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ORIGINAL ARTICLE

Impact of mechanochemical treatment of organophilic Indian bentonites: implications for their rheology

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Abstract

To study and determine the dependency of rheological properties and flow behaviour of organobentonites on mechanochemical modification viz. grinding and preparation temperature of organobentonite, stearyldimethylbenzylammonium-bentonites (SDMBA-bentonites) were prepared by interacting stearyldimethylbenzylammonium chloride with Indian bentonite at different reaction temperature of 40, 60, 80, 90 and 100 °C and the products were ground and passed through sieve (micronization) of 100 mesh BSS (< 150 µm) and also the product obtained at 40 °C was further processed for micronization using 150 (< 105 µm), 240 (< 63 µm) and 350 (< 45 µm) mesh BSS sieves. As there was increase in the micronization and the reaction temperature, the bulk density and particle size decreased with simultaneous increase in the surface area of SDMBA-bentonites. The enhancement of the viscosity, rheological parameters and gel index of the toluene dispersions of these SDMBA-bentonites was also observed. The decrease in particle size and bulk density with simultaneous increase in specific surface area and swelling in nitrobenzene SDMBA-bentonites leads to the formation of larger hydrogen bond network to generate improved rheological properties by increased magnitude of chemical interaction between SDMBA cations and toluene. The rheological behaviour study revealed that all the toluene–SDMBA-bentonite dispersions exhibit the shear-thinning flow behaviour and the micronization and reaction temperature influence the degree of shear-thinning, stability of the gel structures and yield stress of the dispersions. The incorporation of a mixture of 5 vol% of H_2O in methanol as polar activator studied in the range of 33–100 wt% of SDMBA-bentonite reinforced the rheological properties, viscosity and gel volume, degree of shear-thinning, stability of the gel structures and yield stress of the toluene–SDMBA-bentonite dispersions. The SDMBA-bentonites with polar activator having concentration of 65 wt% exhibited the optimum rheological reinforcement. The rheological properties were found to be more enhanced by the ultrasonication relative to conventional stirring/shearing. Power law and Casson equations have been used to describe the rheological properties of the toluene–SDMBA-bentonite dispersions.

Keywords Bentonite · Organophilic · Rheology · Viscosity · Yield stress · Gelation

Introduction

Modification of clays by the interaction with organic moieties such as amines, quaternary ammonium compounds, quaternary phosphonium compounds, amides, polymers etc. has been extensively studied (Mortland 1970; Theng 1974, 1977, 2012; van Olphen 1976, 1977). Over past several years, scientists and researchers have dedicated their efforts towards the development of organoclays for their application as rheological modifier/thixotropic agent in products like paints, inks, adhesives, greases, varnishes, cosmetics, and medicines, etc. (Jones 1983; Murray 1991, 1999, 2000, 2007; Chtourou et al. 2006). The research has been focused with the perception of the adsorption of the organic liquids/media on organoclays during formation of dispersions; as well as swelling and thixotropic gel forming ability/behaviour of the dispersions produced (Jordan 1949; Jordan et al. 1950; Dekany et al. 1975, 1986a, 1986b, 1986c; Szanto et al. 1986).

The bentonite modified with diallyldimethylammonium chloride (DADMAC) and dodecyltrimethylammonium chloride (DTC) has been used as rheology modifier for paper

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coating performing as pseudoplastic fluid through their thickening and promoting rheological function (Liang et al. 2015). Paiva et al. (2008) have presented an overview on organoclay prepared using Qauts and biomolecules such as enzymes. The synthesis of these organoclays, their properties and applications in diverse field are described this research performance. The investigations reported so far are particularly focused on bentonite and polymer nanocomposites, an important area of the nanotechnology. The correlation between the degree of exfoliation of organoclay and the solvent used as dispersing agent has been studied by Ho and Glinka (2003). They have explained the behaviour with Hansen's solubility parameters, $\delta_{\mathrm{o}}^2 = \delta_{\mathrm{d}}^2 + \delta_{\mathrm{p}}^2 + \delta_{\mathrm{h}}^2$. The smectite nanocomposites (organoclay composites) have been reported to enhance the latex goods such as natural rubber, carboxylated styrene butadiene rubber lattices; their blends have been studied for their rheological behaviour and correlation with intercalation and exfoliation (Stephen et al. 2006). Sarkar et al. (2011) have studied the intercalation behaviour of two bentonites from Indian origin and their comparison with that of a high-purity commercial montmorillonite. They have observed the influence of Mg^{+2} and Fe^{+3} on the CEC which lead to the organic loading. In this study, rheological and colloidal behaviour of dispersions formed during the interaction of hexadecylamine (HDA) and Na-bentonite for preparation organoclay has been studied. The rheological and electrokinetic behaviour of aqueous montmorillonite dispersions was investigated as a function of solid content and HDA concentration (Yürdü et al. 2005).

The influence of the nature of clay, modifying ions/species and properties such as dielectric constant of organic media on physical gelation of organoclay in organic media has been studied (Gherardi et al. 1996). The interactions between anisotropic and swollen clay particles were reported to be accountable for gel formation of organoclay dispersion in organic media (Moraru 2001). The studies on effect of properties of the modifying organic moieties and the solvent/organic media on organoclay dispersions have been well documented in the literature (Jones 1983; Dekany et al. 1975, 1986b, 1986c; Hanley and Muzny 2003; Connolly et al. 2006; Powell 1982; Burba and McAtee 1981; Sobisch and Lerche 2000; Gast and Mortland 1971; Cody and Reichert 1986; Pluart et al. 2004). The effect of the organoclay preparation parameters on organoclay products has been studied (Theng 1974; Mortland 1970; Somani et al. 1991). Gonzaga et al. (2007) have studied the effect of two methods—the conventional method and direct method for the preparation of organoclays (organosmectites–organobentonites) on the physicochemical properties and applications of the organoclays derived. (Bhatt and Pandya 1992; Bhatt 1995) have systematically studied the preparation of organoclays under different preparation parameters and correlated their influence of these parameters on the surface properties of the organoclays prepared. Deligianni and Ekonomakou (http://eke.gr/j/images/files/keramika.pdf) have published a report on the research study on optimization of organophilization process and the effect of the processes on the properties of the organoclay nanocomposite products. Bhattacharya and Mandot (2014) derived the conclusions form the study of the cetyltrimethylammonium bromide (CTAB)-modified montmorillonite preparation and their surface and thermal properties with the conclusion that the incorporation of the CTAB augments the thermal stability of the Na-MMT. Hongping and others (2010) have reported the investigation of syntheses of organomontmorillonites and attempted to correlate the parameters with the properties. They have studied the different clays and different quaternary ammonium salts for these investigations. Thus, plenty of studies/investigations have been reported in the literature for effect of modification parameters of organoclays on the properties of organoclays produced. But the scanty literature on influence of the some particular preparation parameter on rheology of organoclay produced is documented. Recently, Calabrese et al. (2016) have reported the synthesis of non-ionic surfactant modified organoclay by functionalizing K10-montmorillonite with bio-compatible surfactant Tween 20. Further they have exercised the efforts to establish the correlation of the synthesis parameters and the physicochemical characteristics of the organoclays during this study. Further, the effect of the organoclay preparation parameters on organoclay products has been reported, but no reference was cited for systematic study on how the organoclay preparation parameters control and influence the flow/rheological properties of the organoclay dispersions. The objective of the present study was to investigate the influence of the different organoclay preparation parameters on the flow behaviour and rheological properties of the organic media-organoclay dispersion systems and to study their correlation and fitting of the data obtained to Power law and Casson models.

Materials and methods

Materials

Raw bentonite was procured from Barmer district, Rajasthan, India. Quaternary ammonium compound–stearyldimethylbenzylammonium chloride (SDMBAC) was obtained from Sigma Aldrich and used without further purification.

Preparation of SDMBA-bentonites

Raw bentonite was beneficiated by the sedimentation of 1% w/v clay suspension. The sedimentation technique based on Stokes' Law is simple and cost effective;

$$r^2 = \frac{9\eta h}{2(d1 - d2)gt}$$

where r denotes radius of given particle (assuming spherical, μ); h denotes height (cm) through which it falls in time "t" in minutes; g denotes Acceleration due to gravity; $d1$ and $d2$ denote densities of solid and liquid respectively; and η denotes viscosity of water.

The clay suspension was prepared by soaking the clay lumps in deionized water, in pre-calculated amount, overnight and stirred for about 30 min. The suspension was then allowed to stand for pre-calculated time and/or height using Stokes' law to obtain the particles having less than 2 μ (clay fraction) and to remove non-clay fraction and other impurities. The supernatant was collected as beneficiated bentonite suspension.

Recasting the XRF chemical analysis yields the following structural formula of the smectite present in the beneficiated bentonite is:

$(Si_{3.7}Al_{0.3})(Al_{1.33}Mg_{0.21}Fe_{0.46})O_{10}(OH)_2,\ X \rightarrow Na_{0.094},\ K_{0.06},\ Ca_{0.2}.$

Properties and chemical composition of pristine and beneficiated bentonite are carried out as per standard methods given in IS: Specification for bentonite [IS: 6186-1986 (R2003)] and XRF and results are presented in Table 1.

