Çukurova Üniversitesi Mühendislik Mimarlık Fakültesi Dergisi, 33(2), ss. 125-138, Haziran 2018
Çukurova University Journal of the Faculty of Engineering and Architecture, 33(2), pp. 125-138, June 2018

Bead Size Distribution Dependency on Reactor Geometry and Agitation Conditions of Polystyrene Production with Suspension Polymerization

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Geliş tarihi: 01.08.2017 *Kabul tarihi: 29.06.2018*

Abstract

The relation between the reactor geometry and agitation conditions on particle size distribution for suspension polymerization of polystyrene was analyzed. The reactor geometries were selected as cylindrical and spherical, respectively. Mechanical agitation was provided via double-impeller Marine type propeller at 1600 rpm and 2000 rpm. The diameters of the reactors were selected approximately the same for cylindrical and spherical reactors in order to keep effective mixing area similar in both geometries. All experiments were conducted around 8 hours to complete the polymerization reaction. Particle size distribution analyses showed that at faster agitation conditions in cylindrical reactor narrower and smaller particles are obtained as expected. On the other hand, in spherical reactor, vortex formation and non-uniform particle size distribution were observed at faster agitation. Interestingly, when agitation speed was decreased in spherical reactor, quite narrower and smaller particle size distributions with respect to cylindrical reactor were obtained. However, the number and average molecular weight analyses suggested that the particles obtained from spherical reactor has a lower molecular weight distribution than particles from cylindrical reactor. This was attributed to the decrease in effective mixing area due to the non-homogenous changes of the distance between reactor walls and impellers throughout the spherical reactor. The geometry change to spherical geometry obviously causes diminishing in mass transfer of initiators and suspension stabilizers so that a shortening of polymer chains lead to a slight increase in polydispersity index.

Keywords: Suspension polymerization, Polystyrene, Mixing, Particle size distribution

Polistirenin Süspansiyon Polimerizasyonuyla Üretiminde Tanecik Boyutu Dağılımının Reaktör Geometrisi ve Karıştırma Koşulları ile İlişkisi

Öz

İlgili çalışmada, süspansiyon polimerizasyonu yoluyla elde edilen polistirenin reaktör geometrisi ve karıştırma koşullarına bağlı olarak parçacık büyüklüğü ve ortalama moleküler ağırlık dağılımları incelenmiştir. Karıştırma işlemi, ikili marin tipi pervaneli bir karıştırıcı ile 1600 dev/dak ve 2000 dev/dak olmak üzere iki farklı karıştırma hızında gerçekleştirilmiştir. Etkin karıştırma alanını kaybetmemek için her iki reaktörün de çaplarının birbiriyle uyumlu olmasına dikkat edilmiş, ayrıca polimerizasyonun

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tümüyle bittiğinden emin olmak için tüm deneyler yaklaşık 8 saat sonunda kesilmiştir. Silindirik reaktörde beklenildiği üzere artan karıştırıcı hızıyla küçük çaplı taneciklerin arttığı ve dağılımın bu aralıkta yoğunlaştığı gözlenirken, küresel reaktörde ise yüksek karıştırıcı hızının vorteks oluşumuna ve tanecik boyutlarının kontrolsüze gelişmesine neden olduğu ancak düşük hızlarda ise çok daha etkin bir yoğunlukta küçük tanecik aralığının elde edildiği görülmüştür. Öte yandan, ortalama moleküler ağırlığı dağılımı tayinleri küresel reaktörde elde edilen polistirenin silindirik reaktörde elde edilenlere göre daha düşük moleküler ağırlık dağılımına sahip olduklarını ortaya koymuştur. Bunun nedeninin küresel reaktörde, karıştırıcı pervanelerinin reaktör duvarlarına göre yukarıdan aşağıya sabit mesafede olmayışı ve dolayısıyla silindirik reaktöre nazaran etkin bir kütle ve ısı transferinin sağlanamayarak polimer zincirlerinin kısalmasına ve polidispertiste endeksinin yükselmesine yol açtığı düşünülmektedir.

