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TECHNICAL PAPER

Aqueous Dispersions of Latex Compounding Ingredients by Wet Ball Milling: Effect of Ball Size and Milling Time on Dispersion Quality

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Abstract Preparation of nanomaterials, their functionalization, evaluation and usage for potential applications are the main objectives in materials science research. Preparation of ultra-fine/nano-sized particle dispersions and their stabilization is a great challenge among researchers where the high surface area and energy impedes the effective usage of nanomaterials. This study presents the effect of ball milling on size and stability of aqueous dispersions of latex compounding ingredients such as china clay, zinc diethyldithiocarbamate, zinc 2-mercapto benzothiazole and butylated reaction product of p-cresol and dicyclopentadiene (wingstay L). The particle size and stability have been assessed through dynamic light scattering technique and sedimentation test. By using lower sized balls for milling, the particle size of latex compounding ingredients can be reduced to a great extent.

Keywords Ball milling · Ball size · Latex compounding ingredients · Dispersions · Stability

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1 Introduction

From the beginning of the era of nanoscience and nanotechnology, researchers are looking for the preparation of nano-sized materials through simple and easiest methods which can be scalable commercially. Grinding is one of the most important operations used in chemical, pharmaceutical and food industries for the size reduction of materials [1]. Ball milling is a technique used for particle size reduction and can also be used for preparing dispersions and for mixing of materials. The grinding or milling process is accompanied by the use of ceramic/steel balls along with the material to be comminuted in a cylindrical vessel or jar which rotates with a specific speed. Describing and understanding the milling process is very sophisticated because it is driven by several parameters like type of the mill, nature of milling (dry or wet), milling speed, ball size and type, ball to powder weight ratio, time of milling, temperature of milling etc. As the milling process advances, periodic fracture and coalescence processes continue [2]. The basic fragmentation mechanisms occurring in the comminution process includes: abrasion (occurs when low intensity stress is applied), cleavage (occurs when slow and relatively intense stresses are applied) and fracture (occurs by rapid application of intense stresses) [3]. In the long milling process, the lower sized particles generated undergoes agglomeration owing to its high specific surface area [4].

For the manufacture of latex based products, it is essential to add insoluble compounding ingredients to the latex as dispersions. Addition of ultra-fine/nano particle dispersions of compounding ingredients to the latex results products with superior quality and improved properties and can impart novel functionality to the product. Preparation of stable colloidal dispersions in the ultra-fine/nano size

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range is difficult because the particle will undergo agglomeration or flocculation. The degree of aggregation or agglomeration of the particles and the morphologies of agglomerated or aggregated structures dictate the final structure and subsequent properties (e.g., solubility, mechanical strength, electrical and thermal conductivity, chemical affinity, etc) [5].

Several researchers reported that the ball size used in a mill has a significant influence on the mill throughput, power consumption and the particle size of the material [6–8]. Effects of ball diameter on the crystalline size, induced strain, and atomic diffusion in Cu-50 % Fe immiscible alloy system has been investigated [9]. Recently, the effect of different ball size on particle size and stability of aqueous dispersions of zinc oxide by ball milling has been attempted [10].

Use of smaller sized grinding media increases the milling efficiency and results in finer products having good quality. However, the main difficulty associated with the use of smaller ball size is the difficulty in discharging the ground material from the milling vessel, especially for dry (powder type) materials. By reducing the grinding media size, the number of contact points between the charge and grinding media can be increased which results in improved shear and collision and are beneficial for particle size reduction.

The aim of the present work is to optimize the process parameters for the preparation of chemical dispersions of latex compounding ingredients (LCI) viz. china clay, zinc diethyl dithiocarbamate (ZDEC), zinc 2-mercapto benzothiazole (ZMBT) and butylated reaction product of p-cresol and dicyclopentadiene (wingstay L). Effect of varying the ball size (¼, ½, ¾ in. and composite balls) and milling time on particle size and stability of aqueous dispersions of latex compounding ingredients have been studied. Since most of the latex compounding ingredients are water insoluble, the study assumes greater importance for the latex based industry.