The SDMBA-bentonites were prepared by the interaction (cation exchange) of beneficiated bentonite (cation exchange capacity (CEC) of 93 milli-equivalent/100 g) with SDMBAC at 40, 60, 80, 90 and 100 °C following the procedure described previously (Bhatt and Pandya 1992; Bhatt 1995). The SDMBA-bentonite produced at 40 °C was powdered and sieved through 100 BSS mesh (< 150 µm), 150 BSS mesh (< 105 µm), 240 BSS mesh (< 63 µm) and 350 BSS mesh (< 45 µm) and denoted as SDMBA-bentonite-100M/40C, SDMBA-bentonite-150M, SDMBA-bentonite-240M and SDMBA-bentonite-350M, respectively. The SDMBA-bentonite products obtained by reaction at 60, 80, 90 and 100 °C were pulverized and sieved through 100 BSS mesh and denoted as SDMBA-bentonite-60C, SDMBA-bentonite-80C, SDMBA-bentonite-90C and SDMBA-bentonite-100C, respectively.

Table 1 Characteristics and chemical composition of pristine and beneficiated bentonites

Characteristics	Pristine raw bentonite	Pristine beneficiated bentonite
CEC (meq/100 g)	78	93
Swelling power (cc)	27	33
Gel formation index (cc)	96	100
XRD (glycolated oriented slide)–d spacing	–	17.80
Chemical composition		
Content, wt%		
SiO_2	55.65	55.14
Al_2O_3	23.15	23.30
Fe_2O_3	09.44	08.51
MgO	02.48	03.08
CaO	01.05	00.66
Na_2O	00.99	01.33
H_2O+	07.24	07.98

Characterization of pristine beneficiated bentonite and SDMBA-bentonites

Characterization of the pristine beneficiated bentonite and SDMBA-bentonites prepared in the present investigation was carried out by evaluating particle size distribution, bulk density, surface area and organophilicity. The particle size analysis of the dry powder was performed at a feed rate of 50% and at air pressure of 1 bar on Mastersizer 2000 (laser diffraction particle size analyser for particle size analysis from Malvern Instrument, UK). The specific surface area of the SDMBA-bentonites computed from the particle size analysis data and displayed with the particle size data of the Mastersizer 2000 (laser diffraction particle size analyser for particle size analysis from Malvern Instrument, UK). The bulk density of the SDMBA-bentonites was determined as per the standard method given in the IS: 1420-1959 (I.S.: 1420-1959) using Tap Density Tester (ElectroLab, India). The organophilicity was determined by the method described for Swelling/Gel Index (Jordan 1949) using toluene as solvent. The powder X-ray diffractograms of organoclays were recorded with X-ray diffractometer Miniflex II Tabletop (Rigaku, Japan) with CuKα radiation ($\lambda = 1.54178$) in the 2θ range 2–10. The BET surface area was measured by conventional standard method of nitrogen gas adsorption at liquid nitrogen temperature (77 K) using ASAP 2010 C (Micromeritics, USA). Before adsorption of nitrogen gas, the samples were degassed at the preoptimized condition of 70 °C in case of SDMBA-bentonites and 105 °C in case of upgraded pristine bentonite by purging helium gas at the rate of 14 ml/min.

Preparation of dispersion

The SDMBA-bentonite dispersions in toluene were prepared by applying either stirring or ultrasonicating to the toluene–SDMBA-bentonite mixtures. The experimental procedure used to study the toluene–SDMBA-bentonite dispersions using stirring/ultrasonicating is given below. The SDMBA-bentonite dispersions having 2 wt% SDMBA-bentonite concentration in toluene were prepared to study the effect of the organic density/amount of SDMBA-bentonite (assessable for the reaction with toluene and ultimately influencing their flow behaviour) on behaviour of the rheological properties by varying key variables such as stirring time (5, 15, 30, 60 and 120 min) and stirring speed (250, 500, 750 and 1000 rpm). Under the optimum condition of 30 min stirring time and 500 rpm stirring speed, the effect of SDMBA-bentonite concentration (1, 2, 3, 4 and 5 wt%) on the rheological properties of the toluene–SDMBA-bentonite dispersions was studied. The effect of polar activator was studied by adding a mixture 95v:5v (mixture of methanol and water (methanol/H_2O (95/5))) in the range of 33–100 wt% on basis of the SDMBA-bentonite to the previously mixed and being constantly stirred toluene–SDMBA-bentonite-mixtures having optimum SDMBA-bentonite concentration of 2 wt% at time as near to initiation of stirring and the mixtures were further stirred for the optimized time of 30 min and speed of 500 rpm.

For the ultrasonication studies, similar procedure was adopted except that the time of ultrasonication (Transsonic T660H, ELMA) was 10 min (optimized from 10, 20 and 30 min studies) for each test.

Determination of rheological properties

The rheological properties, viz. viscosity and gel volume (also known sediment volume) were measured on the toluene–SDMBA-bentonite dispersions with viscometer Model LV DV-II + Pro (Brookfield, USA), using the SC4-18 spindle at the shear rate of 39.6–264 (s^{-1}) at 25 °C and the standard cylinder method, respectively (Jordan 1949; Sobisch and Lerche 2000). The volume of the sedimented dispersion was measured after 24 h. Two rheological models Power law (Ostwald-deWaele) model (Eq. 1) and Casson model (Eq. 2) were tested for investigating flow behaviour of the dispersions.

$$\eta_a = \mu\gamma^{\cdot(n-1)} \quad \text{OR} \quad \text{Log}\,\eta_a = \text{Log}\,\mu + (n-1)\,\text{Log}\,\gamma^{\cdot} \tag{1}$$

$$\eta^{1/2} = \eta_\infty^{1/2} + \tau_0^{1/2}\gamma^{\cdot -1/2} \tag{2}$$

where η denotes viscosity and $\gamma^{\cdot}$ denotes the shear rate.

Values of n in the range $0 < n < 1$ confirms the non-Newtonian shear-thinning flow behaviour of the dispersions and the μ values reflect the stability of the gel structures (I.S.: 1420-1959; Iwasaki et al. 1989; Schoff and Kamarchik 1997). In case of Casson model curves, the square of the slope is τ_0, the yield stress and the square of the intercept is η_∞, the viscosity at infinite shear rate.

Results and discussion

Effect of preparation parameters of SDMBA-bentonite on surface/physicochemical properties

The characteristics of the pristine beneficiated bentonite and SDMBA-bentonites influenced by the preparation

Table 2 Characteristics of SDMBA-bentonites

Characteristics/ SDMBA-bentonites	SDMBA-bentonite 100M[a]/40C[b]	SDMBA-bentonite 150M[a]	SDMBA-bentonite 240M[a]	SDMBA-bentonite 350M[a]	SDMBA-bentonite 60C[b]	SDMBA-bentonite 80C[b]	SDMBA-bentonite 90C[b]	SDMBA-bentonite 100C[b]	Pristine beneficiated bentonite
Particle size distribution % finer than (μm)									
0.1	03.95	02.01	01.90	01.89	01.47	01.29	01.14	01.32	13.12
0.5	25.37	15.08	14.13	14.22	08.52	05.99	05.55	06.00	113.49
0.9	88.54	72.34	46.51	46.59	70.19	36.01	33.03	36.03	294.93
Specific surface area (m^2/g)	0.6478	1.0738	1.2210	1.2320	1.6528	1.9711	2.1993	1.9824	0.2463
Bulk density (g/cm^3)									
Loose	0.51	0.49	0.42	0.42	0.36	0.33	0.30	0.33	0.81
Taped (50 strokes)	0.75	0.72	0.60	0.61	0.51	0.49	0.45	0.48	1.09
BET surface area	3.90	3.75	3.65	3.66	3.45	3.30	3.21	3.33	93
Swelling in nitrobenzene (cm^3)	87	89	90	90	92	93	95	93	02

SDMBA-bentonite 100M and SDMBA-bentonite 40 °C are same and hence denoted as SDMBA-bentonite 100M[a]/40 °C[b]

[a] SDMBA-bentonite prepared at 40 °C and crushed and sieved through 100, 150, 240 and 350 BSS mesh

[b] SDMBA-bentonite prepared at 40, 60, 80, 90 and 100 °C and crushed and sieved through 100 BSS mesh

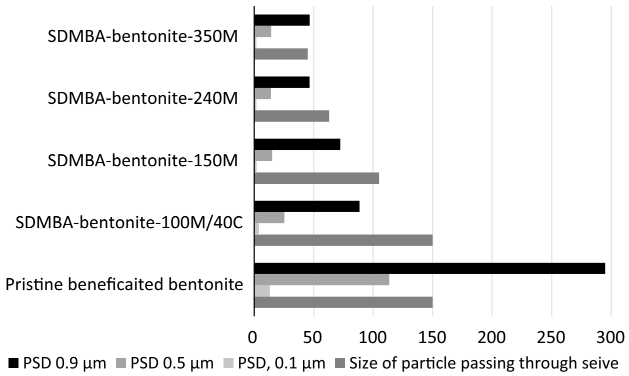


Fig. 1 Effect of micronization on particle size distribution of SDMBA-bentonites prepared at 40 °C