Anahtar Kelimeler: Süspansiyon polimerizasyonu, Polistiren, Karıştırma, Parçacık boyut dağılımı

1. INTRODUCTION

Heat and effective mass transfer is of crucial importance in every system, either chemical or physical changes take place [1-4]. This can be provided by a homogeneous mixing. Therefore, a careful analysis on mixing regimes is necessary to predict the whole system behavior. Especially for mixing sensitive reactions the close relationship between agitation speed, agitator properties and reactor geometry have to be determined [5].

Expandable Polystyrene (EPS) production via suspension polymerization is one of the mixing sensitive processes applied in industry. During this semi-batch type process, styrene monomer gets dispersed in deionized water by mechanical agitation and polymerization takes place in droplet phase with free radical mechanism. Initiators are also used together with suspension stabilizers which prevent coagulation or gel formation [6-8]. A successful EPS production results in spherical beads with a particle size range between 100-2500 μm [7]. The spherical beads are important according to the sectors they are used. For instance, filling materials for construction is desired to be between 1500-2500 μm ranges while for insulation boards this range is between 800-1200 μm. On the other hand, packing and decorative items are ranging between 400-800 μm and even below. Consequently, it is critical to produce EPS beads in a desired range for different industrial areas. Indeed, the initial droplet formation determines the bead size distribution and it is depended on either break-up of droplets or coalescence of polymerized particles [9,10].

The target particle size distribution (PSD) in industrial production is achieved through an optimum reactor design and agitation conditions together with suspension stabilizers. In fact, because there is no possibility to change the reactor geometry and agitator type for each time at large scale productions, the most applicable parameters to obtain different size ranges are chemical additions and the agitation speed control [7]. Since chemical additions might be more costly in order to optimize the whole system in means of changes in viscosity and reaction conditions, the latter method -agitation speed control- is more preferred. Even though in literature the effect of different initiators, suspension stabilizers, and agitation conditions on polymerization rates and polystyrene bead size formation of polystyrene has widely been investigated, the sole reactor geometry and agitation conditions on resulting PSD is not explicitly studied. The aim of this study is to track the particle size distribution (PSD) of polystyrene particles obtained via suspension polymerization as a function of reactor geometry and agitation conditions.

2. LITERATURE

In literature, different aspects of suspension polymerization of styrene, methylmetacrylate (MMA) and similar materials were investigated. Unfortunately, most of them focused different parameters and it is hard to make a summary in means of reactor, agitation conditions and bead size distribution together. The summary of different studies can be found in Table.1. Hence, the close relationship between bead size formation, agitation conditions and polymerization has been shown in various studies carried out with polystrene [11-21], there are also different studies investigating only the polymerization effect on suspension agent amount [16,20,24,26,33], impeller type and/or polymerization degree [24].

In general, it is assumed that the particle size formation takes place according to two different mechanisms; the coagulation rate of the droplets and the breakage of droplet rates. Addition to this, the agitator design studies showed that [18] the ratio of agitator diameter to tank diameter is the key parameter to define the droplet size formation mechanism. If this ratio is low, breakage phenomena is more effective because of isotropic turbulence and the particles smaller than 1000 μm would be expected. In case of higher ratios, the velocity gradient around reactor wall is more effective [10]. Therefore, as a rule of thumb, if the initial emulsion is polydisperse, then suspension polymerization will result in a relatively wide particle size distribution with particles bigger than 1000 μm but also smaller particles than 600 μm. In fact, depending on the agitator type, a turbulent flow area may be created with a turbine type agitator which leads to changes in PSD. Moreover, increasing the agitator diameter was reported to decrease the particle size distribution due to the energy dissipation rate within this area [17].