2 Experimental

Details of the chemicals used in this study are given in Table 1. Wet ball milling was performed in a stainless steel vessel having a capacity of 2.5L (20.5 cm diameter × 15.5 cm height). High performance inert Al_2O_3 ceramic balls with different sizes viz. ¼ (small), ½ (medium) and ¾ in. (large) in diameter were used in this study. In all the cases, powder to ball-weight ratio was maintained as 1:5. Mixture of balls (composite) with different sizes (i.e. ¼, ½ and ¾ in.) were also used to examine the grinding efficiency. Balls of different sizes (composite formulation) were configured in such a way that the free volume between the balls was minimum. The free volume was minimum for ball mixtures in the weight ratio 2:1:2 (large:medium:small). Free volume determination in a composite ball mixture has been explained later. Disodium methylene *bis*-naphthalene sulphonate (Dispersol F) was used as capping agent (CA) and was added prior to the starting of the ball milling. The concentration of dispersion was maintained at 30 % and the milling was carried out at 35 rpm. Samples were withdrawn at regular intervals of time (say 3, 6, 9, 12, 15, 18, 24, 30 and 45 h). The first recording of particle size for each chemical was carried out after 30 min of ball milling. Particle size, specific surface area and cumulative size distributions of dispersions were measured using a particle size analyzer (Mastersizer 3000, Malvern, UK) by dynamic light scattering (DLS) technique. Sedimentation test was used to examine the stability of wet ball-milled dispersions after different milling intervals.

2.1 Free Volume Determination

For every ball sizes (say ¼ in.), the free volume was measured after fully immersing a definite quantity of balls in a beaker with water. The weight of water is equivalent to the available free volume between the balls of a particular size. For composite ball system, different ball combinations were taken and the one having the minimum free volume was selected. It might be pointed out here that lower the free volume, higher was the grinding efficiency.

2.2 Determination of Stability of Dispersion

Around 1–2 g of each ingredients wet milled at various intervals (0.5, 3, 6, 9, 12, 15, 18, 24, 30 and 45 h) with different ball sizes (¼, ½ and ¾ in.) were added to about 20 ml distilled water taken in a measuring vessel. The depth of sedimentation column was recorded after 24 h. Higher the length of the column; better the stability of the dispersions. The sedimentation percentage of aqueous dispersions was determined by the following equation:

The sedimentation percentage of aqueous dispersions

$$= \frac{H}{H_0} \times 100\,(\%)$$

where H (cm) is the length of the sedimentation column and H_0 (cm) is the total length of suspension [11]. Higher the magnitude, better was the dispersion stability.

3 Results and Discussion

3.1 Effect of Ball Size and Milling Time on D[4, 3]

The size of the particles which constitute the bulk of the dispersion volume is known as De Brouker Mean and is represented by D[4, 3]. It also gives an idea about the

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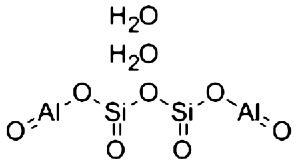
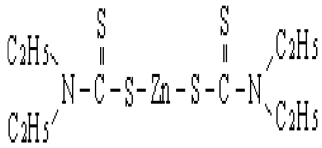
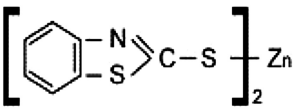
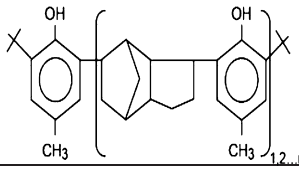
Table 1 Details of latex compounding ingredients

Ingredients	Molecular weight	Water solubility	Structure
China clay	258.2	0.1 % max	
Zinc diethyl dithiocarbamate (ZDEC)	361.91	Insoluble	
Zinc 2-mercapto benzothiazole (ZMBT)	397.9	Insoluble	
Butylated reaction product of p-cresol and dicyclopenta diene (Wingstay L)	650 (Avg)	Insoluble	

presence of larger particles within the size distribution. The D[4, 3] of wet-milled china clay with balls of different sizes (¼, ½, ¾ in. and their combination) at various milling intervals are shown in Fig. 1. D[4, 3] of china clay decreases with increase in milling time. Particle size (D[4, 3]) of unmilled (0 h milling) china clay is 5 μm and after 45 h of milling with ¼, ½ and ¾ in. balls, it decreases to 1.68, 2.5 and 2.88 μm respectively. As the ball size increases, the free volume between the balls increases which results in particles with higher sizes. The combination of balls in definite proportions reports a particle size of 2.09 μm.

