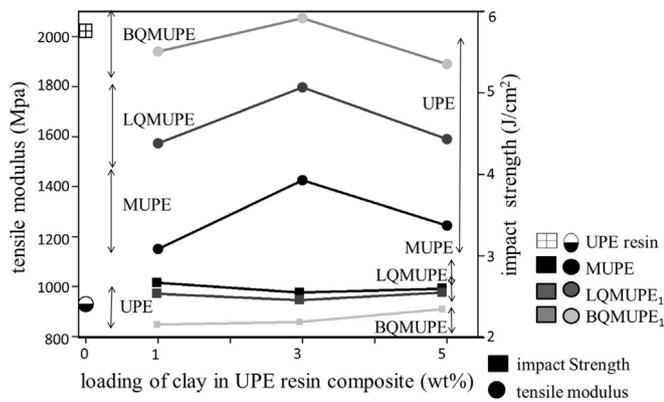


Fig. 5. Impact strength and tensile modulus of composites: impact strength and tensile modulus properties of pristine UPE resin block and polymer nanocomposites of MUPE, LQMUPE₁₈ and BQMUPE₁₈.

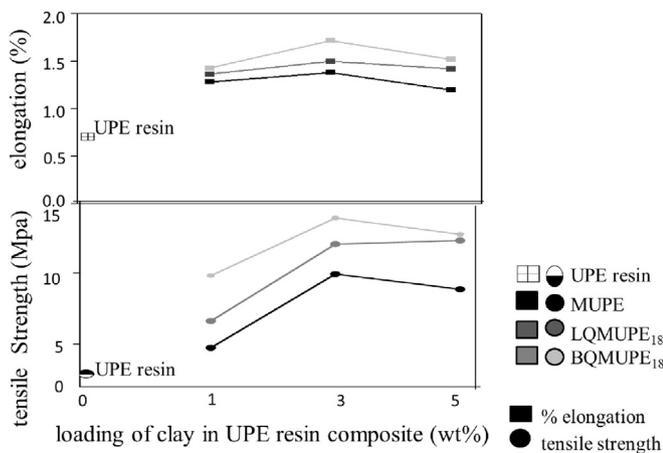


Fig. 6. Elongation and tensile strength measurements of Composites: elongation at break and tensile strength properties of pristine UPE resin block and polymer nanocomposites of MUPE, LQMUPE₁₈ and BQMUPE₁₈.

chain. The values of tensile modulus and impact strength behave inversely accordance with the behavior of the clay such as BQMUPE₁₈ has higher impact strength and lower tensile modulus. Tensile strength and elongation at break of pristine UPE resin block markedly increased from 3 MPa to 14 MPa and 0.7%–1.7% respectively after modified by 3BQMUPE₁₈ (shown in Fig. 6), which is a significant increase, 4.6 times in case of tensile strength and 2.4 times in case of elongation at break compared to pristine UPE. If we increase further loading of the clay, agglomeration starts dominating and adversely affecting by decreasing the tensile strength and elongation.

For the composites modified with LQASMMT₁₈ and P-MMT clays, results are in the similar order but the rise is not much as higher as compared to the BQASMMT₁₈ modified UPE-clay nanocomposite, indicating the role of hydrophobicity of the modifier in altering the mechanical properties of filler loaded nanocomposites.

As loading of the filler increases, polymer chain elongation also increases correspondingly, depending on the type of modifier. With the clay loading increasing in nanocomposite will lead to increase polarity in the polymer chain and polymer chain becomes more flexible due to branching distance increasing. Elongation 0.7%–1.7% increasing after loading of 3 wt% organoclay-BQASMMT₁₈ modified clay. As loading increases to higher wt%, elongation start rupturing the polymer chain and resulting in breaks in polymer chain of the

nanocomposite. Moreover, the elongation is directly related to tensile and flexural strength properties.

Fig. 7 represents the tensile modulus and flexural strength. Toughened nanocomposite give higher flexural strength compared to non-toughened nanocomposite. The toughness in nanocomposite is increased by the filler loading. Addition of organoclay has increased the flexural strength of UPE-clay nanocomposite. Maximum flexural strength on 3BQMUPE₁₈ which is 88 MPa, about double from the pristine UPE resin block at 42 MPa. When loading increased from 3 to 5% the flexural strength is decreased, attributed to the agglomerations of organoclays. Meanwhile increase in the strength with benzyl substitution (BQAS) is because of the higher intercalation and exfoliation of clay in the polyester resin which serves to effectively decrease the number of cross link in the nanocomposite. As described in Figs. 5 and 7, tensile strength and modulus, flexural strength, hardness and elongation have direct proportionality with the type and amount of filler loading while impact strength is inversely proportional to it. As the stiffness or hardness increased by increasing the loading of clay in the matrix increased tensile strength and modulus but due to the high hardness it would be broken easily through kinetic energy given by hammer and decreased the impact resistance. At higher loading the value of impact strength is low because of the high stress concentration points present in nanocomposite.