Interesting outcomes have been reported in literature according to the change in agitator design. For example, Tanaka and Izumi, [16] who used a totally different agitator design composed of a six-bladed disc turbine assisted with a draft tube, mentioned that mean droplet diameter and final particle size were not affected by impeller height but the draft tube. The longer the draft tube resulted in more uniform particle size distribution and larger particles. But still, they also noted an initial decrease in particle size when agitator speed was increased without mentioning the agitation speed and PSD values. In another study by Yang et al. [39] who also used six bladed impeller type agitator recorded 130 μm at 350 rpm in a smaller flat bottomed reactor system where PVA is used as suspension agent. Similar to this impeller type, Polacco et al. [37] used a six-bladed Rusthon type impeller and obtained 121 μm at 750 rpm in a MMA-water system. They related polymerization degree and mean diameter. In terms of impeller number and design, Nogueira et al. [14] used four flat bladed agitator at 350 rpm for a styrene-water system with PVP as suspension agent and reported a PSD around 700 μm. Simply changing impeller design can lead huge differences in PSD. Also similar 4 flat bladed impeller type with higher agitator speed of 500 rpm decreased the PSD to 100 μm for a MMA-water system [20]. Especially, systems including styrene/IPA-toluene systems with cross linkers, PSD decreased much smaller values between 3.5-9 μm at lower agitator speeds like 120 rpm [36]. A study conducted with 2 flat bladed at 400 rpm with n-butyl chloride noted an increase in PSD up to 80 μm [40].

In terms of suspension agent amount and PSD relation, Platzer et al [29] reported a bead size decrease as HEC amount increased changing between the ranges of 1100-700 μm. Another work which HEC was used as suspension agent [34] also verified that at lower levels of HEC stabilizer increased the particle size rapidly. A different suspension agent for this system, ZnO, was by Widjaja et al [31]. They also observed a decrease with increasing ZnO concentration. TCP has been used for styrene-water suspension polymerization reactions [11, 32]. Some studies conducted with PVA or PVP [14,16,19] but direct effect on PSD was not the focus of research in them.

Both experimental and theoretical studies were carried out with constant reactor geometries and agitator types [9,22-39]. Furthermore, cylindrical type reactors are selected for most of these particle size distribution investigations. Therefore, differently from other studies, particle size distributions in spherical type of reactor at slow and fast agitation conditions were observed in this work. In order to focus only the mixing effects and diminish complicated polymer chemistry, all additive ratios and parameters such as temperature were kept constant. To give a better insight for the effect of reactor geometry, at similar conditions experiments were repeated in a cylindrical type reactor.

3. EXPERIMENTAL

3.1. Experimental System

Suspension polymerization of polystyrene was carried out in a 10 L cylindrical and a 6 L spherical boro-silicate glass reactor at atmospheric pressure, separately. In order to keep the effective mixing area and polymerization rates constant, the same agitator was used for both systems. The diameters (D) of the reactors were selected as 20 cm and 22 cm for cylindrical and spherical, respectively. Actual height of the cylindrical reactor was 33 cm but since ¼ of the reactor was not filled, effective height (L) that mixing took place was decreased to 24.75. Therefore, L/D ratio of cylindrical reactor was around 1.24. Similarly, L/D ratio of spherical reactor was calculated 0.75 when the effective height decreased to 16.5 cm. The reactors were placed in a heating mantle with appropriate diameter. Heating was provided by this heating mantle while cooling was done under air circulation with a vent. Temperature was tracked with a thermocouple. All the experiments were carried out under atmospheric pressure.

The mechanical agitator was selected as a marine type propeller consisted of double impellers as shown in Figure 1. Only one experiment was carried out with a single-impeller agitator which showed that the mixing was not homogeneous throughout the reactor so all other experiments were done with double impeller agitator. Even if in literature spiral stirrers were reported to provide a relatively turbulent-free and uniform distribution throughout the suspension mixture [24, 33], since in industry they are not likely used, a three bladed impeller agitator was used in this study.

Detailed scheme of the reactor and agitator parameters are given in. Figure 2. The diameter of agitator impeller was 4 cm and the distance between 2 impellers (for the double-impeller agitator) was around 6 cm. Moreover, the agitator was positioned 9 cm above the bottom of the cylindrical reactor while it was lowered for spherical reactor up to 4 cm above its bottom due to vortex formation at higher positions.