Figure 2 shows the effect of ball size and milling time on D[4, 3] of ZDEC. For unmilled ZDEC, the D[4, 3] is 17 μm and irrespective of the ball size, a sharp reduction is observed after 6 h of ball milling and thereafter a gradual reduction in size is observed. The lowest size of 1.9 μm is observed after 45 h of milling with ¼ in. sized balls whereas with ½, ¾ in. and composite balls, the sizes are 2.83, 3.65 and 2.43 μm respectively.

The D[4, 3] profile of ZMBT looks similar to that of ZDEC. The results are shown in Fig. 3. For unmilled ZMBT, the D[4, 3] lies in the range of 7 microns. After 45 h of milling, it decreases to 1.22, 1.72, 3.04 and 1.47 μm by ball milling with ¼, ½, ¾ in. and composite balls respectively. Figure 4 shows the effect of ball size and milling time on D[4, 3] of wingstay L dispersion. It is clear from Fig. 4 that the D[4, 3] of wingstay L is 50 μm and a sharp reduction in size occurs after 6 h of ball milling. The D[4, 3] of wingstay L after 45 h of ball milling using various ball sizes (¼, ½, ¾ in. and composite balls) are 4.4, 5.9, 7.9 and 5.8 μm respectively.

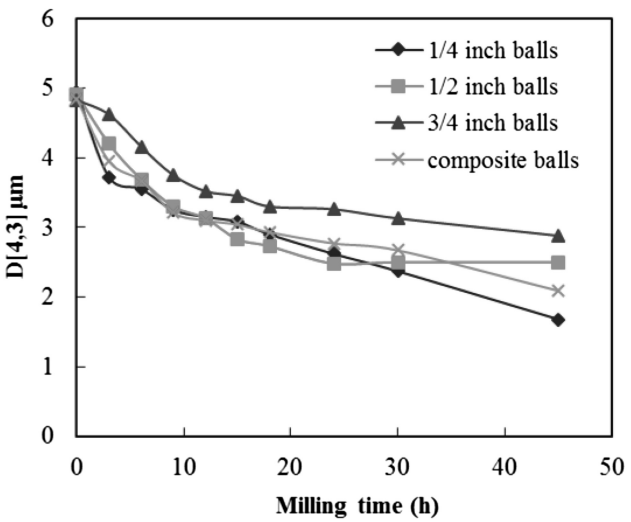


Fig. 1 Effect of ball size on D[4, 3] of china clay dispersions with milling time

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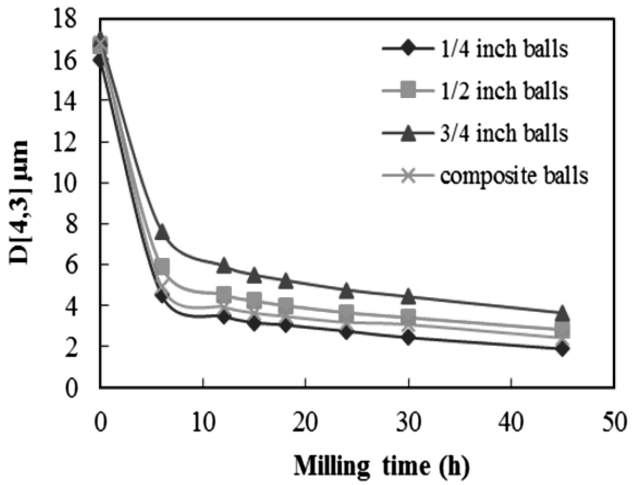