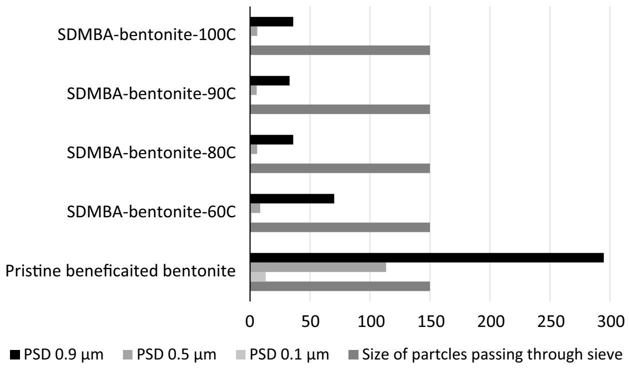


Fig. 2 Effect of reaction temperature on particle size distribution of SDMBA-bentonites prepared by micronization—100 BSS mesh (150 µm)

parameters are given in Table 2. The particle size, BET surface area and bulk density decreased and the specific surface area and swelling in nitrobenzene (organophilicity) increased with the increasing micronization (pulverization by mechanical means/tools and sieving to decrease the particle size) and preparation temperature of SDMBA-bentonites till the micronization reaches 240 BSS mesh (particle size < 63 µm) and temperature is 90 °C then onwards the mechanochemical modification is no much effective. Thus, the micronization of 240 BSS mesh (particle size < 63 µm) and preparation temperature of 90 °C is optimum in the range investigated during this study. This can be more clearly understood from the graphical presentation shown in Figs. 1 and 2. In these figures, SDMBA-bentonites prepared as a function of micronization/reaction temperature versus particle size distribution (PSD) of SDMBA-bentonites produced are presented, respectively. It can be clearly concluded from the figures that the reaction temperature has more influence relative to micronization. The observation that the decrease of particle size and bulk density with simultaneous increase of specific surface area leads to an understanding and also is indirect indication of increase in number of particles per unit volumes. Similar results have been reported for hydrated calcium silicates by Bhatt (1988). Concurrently, decrease in BET surface area [can be considered as hydratable surface area Bhatt (1988)] of SDMBA-bentonites is observed which is assigned to cover up effect, i.e. the surface coverage by modifying organic (SDMBA) cations (Theng 1974; Hendricks 1941; Fripiat et al. 1982; Bhatt 1995). This indicates the increase of SDMBA cations accessibility and coverage in SDMBA-bentonites interlayer gallery and is confirmed by increasing organophilicity and with simultaneous decrease in BET hydrated surface area (Hendricks 1941; Bhatt 1995).The results of surface/physicochemical characterization of SDMBA-bentonites clearly indicate the preparation temperature to be more influencing/effective relative to the micronization. The reason for such effect can be explained as follows: the modification of the SDMBA-bentonites by micronization is mechanical means dividing the particles in finer size by collision forces and thereby control the particle size/number of particles per unit volume of the SDMBA-bentonites. This has restricted effect relative to reaction temperature in which the SDMBA-bentonite the particle size/number of particles is controlled by chemical phenomenon occurring at the clay surfaces. During high temperature synthesis, high-degree deagglomeration of tactoids consisted of face-to-face aggregations of several clay platelets occurs due to the more active migration of the hydrated interlayer cations at higher temperature and high repulsion of negatively charged platelets left behind (Fripiat et al. 1982) and/or a “house-of-cards” structure formation appears in which the individual clay platelets are associated mainly by edge-to-face bonding (van Olphen 1977) in the smectite/bentonite–water dispersion. The solubility of SDMBAC at higher temperatures also increases. Thus, both these phenomena contribute to the increase of specific surface area directed by increment of number of particle size per unit volume, i.e. mass fraction (as explained here above) of bentonite particle with simultaneous increase in accessibility and coverage of SDMBA cations ultimately leading to SDMBA-bentonites of finer particle size and lower bulk density. Thus, the preparation parameters such as micronization and synthesis temperature were found to control the particle size and distribution, bulk density, specific and BET (hydratable) surface areas, organophilicity (Table 2) and the number of particles per unit volume. Furthermore, synthesis temperature observed contributing more efficiently relative to micronization.

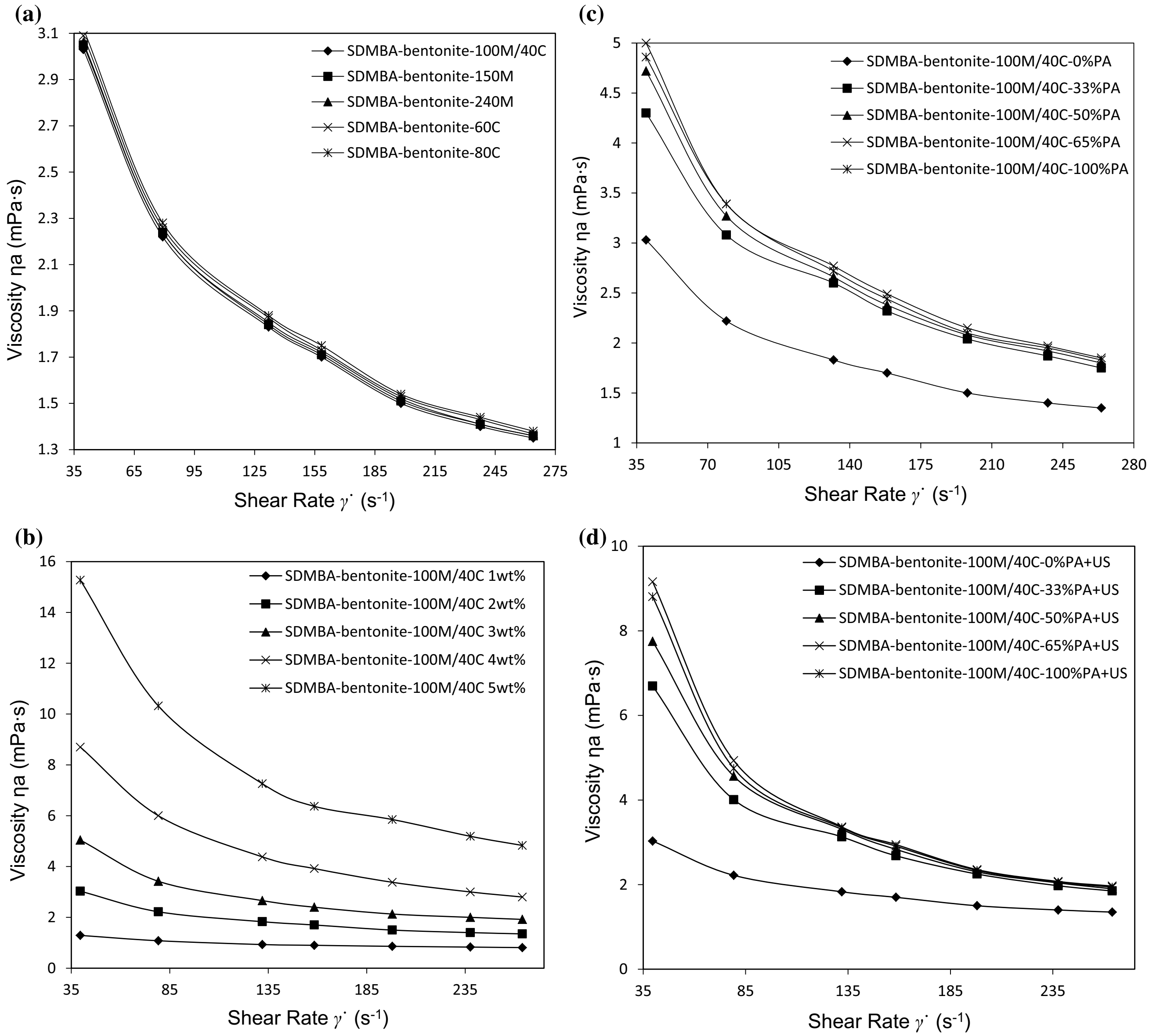


Fig. 3 Flow curves of **a** toluene–SDMBA-bentonite dispersions influenced by SDMBA-bentonites prepared under different preparation parameters, **b** toluene–SDMBA-bentonite dispersions influenced by different SDMBA-bentonite concentrations, **c** toluene–SDMBA-bentonite dispersions influenced by different methanol/H_2O (95/5) polar activator concentration and **d** toluene–SDMBA-bentonite dispersions influenced by different methanol/H_2O (95/5) polar activator concentration and ultrasonication as dispersing tool

Effect of preparation parameters on rheological properties of toluene–SDMBA-bentonite dispersions

The data of rheological properties of the toluene–SDMBA-bentonite dispersions obtained as influenced by the preparation parameters, micronization and synthesis temperature are graphically presented in Fig. 3a and fitted to Power law equation (Oswald model) (Fig. 4a) and Casson model (Fig. 5a). The values of the rheological parameters of these two models are listed in Table 3. The SDMBA-bentonite 90C exhibited the most efficient rheological modification amongst all the five SDMBA-bentonites. The shear-thinning behaviour of the dispersions is attributed to structural breakdown of the smectite particle network when shear is applied (Fig. 3a). As elucidated in Schematic 1, the hydrogen network is enhanced with increase in particle size (mass fraction) that improves the sheer thinning flow behaviour. This values of power law parameters, μ (non-Newtonian coefficient of viscosity) and n (non-Newtonian index of viscosity) (Table 3) increase and decrease, respectively, with the increase in number of particles of SDMBA-bentonites.