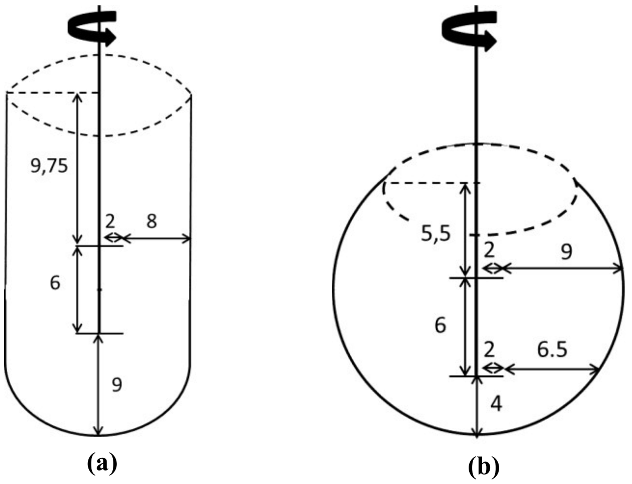
Figure 1. Double-impeller Marine type propeller used for mechanical agitation (Scale is arbitrary)

In order to observe particle size distributions, two agitator speeds as 1600 rpm (referred as slow agitation) and 2000 rpm (referred as fast agitation) were selected among different trials.

3.2. Method

High purity styrene monomer (SM) (purity ≥ 99.99, purchased from Sigma Aldrich), Benzoyl Peroxide (BPO) (purchased from abcr Gmbh) and tricalcium phosphate (TCP) (purchased from Sigma Aldrich) were used without further purification. The recipe was based on Erbay et. al's study [11] with a volumetric deionized water/SM ratio of 50/50. For 10 L reactor, approximately 4.6 L SM and equal amount of DI water was added separately to the 10 L reactor initially under stirring. Besides, 20 g BPO and 4 g of TCP were used as initiator and suspension agent, respectively. The SM and DI amounts were decreased according to for 6 L reactor as 2.76 L SM and equal amount of DI water, 12 g BPO and 2.4 g TCP, respectively. The temperature was slowly increased to 90°C. It is generally the critical temperature for suspension polymerization of polystyrene since above this temperature agglomeration of particles cannot be avoided [5-8]. It was stated by Yang et al. [39] who studied the drop size of styrene monomer in suspension polymerization, the transitional time for a dynamic equilibrium to be established in the dispersions was around 150 min. But to be on the safe side the reaction time of suspension polymerization was kept around 8 hours for all experiments in order to be sure that the polymerization was completed.

Then, the polymer beads were filtered and dried on a filter paper overnight under fume hood. Dried beads were sieved for approximately 15 minutes manually and separated according to particle diameters of 2000 µm, 1600 µm, 800 µm, 400 µm, respectively. These sieve ranges were selected according to industrial EPS size ranges. The sieved particles were weighed and their relative percentage of each set was calculated. Molecular weight distribution analyses were carried out with a Schimadzu RID 10A HPLC system.



(a) (b)

Figure 2. Position of the agitator in (a) cylindrical and (b) spherical reactors. Dashed lines represent the level of the suspension system. The impellers are 30° angled but for simplicity, they are shown as flat here. All dimensions are given in cm

Table 1. Literature values for various suspension polymerization studies

Reactor Properties			Agitator Properties			Suspension System		Bead Size Distribution (µm)	Ref.
Reactor Volume (L)	Reactor L/D (cm/cm)	Baffle Number	Agitator Type	Agitator Diameter (cm)	Agitator speed (rpm)	Suspension System	Suspension Agent: Amount		
20	16.2/28	2	3 curved blade	22.1	350	Styrene-water	TCP: 0.6 phm	845	[11]
							TCP: 1.4 phm	350	
					225		TCP: 1.4 phm	640	
					150		TCP: 0.6 phm	1781	
							TCP: 1.4 phm	1230	
				18	150		TCP: 1.4 phm	740	
				15.2	150			880	
1	NA	NA	4 flat blades	NA	350	Styrene-water	PVP	700	[14]
NA	18/12	2	six-bladed disc + Draft Tube	NA	NA	Styrene-water	PVA	NA	[16]
1	NA/10	4	4 bladed flat turbine	5	500	MMA-water	PVA	100	[19]
1	NA	4	4 bladed flat turbine	5	500	MMA-water	PVA	NA	[20]
30 (Continuous Flow Reactor)	110/101	NA	Paddle impeller, flat	7.55	180-250	Styrene-Toluene	-	NA	[24]
			Ribbon spiral impeller	8.2	80-150				