Fig. 2 Effect of ball size on D[4, 3] of ZDEC dispersions with milling time

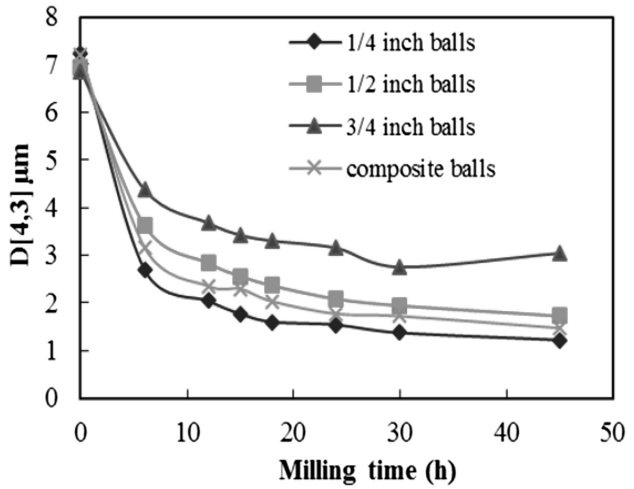

Fig. 3 Effect of ball size on D[4, 3] of ZMBT dispersions with milling time

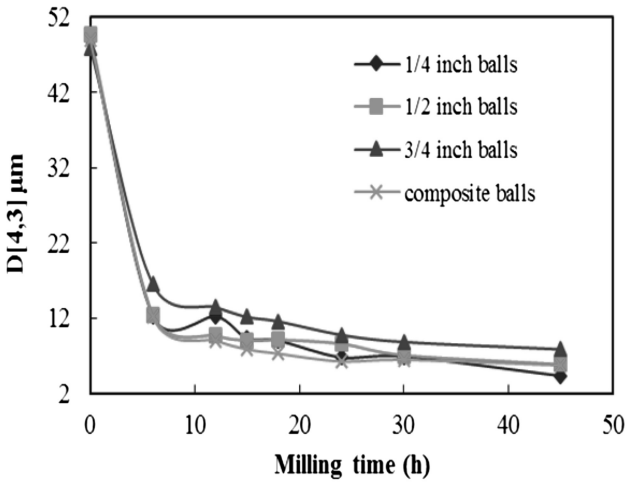

Fig. 4 Effect of ball size on D[4, 3] of wingstay L dispersions with milling time

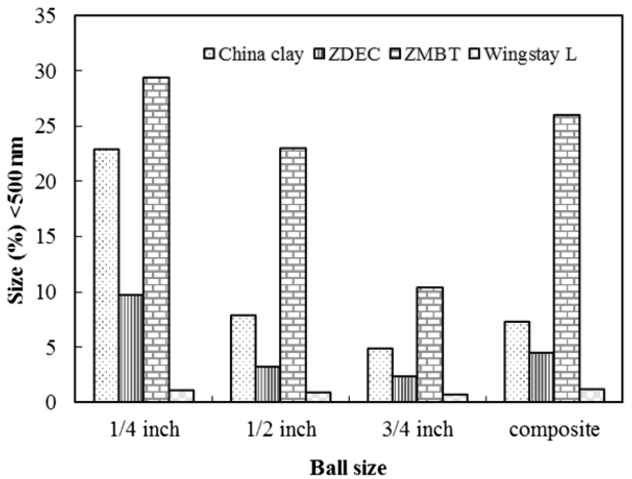

Fig. 5 Size (%) (particle size below 500 nm) of latex compounding ingredients after 45 h of wet ball-milling with ¼, ½, ¾ in. and composite ball sizes

Thus it can be concluded that irrespective of ball size, a significant size reduction is observed for ZDEC, ZMBT and wingstay L after 6 h of ball milling and thereafter size reduction is found to be slow. Interestingly, the size reduction achieved in ball milling with composite balls is at par with that of smaller sized balls. From the results cited above, it is obvious that efficiency of balls in size reduction of aqueous dispersions of latex compounding ingredients follows the order ¼ in. > composite balls > ½ in. > ¾ in.

4 Effect of Ball Size on Size

The effect of ball size on the amount of lower sized particles (i.e. particles having size <500 nm) of latex compounding ingredients (LCI) after 45 h of wet ball-milling is represented in Fig. 5. The size (%) of china clay after 45 h of wet-milling with ¼, ½, ¾ in. and composite balls are 23, 8, 5 and 7.3 % whereas for ZDEC the values are 9.7, 3.2, 2.4 and 4.5 % respectively. Among the LCI used, ZMBT retains highest share of lower sized particles and wingstay L shows lowest share of lower sized particles in all the cases (with different ball sizes). The share (%) of ZMBT is 29.4, 23, 10.4 and 26 % after 45 h of wet-milling with ¼, ½, ¾ in. and composite balls respectively. In the case of wingstay L, the size (%) of lower sized particles obtained after 45 h of wet-milling with ¼ in. and composite balls are nearly the same (1.2 %) and with ½ and ¾ in. sized balls, they are 0.91 and 0.74 % only. The size (%) of lower sized particles (size <500 nm) obtained after 45 h of wet ball-milling is found to be high. However, wet-