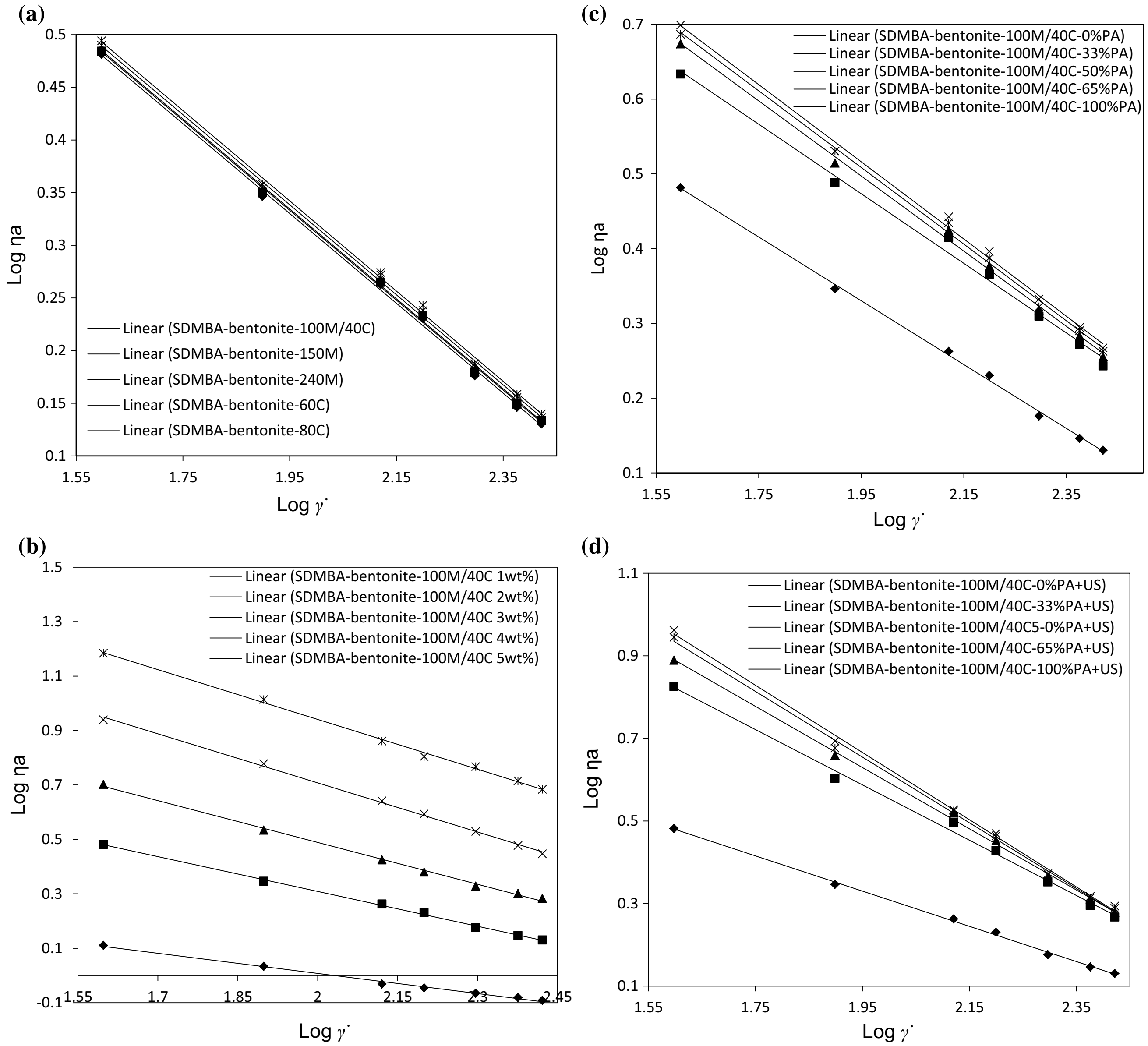


Fig. 4 Power law plots of **a** toluene–SDMBA-bentonite dispersions influenced by SDMBA-bentonites prepared under different preparation parameters, **b** toluene–SDMBA-bentonite dispersions influenced by different SDMBA-bentonite concentrations, **c** toluene–SDMBA-bentonite dispersions influenced by different methanol/H_2O (95/5) polar activator concentration and **d** toluene–SDMBA-bentonite dispersions influenced by different methanol/H_2O (95/5) polar activator concentration and ultrasonication as dispersing tool

This may be ascribed to the increase in the non-Newtonian shear-thinning flow behaviour and stability of the gel structure of the toluene–SDMBA-bentonite dispersions. Casson model parameters (Table 3), τ_0 (yield stress) and η_∞ (viscosity at infinite shear rate) which increased with the increase in number of particles of SDMBA-bentonites are indicative of incremental yield stress of the toluene–SDMBA-bentonite dispersions. It can be deduced that the influence of the SDMBA-bentonites on the degree of shear-thinning, the stability of the gel structure and the yield stress of the toluene–SDMBA-bentonite dispersions decreases in the following order: SDMBA-bentonite 90C > SDMBA-bentonite 100C ≈ SDMBA-bentonite 80C > SDMBA-bentonite 60C > SDMBA-bentonite 350M > SDMBA-bentonite 240M > SDMBA-bentonite 150M > SDMBA-bentonite 100M/40C.

When toluene–SDMBA-bentonite immersion is sheared/stirred, the benzyl group and stearyl chain of the SDMBA cation and toluene come into contact and interact with each other resulting into the swelling of the SDMBA-bentonite particles. SDMBA-bentonites 90C having maximum number of particles imparting maximum SDMBA cations interact