3.3. Structural investigation of composites through microscopy

The distributions of the clay in UPE polymer nanocomposite has been observed by TEM imaging. Micrographs of nanocomposites by TEM are shown in Fig. 8, which reveal the micro structures for polymer-clay nanocomposites treated with 3 wt% clays in UPE resin. The dark and bright regions correspond to the clay/organoclays and the UPE resin matrix, respectively. The Fig. 8A to F, clearly show the existence of organoclay clusters in UPE resin matrix with varying degree of dispersibility. Fig. 8A, corresponds to a 3% P-MMT added nanocomposite. A disordered structure is observed indicating poor clay dispersion attributed to strong inter-platelet interactions in pristine clay leading to effectively restricting polymer chains to enter within the galleries of clay. And therefore, there are some finely exfoliated clay layers and some un-exfoliated individual clay particles seen in the magnified micro-graph of MUPE (Fig. 8D). Fig. 8B and C corresponds to the nanocomposites LQMUPE₁₈ and BQMUPE₁₈ with corresponding 3% LQASMMT₁₈ and BQASMMT₁₈ clays respectively. Since, modification of clay with alkyl ammonium surfactant (LQAS) lowered the electrostatic interactions between clay layers, enlarged their intra-gallery spacing,

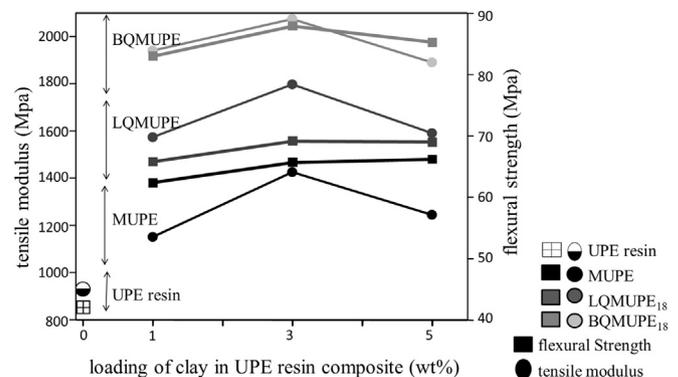


Fig. 7. Tensile modulus and flexural strength of composites: tensile modulus and flexural strength properties of pristine UPE resin block and polymer nanocomposites of MUPE, LQMUPE₁₈ and BQMUPE₁₈.

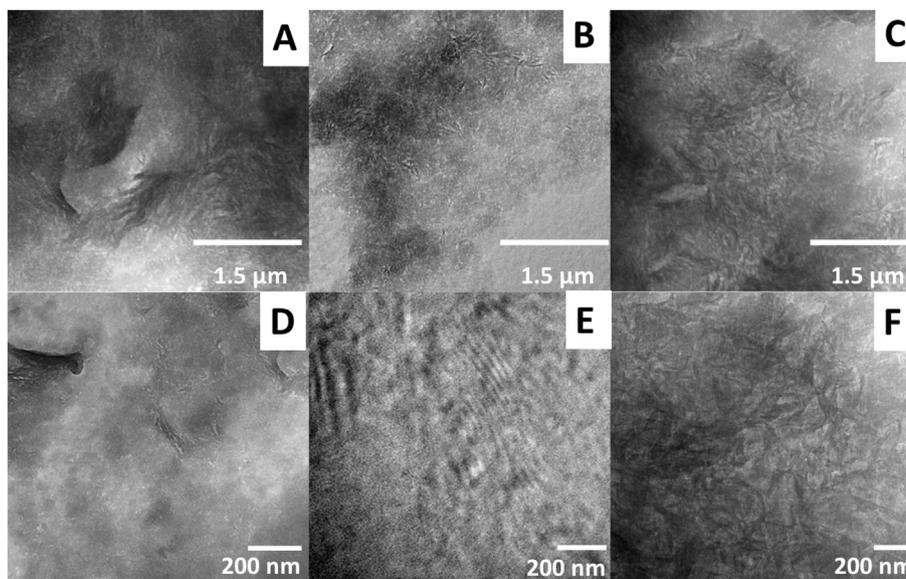


Fig. 8. Transmission Electron Microscopy images of polymer-clay nanocomposites, where dispersion materials are A. P-MMT, B. LQASMMT₁₈ and C. BQASMMT₁₈, respectively (3%W/W) D, E, and F represents of clays represented in A, B and C respectively.

and facilitated exfoliation and thus dispersion of clay in polymer matrix is observed. However in case of benzyl substituent (BQAS), the increase in the *d*-spacing is significant indicating significantly reduced interaction between platelets, which in turn is resulted in highly increased exfoliation shown in Fig. 2C and F. However, in contrast with Fig. 8A, these clusters possess a well aligned structure. This suggests that the hydrophobic/lipophilic clay has higher potential to exfoliate and generate highly ordered and uniform distribution.