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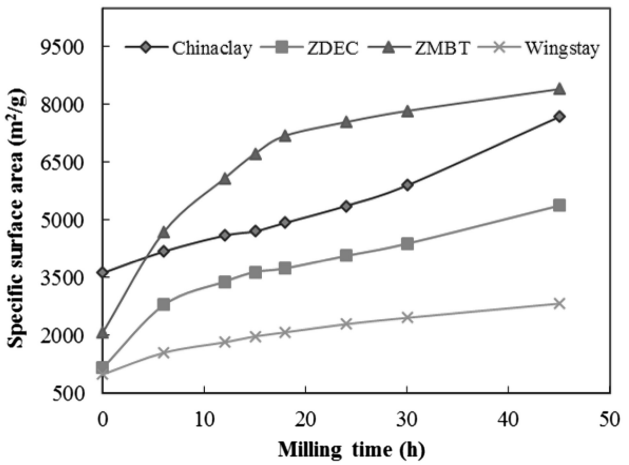

Fig. 6 Specific surface area of aqueous dispersions of latex compounding ingredients wet ball-milled with ¼ in. balls at different milling intervals

milling with lower sized balls (¼ in.) retains highest share of lower sized particles in all the cases.

5 Effect of Milling Time on Specific Surface Area (SSA) of Latex Compounding Ingredients

The effect of milling time on specific surface area (SSA) of latex compounding ingredients milled with ¼ in. balls is displayed in Fig. 6. It can be seen that irrespective of the material used, the specific surface area increases with milling time. However the extent of increase in SSA is different for different materials. The increase in SSA of ZMBT and ZDEC is quite high for the first 15 h of milling and it is more prominent in the case of ZMBT. The SSA of ZMBT is 2087 m^2/g (unmilled) and increases to 6720 m^2/g after 15 h of milling. Whereas the SSA of ZEDC is 1155 m^2/g (unmilled) and after 15 h it is found to be 3653 m^2/g only. The SSA of ZMBT and ZDEC after 45 h of ball milling using ¼ in. ball size are 8398 and 5370 m^2/g respectively. The SSA of unmilled china clay is 3617 m^2/g and it increases to 7675 m^2/g after 45 h of ball milling. The SSA of unmilled wingstay L is 982 m^2/g only and registers the lowest SSA of 2819 m^2/g among the dispersions evaluated after 45 h of ball milling.

6 Effect of Milling Time on Cumulative Size Distribution of Latex Compounding Ingredients

The cumulative size curves of latex compounding ingredients after 6, 12, 30 and 45 h of wet ball milling with ¼ in. ball size is shown in Fig. 7. As anticipated, the particle size of ingredients decreases with increase in