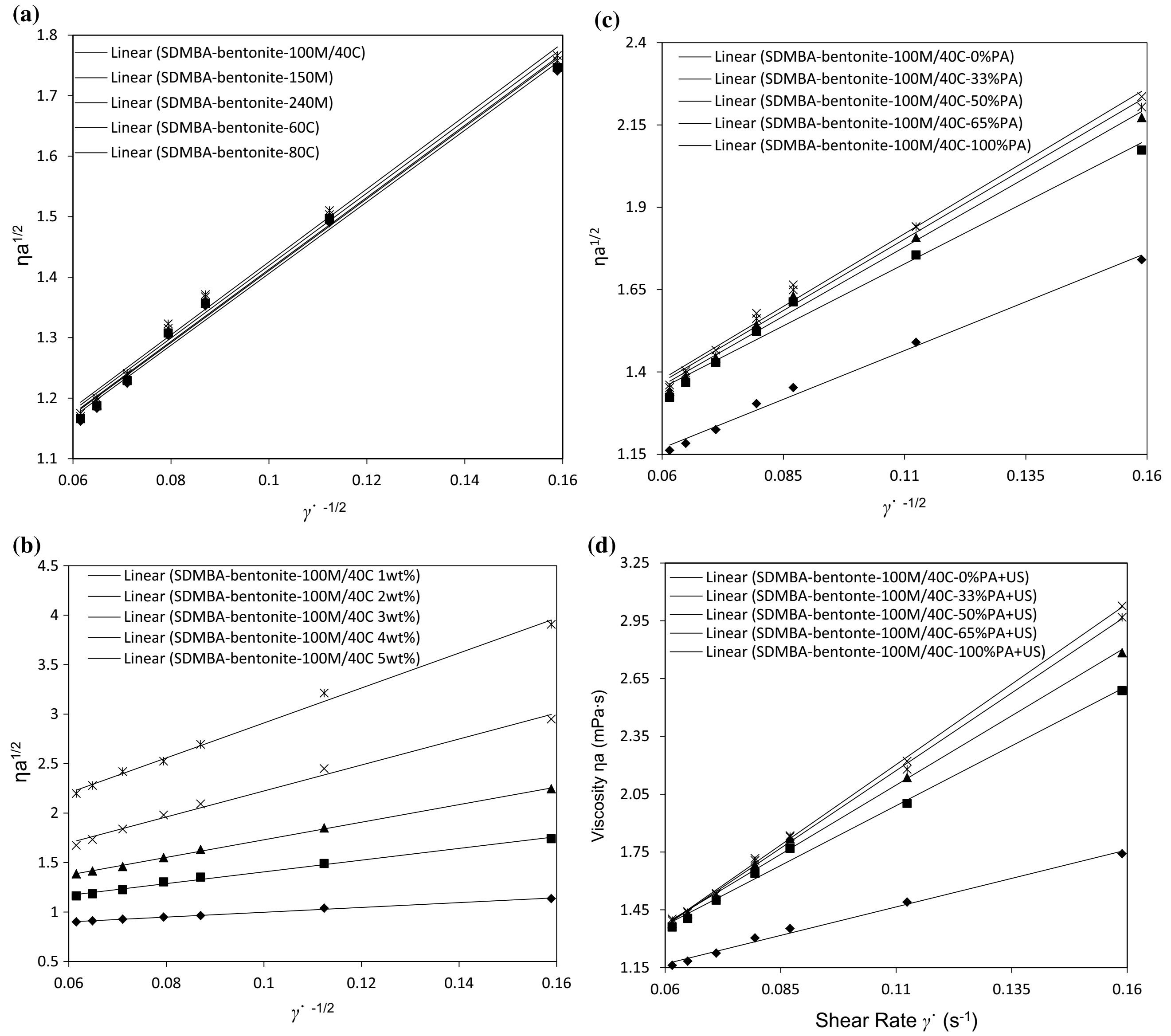


Fig. 5 Casson plots of **a** toluene–SDMBA-bentonite dispersions influenced by SDMBA-bentonites prepared under different preparation parameters, **b** toluene–SDMBA-bentonite dispersions influenced by different SDMBA-bentonite concentrations, **c** toluene–SDMBA-bentonite dispersions influenced by different methanol/H_2O (95/5) polar activator concentration and **d** toluene–SDMBA-bentonite dispersions influenced by different methanol/H_2O (95/5) polar activator concentration and ultrasonication as dispersing tool

most strongly with toluene yielding the maximum swelling amongst all the eight SDMBA-bentonites investigated in the presented study. These swollen particles lead to formation of weak gels which after shearing give high relative viscosity fluids. This indicates that the SDMBA-bentonite 90C with maximum particles have stronger interaction with larger magnitude of swelling forming weak gel and hence better rheological reinforcement, in accordance with Pluart et al. (2004) and Bhatt et al.(2013) who have reported the stronger interaction between organic modifier with higher organic density and toluene. Further, as explained earlier, the organic density of the SDMBA-bentonite increases with increasing particles per unit volume which contributes to the increased chemical interaction magnitude and leads to the swelling of organoclay in dispersion medium. This designates to occurrence of chemical interactions at a molecular level and thereby controlling the rheological behaviour at the micrometre scale. Swelling of the SDMBA-bentonite particles modifies the composition of stacks in the dispersion that determines its gel strength and viscosity. As swelling magnitude increases, the average stack size in the dispersion decreases and more delimitated of clay plates are in dispersion. The average number of plates in the stacks will increase with number of particles and thereby organic density of the

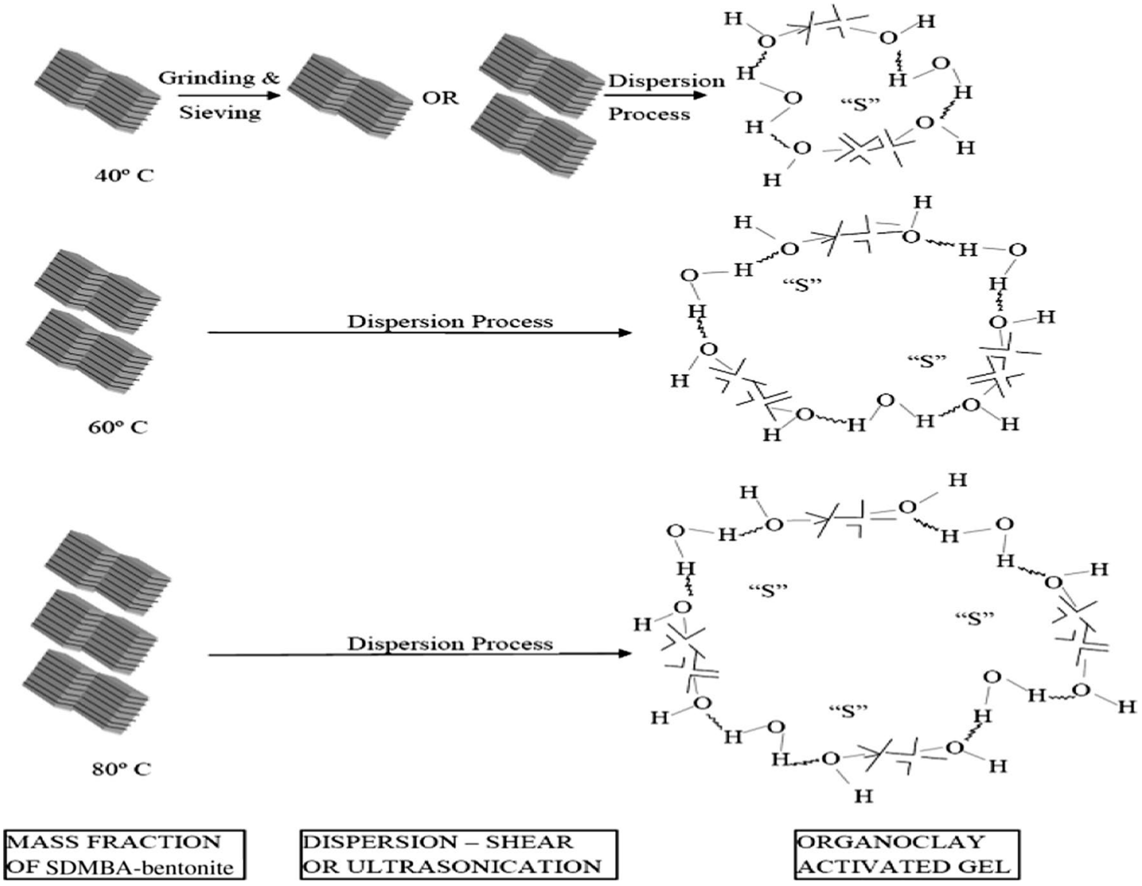
Table 3 Rheological parameters and gel volume of toluene–SDMBA-bentonite dispersions influenced by SDMBA-bentonites prepared under different preparation parameters

Parameters/ SDMBA-bentonites	μ	n	R^2	τ_0	η_∞	R^2	Gel vol. (cc)
Effect of mesh (particle)size of SDMBA-bentonites							
100M[a]/40C[b]	14.521	0.5734	0.9984	35.093	0.6616	0.9928	18
150M[a]	14.635	0.5732	0.9986	35.364	0.6659	0.9929	21
240M[a]	14.696	0.5730	0.9983	35.461	0.6680	0.9922	24
350M[a]	14.764	0.5727	0.9981	35.482	0.6696	0.9919	25
Effect of temperature of SDMBA-bentonite preparation							
100M[a]/40C[b]	14.521	0.5734	0.9984	35.093	0.6616	0.9928	18
60C[b]	14.870	0.5724	0.9984	35.894	0.6726	0.9924	30
80C[b]	15.059	0.5715	0.9982	36.377	0.6758	0.9925	38
90C[b]	15.307	0.5702	0.9984	36.866	0.6815	0.9918	40.5
100C[b]	15.207	0.5706	0.9981	36.609	0.6792	0.9916	40

SDMBA-bentonite 100M and SDMBA-bentonite 40 °C are same and hence denoted as SDMBA-bentonite 100M[a]/40 °C[b]

[a] SDMBA-bentonite prepared at 40 °C and crushed and sieved through 100, 150, 240 and 350 BSS mesh

[b] SDMBA-bentonite prepared at 40, 60, 80, 90 and 100 °C and crushed and sieved through 100 BSS mesh



Schematic 1 Relation between rheology and structure of toluene–SDMBA-bentonite dispersions at various stages

SDMBA cation, which on interaction with solvent decreases generating dispersion with large extent of swelling (Connolly et al. 2006). The ultimate product is a weak gel and high relative viscosity. Moreover, the number of platelets in a stack is not reaching full equilibrium. Presumably, the large-scale aggregation prevents the numbers of platelets in

Table 4 Rheological parameters and gel volume of toluene–SDMBA-bentonite dispersions influenced by SDMBA-bentonites