SEM images of pristine UPE resin block and UPE-clay nanocomposite with 3% (W/W) filler loading are given in Fig. 9, along with the mapping of C, O, Si, Al, Na, K, Cl elements measured by EDAX. Surface morphology in the case of pristine UPE resin block is uniform which means polymer are distributed uniformly (see Fig. 9A1 and A2). However, surface roughness increases in the case of MUPE block, due to agglomerations of the clay in the polymer matrix and very poor distribution, significant amount of clay could be seen clearly in Fig. 9B1 and B2. In case of organoclay loaded resin blocks, LQMUPE₁₈ and BQMUPE₁₈ the SEM is indicative of the distribution of clays within polymer matrix corresponding to their properties. Benzyl substituted surfactant increased *d*-spacing of clay layers significantly and at the same time it hydrophobizes the clay [14], leading to better interaction with hydrophobic polymer chains of UPE resin. This causes extensive exfoliation of organoclay BQASMMT₁₈ in BQMUPE (Fig. 9D1 and D2). In comparison the clay with LQAS modifier, LQASMMT₁₈ is hydrophilic [14] and yet shows little exfoliation in polymer matrix (Fig. 9C1 and C2) for LQMUPE. This is because of the fact that organic modifier with alkyl chain sufficiently increases the *d*-spacing of clay, making the ingress of polymer possible with the interlayer, which leads to some degree of interaction between polymer chains with the chains of organic surfactants of clay and that results in little exfoliation of this clay in polymer matrix despite being hydrophilic.

Moreover, EDAX analysis proved presence of the clays on the surface based on the data of elemental analysis which are absent for the case of pristine UPE resin block (Fig. 9A3). The data of EDAX matches with the morphology seen in micrographs corresponding to UPE, MUPE, LQMUPE and BQMUPE. Fig. 9B3 suggest the presence of the unmodified clay on the surface by EDAX data base with the presence of Si, Al, Cl, Na and K elements on the data analysis.

Additionally, distribution of the clay becomes uniform through the increase in the hydrophobicity, resulted in uniform dispersion of the clay in the polymer matrix can see in Fig. 9D3. While for the clay modified with LQAS₁₈, distribution of the clay becomes less uniform due to lack of extensive exfoliation because of their surface charge and hydrophilic nature (Fig. 9C3). With reference to our previous work in the context of organoclays, the understanding of structure-property relationship is developed. Combining that knowledge with the present work of UPE-clay nanocomposites, the dispersion of clay in polymer matrix and its repercussions on the mechanical properties of the resultant nanocomposites, Fig. 10 is thematic illustration of clay structures and corresponding composites. In case of surfactants having benzyl substituent, the adsorption of these surfactants is governed by higher hydrophobicity, which resists the penetration of water and behave as a hydrophobic in nature, which is distributed uniformly in polymer matrix. However, linear surfactant is going to enhance hydrophilicity of clay due to increase the water adsorption and make agglomerates in polymer matrix.

Since the distribution in the polymer matrix is uniform and have less stress points in the polymer matrix which are modified by hydrophobic clay, enhance the mechanical properties except the impact strength due to the stiffness of the polymer matrix. The tensile and flexural strength is increase 4.6 and 2 times respectively. Moreover, increase the strength by increase in the loading in the filler concentrations, till the saturations. Above the saturation in the filler concentration increase the level of agglomerations and decrease the mechanical properties.