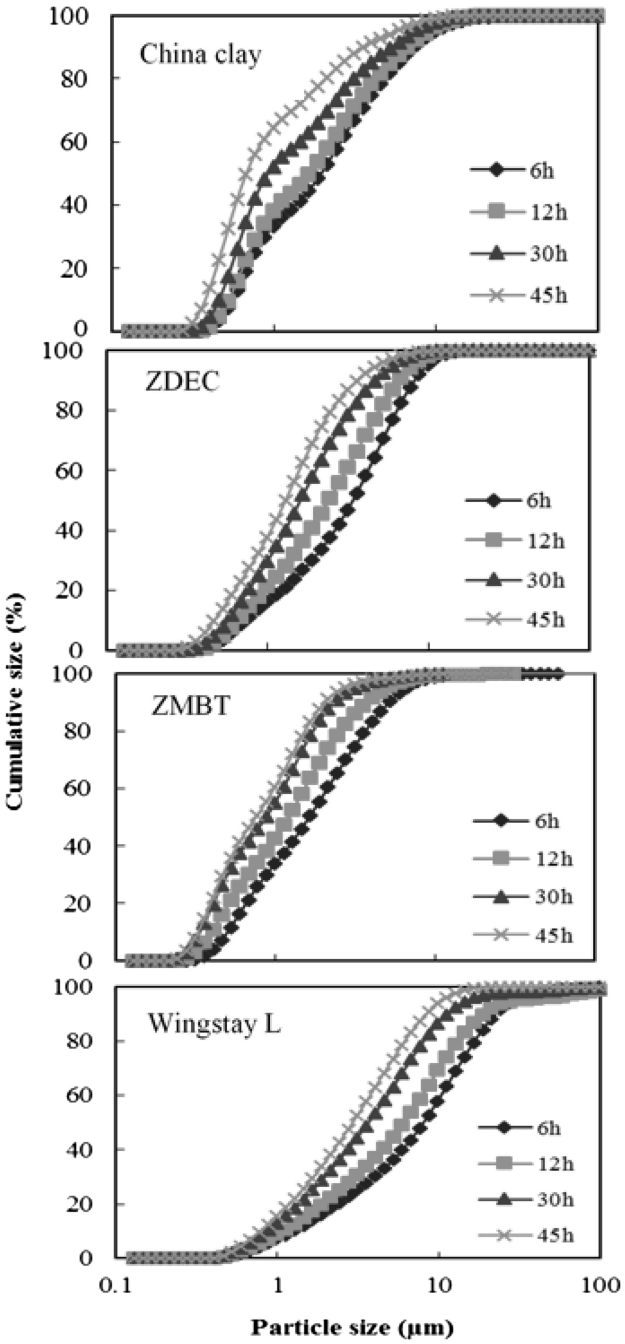

Fig. 7 Cumulative size curves of aqueous dispersions of latex compounding ingredients after 6, 12, 30 and 45 h of wet ball milling with ¼ in. sized balls

milling time. All the compounding ingredients show higher size at 6 h of milling and it significantly reduces after 45 h of milling. A clear shift in peak towards left is evident after 45 h of wet-milling indicating size reduction. The millability of the chemical can be followed from the slope of the curve. The curve is more straightened (slope increases) as higher particles reduces to lower ones at extended milling time.

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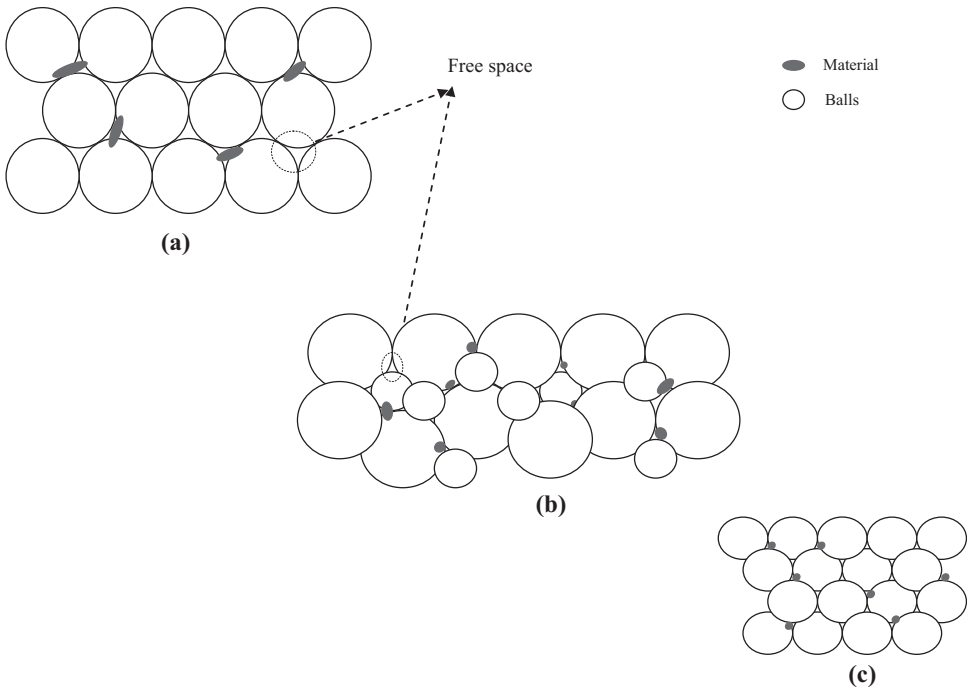

Fig. 8 Schematic representation showing the free volume in large sized balls (**a**), mixture of large and small sized balls (**b**) and small sized balls (**c**)

The reduction in particle size with prolonged milling using smaller sized balls indicates the formation of fresh surfaces during the course of grinding. As the milling time increases, the cumulative size curves moves to the left indicating lower particle size as evident from the increase in specific surface area shown in Fig. 6. With ¼ in. sized balls, there will be more number of balls in a unit volume and free volume will be minimum compared to other sizes. Consequently effective impacts on the dispersed materials will be high which results in particle size reduction.