Parameters	μ	n	R^2	τ_0	η_∞	R^2	Gel vol. (cc)
Effect of concentration of SDMBA-bentonite-100 M/40C							
1% w/w	3.167	0.7535	0.9949	5.944	0.5685	0.9958	10
2% w/w	14.521	0.5734	0.9984	35.093	0.6616	0.9928	18
3% w/w	32.621	0.4876	0.9974	78.918	0.7081	0.9989	21
4% w/w	81.133	0.3992	0.9982	172.056	0.8314	0.9907	27
5% w/w	144.844	0.3899	0.9976	311.876	1.3108	0.9950	30
Effect of 2% concentration of SDMBA-bentonites							
100M^a/40C^b	14.521	0.5734	0.9984	35.093	0.6616	0.9928	18
150M^a	14.635	0.5732	0.9986	35.364	0.6659	0.9929	21
240M^a	14.696	0.5730	0.9983	35.461	0.6680	0.9922	24
350M^a	14.764	0.5727	0.9981	35.605	0.6696	0.9919	25
60C^b	14.870	0.5724	0.9984	35.894	0.6726	0.9924	30
80C^b	15.059	0.5715	0.9982	36.377	0.6758	0.9925	38
90C^b	15.307	0.5702	0.9984	36.866	0.6815	0.9918	40.5
100C^b	15.207	0.5706	0.9981	36.609	0.6819	0.9916	40
Effect of 3% concentration of SDMBA-bentonites							
100M^a/40C^b	32.621	0.4876	0.9974	78.918	0.7081	0.9989	21
150M^a	32.991	0.4873	0.9975	79.709	0.7090	0.9987	24
240M^a	33.136	0.4869	0.9981	79.891	0.7130	0.9989	27
350M^a	33.281	0.4867	0.9980	80.201	0.7147	0.9987	28.5
60C^b	33.504	0.4863	0.9971	81.090	0.7183	0.9989	37
80C^b	33.752	0.4851	0.9980	81.189	0.7185	0.9988	41
90C^b	34.308	0.4829	0.9985	82.223	0.7188	0.9984	43.5
100C^b	34.049	0.4831	0.9985	81.729	0.7187	0.9981	43
Effect of 4% concentration of SDMBA-bentonites							
100M^a/40C^b	81.133	0.3992	0.9982	172.056	0.8314	0.9907	27
150M^a	81.846	0.3987	0.9982	173.554	0.8343	0.9908	32
240M^b	82.111	0.3981	0.9980	173.818	0.8400	0.9905	34
350M^a	82.490	0.3975	0.9979	174.478	0.8418	0.9904	37.5
60C^b	83.311	0.3969	0.9981	176.627	0.8436	0.9910	51
80C^b	84.081	0.3966	0.9981	177.849	0.8481	0.9907	57
90C^b	85.467	0.3962	0.9977	180.043	0.8549	0.9899	58.5
100C^b	84.840	0.3963	0.9977	178.857	0.8489	0.9900	58
Effect of 5% concentration of SDMBA-bentonites							
100M^a/40C^b	144.844	0.3903	0.9976	311.876	1.3108	0.9950	30
150M^a	145.680	0.3902	0.9974	313.857	1.3214	0.9948	36
240M^a	146.319	0.3899	0.9977	314.743	1.3255	0.9950	39
350M^a	146.960	0.3895	0.9978	315.915	1.3280	0.9950	42
60C^b	148.457	0.3886	0.9975	318.908	1.3301	0.9948	57
80C^b	149.968	0.3883	0.9978	322.095	1.3380	0.9951	66
90C^b	152.440	0.3871	0.9977	326.055	1.3486	0.9946	67.5
100C^b	151.321	0.3872	0.9979	323.817	1.3461	0.9951	67

SDMBA-bentonite 100M and SDMBA-bentonite 40 °C are same and hence denoted as SDMBA-bentonite 100M^a/40 °C^b

[a] SDMBA-bentonite prepared at 40 °C and crushed and sieved through 100, 150, 240 and 350 BSS mesh

[b] SDMBA-bentonite prepared at 40, 60, 80, 90 and 100 °C and crushed and sieved through 100 BSS mesh

the stacks to fully equilibrate, although the spacing between the layers appears to be in equilibrium. This may be due to the existence of well-organized platelets at larger length scales in montmorillonite aggregates. Consequently, delamination and hence rheological reinforcement will be incomplete (Connolly et al. 2006). Jamie Fletcher (http://www.

chemeurope.com/articles/e/61207/) has reported similar observations for talc/epoxy system having effect of number of particles on rheological properties of flows. The mechanism by which/how the preparation parameters viz. micronization and synthesis temperature influence the interaction of functional groups of SDMBA-bentonite with solvent and thereby form the disaggregation and deagglomeration of SDMBA-bentonite particles is given in Schematic 1.

Effect of SDMBA-bentonite concentration

Figure 3b displays the viscosities of the toluene–SDMBA-bentonite dispersions having different SDMBA-bentonite concentration in the range from 1 to 5 wt% as a function of shear rate. Power law and Casson plots obtained from these data (Fig. 3b) are presented in Figs. 4b and 5b, respectively. The values of Power law model parameters, μ and n, and Casson model parameters, τ_0 and η_∞, derived from these plots (Figs. 4b, 5b) are given in Table 4. These results reveal that degree of shear-thinning, gel stability, yield stress of these toluene–SDMBA-bentonite dispersions is increased with the increment of SDMBA-bentonite concentration in the range from 1 to 5 wt%. As explained earlier, the magnitude of the interaction between toluene and SDMBA cation plays a dominating role in reinforcing the rheological properties of the toluene–SDMBA-bentonite dispersions. Further, the increase in concentration of SDMBA-bentonite in the dispersions will result the increase in number of particles leading to increase in magnitude of interaction between toluene and quaternary ammonium cation promoting swelling, the smaller the average stack size for the dispersion and ultimately more dispersed particles that leads to weak gels and higher viscosities. As can be seen from the data depicted in Figs. 3b, 4b, and 5b and in Table 4, relation of increase in the SDMBA-bentonite concentration and reinforcement in rheological properties is not linearly proportionate. This may be due to the increased particle volume fraction with the increasing SDMBA-bentonite concentration leaving relatively lesser surface for interaction between SDMBA-bentonite particles and toluene and/or polar activator which results into relatively lesser rheological enhancement. Similar results were obtained for other toluene–organoclay dispersion systems also (Bhatt et al. 2013).

Effect of concentration of polar activator [methanol/H2O (95/5)]

The viscosity data of the toluene–SDMBA-bentonite dispersions having 2 wt% concentration influenced by methanol/H_2O (95/5) polar activator concentration are plotted as a function of shear rate (Fig. 3c) and fitted to Power law (Fig. 4c) and Casson model (Fig. 5c). The rheological parameters obtained by model fitting are listed in Table 5. The nature of the curves in these figures and the values of rheological parameters (Table 5) suggest that the dispersions exhibit non-Newtonian shear-thinning flow behaviour.

Comparing the results of rheological parameters and gel volume for the toluene–SDMBA-bentonite dispersions with/without methanol/H_2O (95/5) polar activator displayed in Tables 3 and 5, respectively, indicates the significant role of polar activator in reinforcing the rheological properties. Besides, increase in number of particles (per unit volume),

Table 5 Rheological parameters and gel volume of toluene–SDMBA-bentonite dispersions influenced by concentration of polar activator—methanol/H_2O (95/5)

Parameters	μ	n	R^2	τ_0	η_∞	R^2	Gel vol. (cc)
Effect of concentration of polar activator on SDMBA-bentonite (100 M^a/40 °C^b)							
33% PA	24.027	0.5347	0.9934	56.698	0.8098	0.9940	19.5
50% PA	29.971	0.4976	0.9975	54.921	0.7300	0.9921	24
65% PA	33.327	0.4838	0.9964	78.059	0.7193	0.9917	27
100% PA	32.218	0.4874	0.9974	75.188	0.7218	0.9911	25.5
Effect of 65% concentration of polar activator on SDMBA-bentonites							
100M^a/40C^b	33.327	0.4838	0.9964	78.059	0.7193	0.9917	27
150M^a	33.721	0.4826	0.9965	78.821	0.7211	0.9916	34.5
240M^a	33.845	0.4825	0.9959	79.037	0.7242	0.9909	39
350M^a	34.002	0.4822	0.9955	79.344	0.7259	0.9905	42
60C^a	34.041	0.4809	0.9955	79.857	0.7350	0.9912	48
80C^a	34.914	0.4800	0.9954	81.283	0.7385	0.9905	60
90C^b	35.253	0.4798	0.9959	82.004	0.7379	0.9907	63
100C^b	34.995	0.4799	0.9956	81.411	0.7334	0.9903	63

SDMBA-bentonite 100M and SDMBA-bentonite 40 °C are same and hence denoted as SDMBA-bentonite 100M^a/40 °C^b

[a] SDMBA-bentonite prepared at 40 °C and crushed and sieved through 100, 150, 240 and 350 BSS mesh