4. Conclusion

The present work throws light on how the nature of filler material affects the mechanical properties of nanocomposites. Organic modification of clays is a versatile tool to obtain organoclays with varying hydrophobicity which seems to be responsible to alter the hardness, tensile strength and thermal stability depending on effective dispersion in polymer matrix. However the amount of organoclay additive should be optimized as in all the cases, loading more than 3% W/W organoclay resulted in formation of agglomerates in nanocomposite which lead to poor mechanical properties

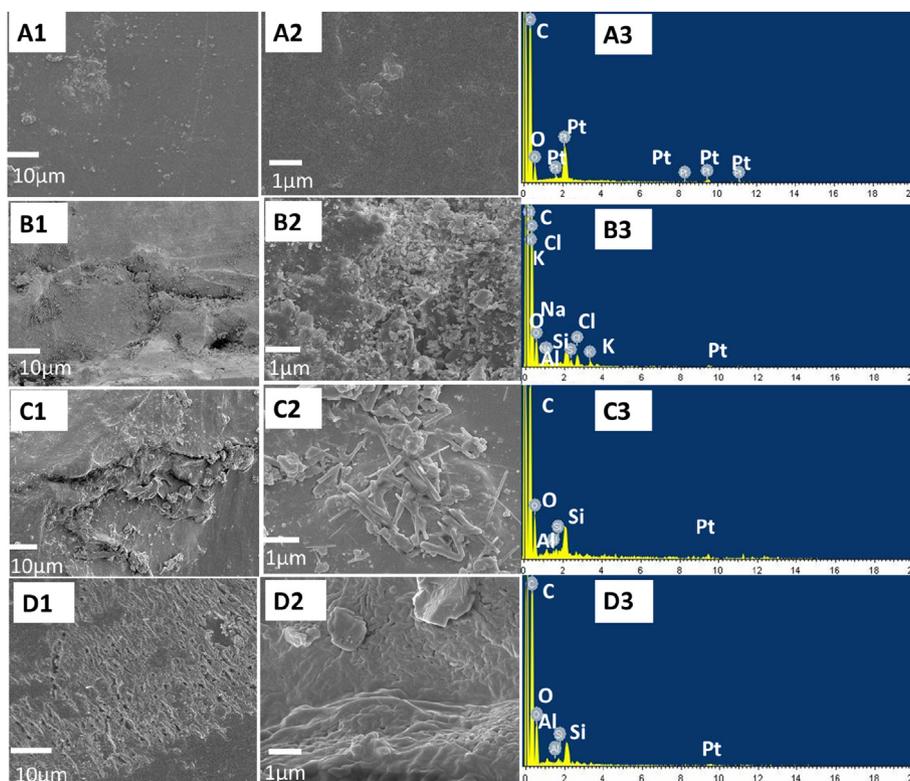


Fig. 9. SEM-EDAX Analysis of polymer-clay nanocomposites: Scanning Electron Microscopy and EDAX elemental analysis images of polymer-clay nanocomposites, where dispersion materials are A. Pristine UPE resin block, B. P-MMT, and C. LQASMMT₁₈ D. BQASMMT₁₈, respectively (3% W/W), meanwhile 1,2 represents the different magnification and 3 represent the EDAX data of corresponding clays.

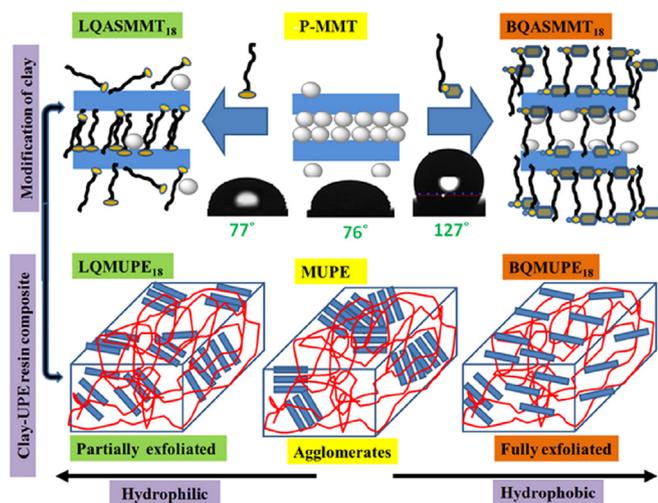


Fig. 10. Schematic diagram of polymer-clay composites corresponding to clay modification: schematic illustration of modification of clays and arrangement of P-MMT and organo-MMT on distribution of clays in UPE resin composites.

of the nanocomposite. The most effective organoclay filler was found to be BQASMMT₁₈ which induced the enhancement of tensile strength by 4.6 times compared to that of pristine polymer. The flexural modulus and elongation also enhanced by modifying nanocomposite by BQASMMT₁₈, benzyl terminated long chain surfactants. From the results reported here, it can be concluded that the lipophilic organoclays modified by QAS surfactants enhance distribution of the clay into the polymer matrix and resulting into higher mechanical strength and higher elongation. The impact

strength is the only parameter which shows a negligible decrease upon addition of organoclays. To the best of our knowledge this is one of the rare report where all three vital parameters such as (tensile strength, tensile modulus, flexural strength) are enhanced for a particular filler material in UPE resin.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2016.05.066>.

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