Schematic illustration showing the effect of ball size on milling efficiency is shown in Fig. 8. The size of grinding medium has an influence on milling efficiency [12]. Large grinding medium is useful since the weight of the balls will exert more kinetic energy to particles. The kinetic energy of the balls is related to ball size by the relation,

$$KE \propto d^4 \quad (1)$$

Thus, large balls transmit high energy and hence the amount of transferred energy per collision increases. However, with increase in ball size, the free space (void space) between the balls also increases (Fig. 8a). This results in reduced ball-to-ball contact and consequently fewer ball-to-material collisions. The free space (void space) can be reduced by using a mixture of balls (composite) with different sizes. A combination of balls of various sizes results in a close packed configuration due to the occupation of small balls in the void spaces (Fig. 8b). Such configuration may presumably result in more ball-to-material impacts [13]. Using smaller sized balls, the total contact points (N) between the balls increases (Fig. 8c). As the ball size decreases, the number of balls (n) in the jar increases as $1/d^3$ (i.e. $N \propto n \propto d^{-3}$). Consequently, the rate of ball-to-ball contacts per unit time increases. As the particle breakage mostly occurs at the contact sites of the balls, smaller balls possess increased number of contact points between the balls [14]. Thus, the rate of breakage of particles by smaller sizes is higher [15]. Also, by reducing the ball size, the amount of entrapped powders increases and may result in fine particles of uniform size.

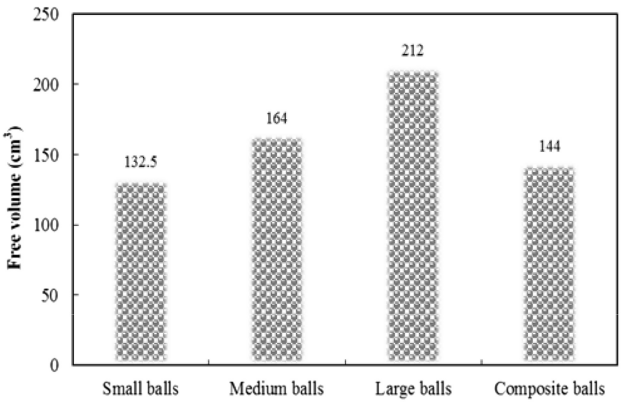

Fig. 9 Free volume available for ¼ (*small*), ½ (*medium*), ¾ in. (*large*) and composite ball systems

Figure 9 shows the free volume present in different systems each consisting of small (¼), medium (½), large

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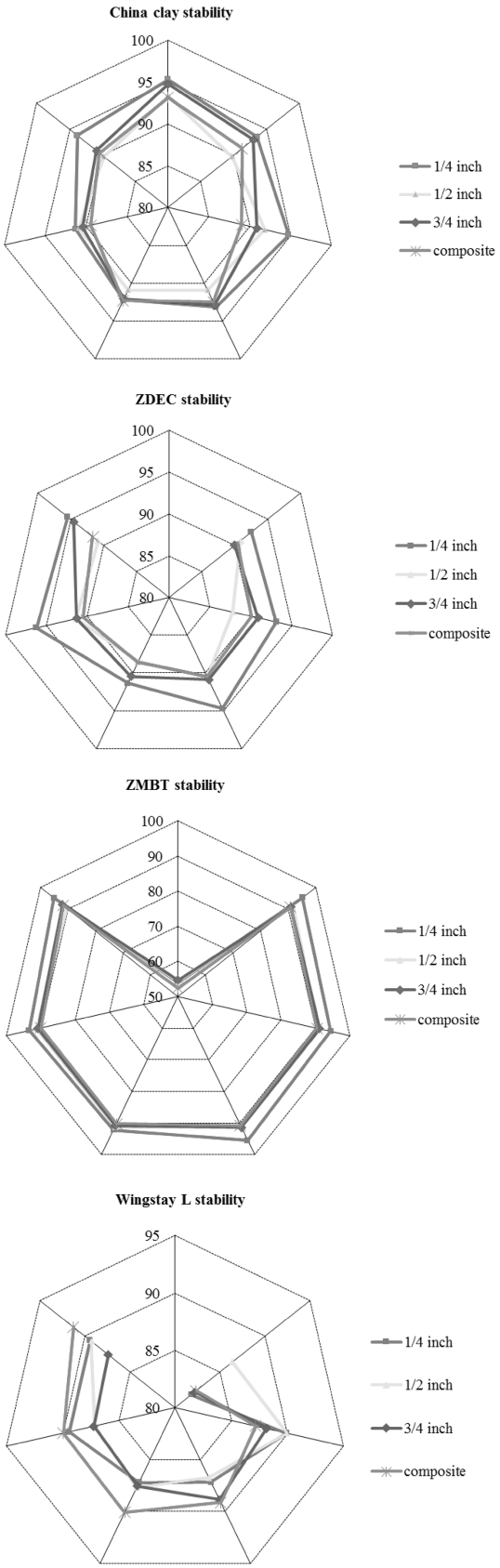