[b] SDMBA-bentonite prepared at 40, 60, 80, 90 and 100 °C and crushed and sieved through 100 BSS mesh

the incorporation of polar activator methanol/H_2O (95/5) adds to the interaction magnitude by imparting the hydrogen bond network to the dispersion media by the action of gelation. Consequently, dispersions exhibit improved rheological properties. As can be seen from Table 5, with increase in concentration of methanol/H_2O (95/5), the μ and τ_0 increased and n and η_∞ decreased initially and then the trend reversed, appearing a maximum value at 65 wt%. This is ascribed to the polar activator acting as a gallant till 65 wt% concentration and then as degellant. This can be elucidated as follows. The polar activator methanol/H_2O (95/5) molecules having an affinity for silicate surface enter the interlayer through wedge disrupting van der Waal forces (which tend to hold the clay aggregate together) and come in contact with the silicate surface of the SDMBA-bentonite. This will allow the functional groups of the quaternary ammonium cation to radiate away from the clay surface and free to “solvate” in toluene by chemical interaction to have much higher affinity for toluene than the inorganic clay surface has (Dekany et al. 1986b; Burba and McAtee 1981). Simultaneously, the mobility of ammonium ions over the surface is increased (Gast and Mortland 1971; Cody and Reichert 1986). Consequently, the hydrogen bond and van der Waals interactions between solvent and/or polar activator and quaternary ammonium cations come into existence. These interactions contribute to the disaggregation of the SDMBA-bentonite particles by hydrogen bonding bridges through hydrogen bond interaction between adjacent clay platelets edge-to-edge and/or edge-to-face hydrogen bond network and gel matrix to form (Dekany et al. 1975, 1986b and 1986c; Sobisch and Lerche 2000). With increase in amount of methanol/H_2O (95/5) molecules, the increase in covering silicate surfaces to lift up the quaternary ammonium cations and the disaggregation of particles by hydrogen bonding continues contributing to increment in the extent of hydrogen bond network followed by greater gelation. The performance of polar activator as gallant continues till the balance between the effects of covering silicate surfaces to lift up the organic ions and the aggregation of particles by hydrogen bonding followed by the gelation and then the effect of degelation occurs. In the present investigation, this value is 65 wt%. Incorporation of methanol/H_2O (95/5) beyond this amount is assumed to be adsorbed at the clay platelet edges, breaking the edge–edge structure to give a parallel alignment of plates. Consequently, the hydrogen bond network is disturbed/destroyed and the balance to form gelation is disturbed and resultant is the act of activator that is degellant (Jones 1983; Gast and Mortland 1971; I.S.: 1420-1959). In this support, a concentrated organophilic clay gel was reported to develop dilatants characteristics at high polar activator doses and particular difficulty observed with solvent being polar such as ester or alcohol (Jones 1983). Further, it can be inferred from Figs. 3c, 4c and 5c and Table 5 that the larger number of particles (per unit volume) leads to the increased scope of hydrogen bond network directing the greater rheological reinforcement of the toluene–SDMBA-bentonite dispersions.

The rheological data of the toluene–SDMBA-bentonite dispersion using methanol alone as polar activator 65 wt% (not given) were found to be inferior to those obtained with methanol/H_2O (95/5) 65 wt% given here above. Substantial role of water as polar activator has been observed by several investigators (Jones 1983; Dekany et al. 1986c; Gherardi et al. 1996; Powell 1982; Burba and McAtee 1981; Sobisch and Lerche 2000; Gast and Mortland 1971; Cody and Reichert 1986; Jones 1963). The water and the organoclay are being strongly synergistic in their viscosifying effect and water being an effective hydrogen bonder plays a vital role in activating swelling process and stabilizing organoclay gel systems (Jones 1983). Water molecules are dominant in stabilizing the network structure by hydrogen bond formation between silanol groups of different platelets or platelet aggregates (Sobisch and Lerche 2000). Thus, water molecules help in forming edge-to-edge hydrogen bond network in clay dispersion which consequently leads to development of gel matrix (Powell 1982). Moraru (2001) have observed water molecules to contribute to the formation of giant dipoles on the organomontmorillonite and of hydrogen bridges between interacting particles and the dipolar repulsion is a driving force in the swelling process, after the initiating effect of the polar activator. The adsorbed water act as mobile protons and the dissociation degree of such adsorbed water is 10^6 higher than in bulk (Fripiat and Stone 1978).

The rheological properties, gel volume and viscosity, of these toluene–SDMBA-bentonite dispersions exhibit the analogous trend (Table 5). As seen earlier, the incorporation of polar activator methanol/H_2O function by wedging the SDMBA-bentonite particles and allow the functional groups stearyl chain of organic modifier quaternary ammonium compound to radiate away from the clay surface to free to solvate in the organic liquid toluene due to have a much higher affinity for the organic solvent than the inorganic clay surface. The mechanism is given in Schematic 2 explaining further full deagglomeration of organoclay particles and followed by shear forces to produce gel formation.

Effect of ultrasonication

The rheological properties of the toluene–SDMBA-bentonite dispersions with methanol/H_2O (95/5) as polar activator determined using ultrasonication as dispersing method for the optimum time of 10 min are depicted in Fig. 3d as a function of shear rate. Rheological parameters derived from the Power (Fig. 4d) and Casson (Fig. 5d) plots of these data (Fig. 3d) are presented in Table 6. It can be inferred from the comparison of the data in Figs. 3c, d, 4c, d and

Table 6 Rheological parameters and gel volume of toluene–SDMBA-bentonites-dispersions influenced by concentration of polar activator—methanol/H_2O (95/5) and ultrasonication

Parameter	μ	n	R^2	τ_0	η_∞	R^2	Gel vol. (cc)
Effect of concentration of polar activator and ultrasonication on SDMBA-bentonite (100M[a]/40[b])							
33% PA + US	78.253	0.3302	0.9957	154.182	0.3903	0.9940	21
50% PA + US	118.878	0.2586	0.9982	207.015	0.2653	0.9968	27
65% PA + US	179.432	0.1856	0.9982	265.918	0.1342	0.9991	33
100% PA + US	160.990	0.2041	0.9978	259.564	0.1604	0.9985	28.5
Effect of 65% concentration of polar activator and ultrasonication on SDMBA-bentonites							
100M[a]/40C[b] + 65% PA + US	179.432	0.1856	0.9982	265.918	0.1342	0.9991	33
150M[a] + 65% PA + US	181.01	0.1852	0.9983	281.162	0.1345	0.9992	45
240M[a] + 65% PA + US	181.55	0.1851	0.9984	281.740	0.1357	0.9991	54
350M[a] + 65% PA + US	182.39	0.1849	0.9983	282.737	0.1359	0.9991	57
60C[b] + 65% PA + US	184.16	0.1846	0.9980	285.569	0.1362	0.9989	63
80C[b] + 65% PA + US	186.90	0.1832	0.9982	287.920	0.1369	0.9989	75
90C[b] + 65% PA + US	193.37	0.1806	0.9982	295.551	0.1373	0.9992	76.5
100C[b] + 65% PA + US	192.40	0.1808	0.9982	294.291	0.1372	0.9988	76.5

SDMBA-bentonite 100M and SDMBA-bentonite 40 °C are same and hence denoted as SDMBA-bentonite 100M[a]/40 °C[b]

[a] SDMBA-bentonite prepared at 40 °C and crushed and sieved through 100, 150, 240 and 350 BSS mesh

[b] SDMBA-bentonite prepared at 40, 60, 80, 90 and 100 °C and crushed and sieved through 100 BSS mesh

5c, d and Tables 5 and 6 that the rheological reinforcement by the polar activator under the influence of shearing and ultrasonication exhibits the identical behaviour of the SDMBA-bentonites with methanol/H_2O (95/5) 65 wt% being the optimum value. The SDMBA-bentonite synthesis temperature is found to be more effective than mechanical grinding. Of course, it can be deduced from the rheological magnitude and values of rheological parameters (Tables 5, 6) obtained for both the dispersing methods indicate the ultrasonication to be superior to the shearing. This suggests that the dispersions obtained from the ultrasonication exhibit the nature similar to that of shear-thinning for all the toluene–SDMBA-bentonite dispersions, but the rheology reinforcement is remarkably higher for the dispersions prepared under influence of ultrasonication. It can be deduced that the mechanism of rheological reinforcing the toluene–SDMBA-bentonite dispersions by shearing and ultrasonication is identical, but intense ultrasonic cavitation produced by ultrasound during ultrasonication plays dominant role by imparting the energy higher than the shearing and affect directly to micro-level leading to the stronger interaction between quaternary ammonium cation and toluene and/or polar activator methanol/H_2O (95/5) contributing to larger degree of hydrogen bond network and weak gel resulting the higher rheological reinforcement. The cavitation phenomenon occurred during ultrasonicating results in micro-turbulences and micro-jets of up to 1000 km/hr on implosion. Large particles are subject to surface erosion (via cavitation collapse in the surrounding liquid) or particle size reduction (due to fission through inter-particle collision or the collapse of cavitation bubbles formed on the surface). This leads to sharp acceleration of diffusion, mass-transfer processes and solid-phase reactions due to crystallite size and structure changing (Hielscher 2007). This entire mechanism contributes to the break up aggregates of clay particles to such an extent that the centre of each aggregate is exposed to solvent contributing to higher degree of disaggregation forming edge-to-edge hydrogen bond network and weak gel matrix with higher viscosity. Thus, the not only mechanical effects of ultrasonic cavitation but also the chemical reactions by the cavitation energy (sonochemistry) plays dominant role and overall rheological enhancement of the toluene–SDMBA-bentonite dispersions is superior than that obtained by conventional shear method (Hielscher 2007).