Table 1 (continue)

2	NA	NA	NA	14	190-1300	Styrene-Toluene	-	NA	[26]
9.2	NA	4	NA	NA	2000	Styrene-water	TCP: 10.45 g	NA	[32]
0.125	NA	-	Shaker	-	-	Styrene-polar system	NA	NA	[38]
240	96/57.6	2	3 curved blade	36	150	Styrene-water	HEC: 0.03%	1100	[29]
							HEC: 0.04%	900	
							HEC: 0.06%	750	
							HEC: 0.08%	700	
0.2	NA	NA	NA	NA	NA	Styrene-water	ZnO: 0.03 g	550	[31]
							ZnO: 0.05 g	150	
NA	200/D	NA	2 bladed spiral stirring	NA	NA	Styrene-water	NA	NA	[33]
2	NA	NA	NA	NA	150	Styrene-water	HEC: 0.4 / 0.1	280 / 450	[34]
					200		HEC: 0.4 / 0.1	200 / 380	
					300		HEC: 0.4 / 0.1	150 / -	
					400		HEC: 0.4 / 0.1	150 / -	
					500		HEC: 0.4 / 0.1	140 / 1300	
1000	NA	NA	NA	NA	210	VCM-Water	-	200	[35]
					230			120	
					250			70	
1	NA	NA	4 bladed	NA	120	Styrene-IPA/Toluene System DVB:CrossLinker	PVP: 13 wt% DVB wt %: 0	4.5	[36]
							DVB wt %: 0.75 (IPA:100%)	3.5	
							DVB wt %: 1.5 (IPA/T: 93/7)	5.2	
							DVB wt %: 1.5 (IPA/T:86/14)	9.1	
1	NA	NA	45° six-bladed Rusthon type	5.5	750	MMA-water	HEC: 0.6g /100 g water	121	[37]
Flat bottom	NA/14.4	4	six-bladed disc	7.2	350	Styrene-water	PVA	130	[39]
4.5	24.1/15.2	-	2-bladed flat impeller	12.7 and 9.8	400	n-butylchloride	PVA: 1 g/L	70	[40]
							HPMC: 1g/L	90	
					500		PVA: 1 g/L	45	
							HPMC: 1g/L	80	
					700		PVA: 1 g/L	40	
							HPMC: 1g/L	40	

4. RESULTS AND DISCUSSION

4.1. Particle Size Distribution (PSD) Analyses

PSD as a function of agitator conditions in cylindrical reactor are given in Figure 3.

Particle size distributions obtained from cylindrical reactor with single-impeller (1x3) and double-impeller (2x3) agitators for slow (1600 rpm) and fast (2000 rpm) agitation conditions. Single impeller (1x3) experiment could be done only for fast agitation speed due to the unstable suspension conditions at lower speed. Hence, even at fast agitation, abnormal changes in viscosity and vortex formation, which are indications of non-homogenous mixing, were observed. Therefore, all other experiments were carried out with double impeller agitator. The dominant particle size range for single impeller agitation was found to be populated between 800-1200 µm (40%). However, bigger particles whose size range is between 1200-2000 µm were found to be more than the smaller particles whose size range is between 1200-2000 µm. Generally, this result would be expected for slow agitation conditions for cylindrical reactor geometries. Therefore, it shows that with single impeller, the coagulation rate of the droplets is more effective than the breakage rate of droplets. Hence, this agitator is not able to provide enough energy dissipation rates.