◀**Fig. 10** Effect of ball size and milling time on stability of china clay, ZDEC, ZMBT and wingstay L dispersions

(¾ in.) and combination of balls having these sizes. The free space (free volume) present in the given system containing large balls are quite high (212 cm^3) compared to medium (164 cm^3) and smaller (132 cm^3) sized ball systems. This results in reduced ball-to-ball contacts and fewer impacts. This can be ascribed to the reduced grinding efficiency observed for milling with large (¾ in.) balls. Among the different ball combinations tried, small, medium and large balls in the ratio 2:1:2 by weight shows the lowest free volume of 144 cm^3, which is comparable to 132.5 cm^3 offered by smaller (¼ in.) sized balls.

7 Stability of Dispersions

The radar plots showing the stability of china clay, ZDEC, ZMBT and wingstay L dispersions, wet-milled with different ball sizes (¼, ½, ¾ in. and composite balls) at different milling intervals (6, 12, 18, 24, 30 and 45 h) are shown in Fig. 10. [The increasing order of milling time to be considered in a clockwise fashion].

china clay shows better stability (95 %) after 12 h of milling with ¼ in. sized balls. The better stability at lower milling time is expected to be due to the enhanced dispersion capability of china clay compared to other water insoluble latex compounding ingredients. ZDEC shows highest stability (96.24 %) after 30 h of wet-milling with ¼ in. balls. In case of ZMBT also, grinding with smaller sized balls (¼ in.) shows better dispersion stability. Grinding with large, medium and combination of balls having different sizes are nearly the same in the case of ZMBT. Compared to other dispersions, the dispersion stability of wingstay L is found to be low i.e., a value of 90 % or above is highly desirable. The presence of highly complicated non-polar nature of wingstay L prevents the easy dispersion in water even after prolonged period of milling (45 h). Interestingly, stability of wingstay L dispersion is found to be good (91.28 %) after 45 h of wet ball-milling with composite balls. To improve the stability further, addition of suitable colloid stabilizer should be exercised while preparing wingstay L dispersion.

8 Conclusions

The effect of wet ball-milling on particle size and dispersion stability of aqueous dispersions of latex compounding ingredients (china clay, ZDEC, ZMBT and wingstay L)

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ball milled with different ball size was studied. Irrespective of the ball size, prolonged milling resulted particle size reduction of the chemicals. However, maximum size reduction was achieved with smaller sized balls. By reducing the ball size, the number of effective impacts could be increased. The amount of free volume (space between the balls) was minimum in small sized balls. Both of these contributed to the effective grinding of the materials. Using composite balls i.e. large (¾), medium (½) and small (¼ in.) together for wet ball milling resulted competent size reduction and was at par with that offered by smaller sized balls. The optimum ball combination was in the ratio 2:1:2 (by weight) respectively corresponding to large, medium and small sized balls. The D[4, 3] of china clay, ZDEC, ZMBT and wingstay L were 1.68, 1.9, 1.22 and 4.4 μm respectively after 45 h of milling with small (¼ in.) sized balls. The dispersion stability was also found to be good. However, wingstay L dispersions with considerable stability could be achieved by wet ball-milling using composite balls.

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