Thus, all the SDMBA-bentonites might get disaggregated up to the extent such that the centre of each aggregate is exposed to toluene under the influence of ultrasonication which may not be the case with shear method. Consequently, higher degree of hydrogen bond network is formed and weak gel achieved producing better rheological reinforcement following the mechanism described in earlier pages for the study of organic density and polar activator parameters. The hydrogen bond network produced by the SDMBA-bentonites prepared at 60, 80, 90 and 100 °C synthesis temperatures may be ascribed to finer particle size and decrease in bulk density, i.e. the larger number of particles relative to that of the SDMBA-bentonites prepared at 40 °C and meshing to 100, 150, 240 and 350 BSS mesh. It can be seen from the Schematic 1 that how particle size and number of particles of organoclay dominate the resulting dispersion/gel irrespective of the dispersion method used.

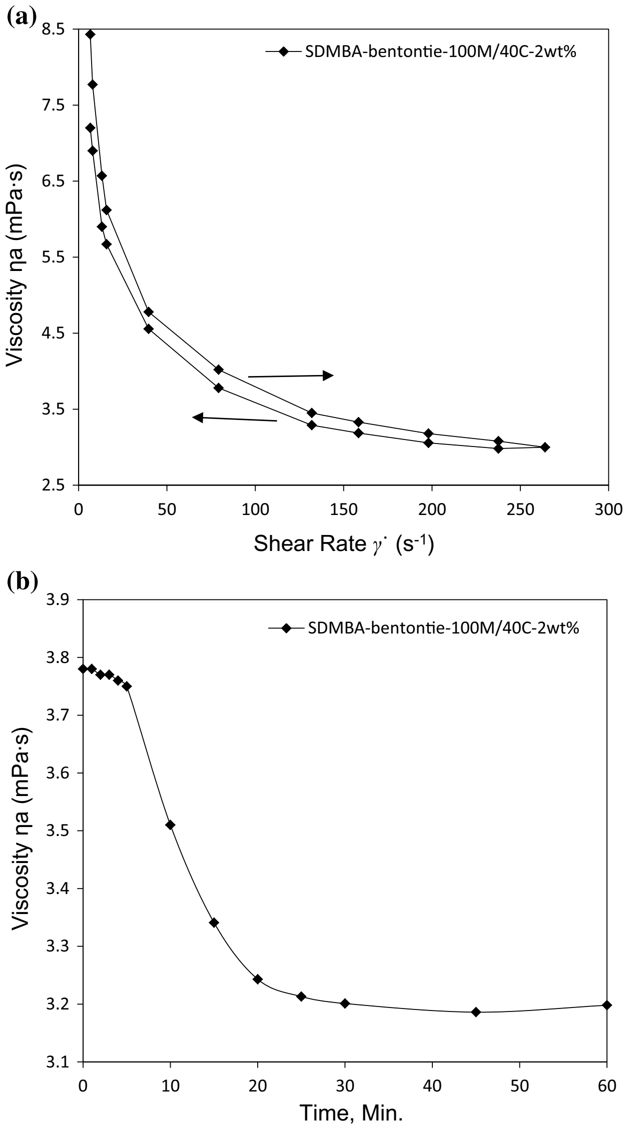


Fig. 6 Effect of **a** increasing and decreasing shear rate on viscosity of toluene–SDMBA-bentonite dispersions having 2% (w/w) concentration, and **b** time on viscosity of toluene–SDMBA-bentonite dispersions having 2% (w/w) concentration

Thixotropy of dispersions

To check whether the toluene–SDMBA-bentonite dispersions are thixotropic, we have measured the viscosity of the dispersions during increasing–decreasing shear rates in the range 6.6–264 (s^{-1}) and also at the shear rate of 79.2 (s^{-1}) for 30 min of shear time. The viscosity data of the toluene–SDMBA-bentonite-dispersion determined as a function of increasing–decreasing shear rates and as a function of time for toluene dispersion in SDMBA-bentonite of 2 wt% concentration has been graphically presented in Figs. 4b and 6a, respectively. The nature of flow curve (Fig. 6a) of the toluene–SDMBA-bentonite-dispersion obtained during decreasing shear rate present a strongly marked shear-thinning behaviour. Hysteresis effect observed for the toluene–SDMBA-bentonite-dispersion (Fig. 6a) and the area of the “hysteresis loop” of the flow curves, which is a measure of the degree of hysteresis, is positive confirming the behaviour of the toluene–SDMBA-bentonite dispersion system to be thixotropic. This “hysteresis loop” is caused by the decrease in the fluid’s viscosity with increasing time of shearing.

The nature of curve, i.e. decrease in viscosity with time at constant shear rate of 79.2 s^{-1} (Fig. 6b) also supports the thixotropic behaviour of the toluene–SDMBA-bentonite-dispersion. Analogous results were obtained for other toluene–SDMBA-bentonite dispersions with/without incorporation of methanol/H_2O polar activator. The flow behaviour of these dispersions demonstrates first the usual shear-thinning effect due to structural breakdown of the network then a shear-thickening effect. This may be ascribed to an increase in suspended particle aspect ratio which directs to an antithixotropic behaviour of the dispersions as revealed by the viscosity values during the decreasing stress rate. The conclusions reported by Pluart et al. (2004) for their study of Tixogel/DGEBA dispersion support these observations.

Conclusions

Stearyldimethylbenzylammonium cations used to prepare organoclays from Indian bentonite were densely packed between the bentonite/montmorillonite layers with an almost complete surface coverage. The preparation parameter, synthesis temperature was found to influence the physicochemical properties like particle size, bulk density and organophilicity more efficiently relative to the grinding/meshing (micronization). Mixing of the SDMBA-bentonites with toluene under the influence of shearing or ultrasonication produced the toluene–SDMBA-bentonite dispersions. The toluene–SDMBA-bentonite dispersions have an unstable texture, which can be easily destroyed by weak shear stress and recovered thixotropically by releasing the stress. Thus, the toluene–SDMBA-bentonite dispersions under study exhibit thixotropic shear-thinning flow behaviour. The nature of the viscosity vs. shear rate curves, the plots and parameters of the flow models, Power law and Casson, indicate that the degree of shear-thinning, gel stability and yield stress increased with the (1) increasing in synthesis temperature and or grinding/meshing the particles (reduction of particle size), (2) increasing SDMBA-bentonite concentration, and (3) increasing polar activator methanol/H_2O (95/5) concentration with an optimum value of 65 wt% on clay basis. Rheological enhancement by SDMBA-bentonite prepared at 90 °C is attributed to the strongest interaction of stearyl chain and benzyl group of SDMBA with toluene due to the largest number of particles, i.e. smallest particle size and largest specific surface area leading to maximum surface exposure of the SDMBA-bentonite particles and resulting into highest organic density and interaction of the SDMBA cations with toluene an organic solvent and/or methanol/H_2O (95/5) a polar activator. Proportionately, nonlinear improvement of rheological properties of the toluene–organoclay dispersions with increasing organoclay concentration may be attributed to the increasing particle volume fraction leading to relatively lesser surface for interface interaction between organoclay particles and toluene molecules which results to relatively lesser rheological improvement. The enhancement in rheological properties of the dispersions is ascribed to the disruption of the two adjacent silicate sheets of organoclay particles through wedging by polar activator methanol/H_2O (95/5) producing a larger hydrogen bond network. Using ultrasonication as dispersing method enhanced the viscosity and rheological parameters and gel volume remarkably higher compared to shearing. This improvement of rheological properties by ultrasonication may be due to the intense ultrasonic cavitation that may impart the energy required to break up clay particles aggregates to such an extent that the centre of each aggregate is exposed to solvent contributing to higher degree of disaggregation, forming edge-to-edge hydrogen bond network and weak gel matrix with higher viscosity. All the toluene–organoclay dispersions exhibited analogous flow behaviour under the parameters studied. The overall combination of the three interactions: (1) chemical interaction between organic modifier-SDMBA and solvent-toluene, (2) hydrogen bonds and (3) van der Waals attraction between organic modifier and solvent determines the strength and stability of rheological properties, viscosity and gel volume of the toluene–organoclay dispersions. Further, the chemical interaction between organic modifier-SDMBA and organic solvent-toluene can be controlled by the surface properties of SDMBA-bentonites governed/tailored by the preparing parameters, micronization, i.e. grinding + meshing and synthetic temperature.

More brain storming approach in this route for modifying Indian bentonite to prepare the organoclays of desired surface characteristics and the use of ultrasonication for preparing dispersions of organoclays to be used as thickening or thixotropic agents in various industrial–rheological applications will open the new track for application of such dispersion systems, and more exhaustive work in this area will contribute to develop this as technology.

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