The most similar impeller system to this study was conducted by Erbay et al. [11] and Platzer et al. [29] with three curved blade agitator. However, Platzer et al. [29] worked on a 240 L reactor with an agitator with 36 cm diameter at 150 rpm and investigated on the suspension agent amount effect (HEC) as a function of PSD. Erbay et al. [11] conducted a detailed research on both suspension agent amount (TCP), agitator diameter and agitator speed. They concluded that the effect of agitator parameters have a strong influence rather than TCP amount. However, their results also show that as TCP amount is decreased, PSD increases. For the same TCP amount, and at the same agitator diameter, they showed that as speed is decreased, an increase in PSD can be tracked. When agitator diameter and PSD change is compared at the same speed and TCP amount, it wa seen that the increase in diameter results in increase in PSD as well. Unfortunately, since there are many different parameters in these studies including impeller, design, reactor volume, baffles and even suspension system, these results are not directly comparable to each other and the related study.

After the impeller number was doubled (2x3), the vortex vanished, agitation deviation decreased and a homogenous mixing throughout the reaction was observed at the same agitation speed. Moreover, a drastic shift from the distribution curve towards smaller particle size range was observed. The particle size range narrowed to 400-1200 µm with the highest particle size range population between 400-800 µm (52%). Consequently, the density of bigger particles nearly disappeared and only a small portion of particles between 1200-1600 µm was formed. The ratio of smaller particles below 400 µm is increased when compared to single-impeller agitator. It is known that narrower and smaller bead size distributions can be formed by increasing the agitation speed [9,11,35,41] during suspension polymerization reactions. This is not only valid for styrene-water suspension systems but also different suspension systems like VCM-water as reported by Choi et al. [35]. They observed a shift of PSD to smaller sizes when the agitation speed was increased due to the higher breakage rate at the early stages of the polymerization.

Hence, adding an extra impeller has a similar effect that shows the enhancement of effective mixing area and the importance of selecting the correct number of impellers at the design level. When the agitation speed was decreased to 1600 rpm with double-impeller agitator, the particle sizes get bigger. However, the ratio of the particles over 2000 µm is the dominating range (41%) which is not within the targeted zone. Therefore, 1600 rpm seems already the critical speed under which will result in unwanted bigger particles at this reaction conditions.

On contrary to cylindrical reactor, when the agitator mounted at the same position in spherical reactor, 1600 rpm was not fast enough to enable homogeneous mixing so the speed was increased to 2000 rpm during the experiment. However, in the end of the experiment, agglomerated and needle like particles were obtained. Due to change in geometry, the effective mixing zone couldn't be well controlled at this agitation conditions with the agitator position for this geometry.

After the agitator was mounted at lower position within the spherical reactor, it was found that even slower agitation speed was good enough to have small spherical shaped particles in the size range between 400-800 µm with a ratio of 67.8%. Surprisingly, this range could be obtained up to 52% in cylindrical reactor only at faster speed. When the speed was increased to 2000 rpm in spherical reactor, particles get smaller than 400 µm and couldn't be analyzed so the results for fast agitation are not shown in this study. The comparison of spherical reactor results to cylindrical together is given in Figure 4.

The results are summarized in Table 2. It shows that there is a tendency to obtain narrower and smaller particle size distribution at faster agitation conditions in cylindrical reactor. On the other hand, even narrower and smaller particle size distributions can be obtained in spherical reactors by just mounting the agitator at lower position rather than increasing the speed. This can be attributed to the effective turbulent flow area created by decreasing the distance of the reactor bottom and agitator in spherical geometry. Because in this geometry, the axial flow pattern cannot be maintained as in the cylindrical geometry, the random flow pattern causes particles to break into droplets. This random flow pattern leads to high percentage of narrow bead size distribution which seems energetically favored with slower rate. However, at this point, the question to be answered shows up if this random mixing is enough for the mass and heat transfer through the reactor. In order to answer, molecular weight distributions were determined and compared at slower agitation conditions for both reactor types. Besides, to make a complete picture, fast agitation with single impeller results were also analyzed. Since at faster agitation, there were already agglomerated and non-homogeneous shaped particles in spherical reactor, the mixing regime seems already not homogeneous. Therefore, for this case no molecular weight distribution analysis was done. Detailed GPC analysis is discussed in next section.

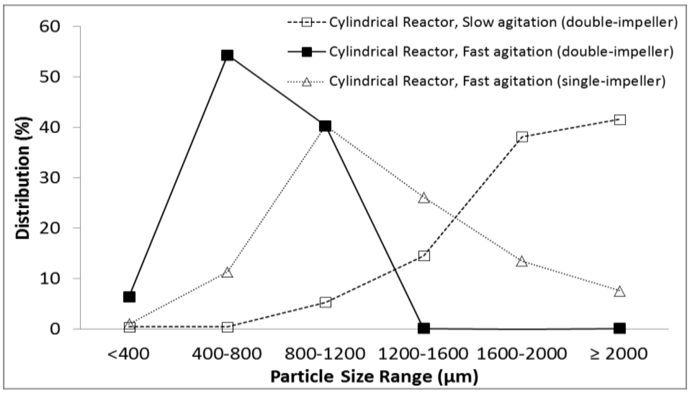


Figure 3. Particle size distributions obtained from cylindrical reactor with single-impeller (1x3) and double-impeller (2x3) agitators for slow (1600 rpm) and fast (2000 rpm) agitation conditions

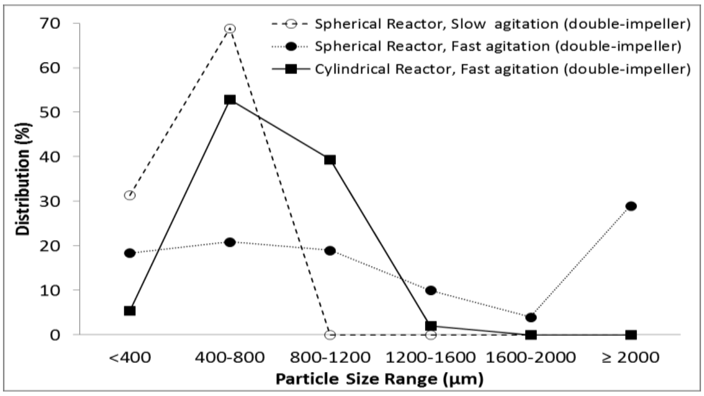


Figure 4. Particle size distributions in spherical reactor for slow (1600 rpm) and fast (2000 rpm) agitation conditions compared to the size distribution in cylindrical reactor for fast (2000 rpm) agitation condition with double-impeller (2x3) agitator for all cases.

Table 2. The summary of suspension polymerization of polystyrene in different reactor geometries and agitation conditions

Vol. (lt)	Agitator Speed (rpm)	Impeller Number	Dominating Size Range (µm)	Perc. (%)	Visual Observations
6	2000	2x3	≥ 2000	28	Higher amount of agglomerated particles & needle formed particles
	1600	2x3	400-800	67.8	Spherical shaped particles at smaller sizes with narrower distribution*
10	1600	1x3	800-1200	40	Vortex formation, abnormal changes in viscosity
	2000	2x3	400-800	52	Narrower bead size distribution
	1600	2x3	≥ 2000	41	Bigger particles above target zone

*Agitator at lower position

4.2. Molecular Weight Distribution Analyses

In order to understand the degree of effective heat and mass transfer for different agitation conditions, molecular weight distribution analysis were done and results are given in Table 3. The ratio of weight average molecular weight over number average molecular weight (M_w/M_n), which is known as the polydispersity index (PDI), describes how far away the distribution is from uniformity. Hence, in this study, both the values of M_w and M_n for each system were considered to understand the strong relation between the reactor geometry, number of impellers, and agitation speeds. Actually for both cases PDI was used as an indication for poor or good mixing. When the mixing was assumed to be good enough, PDI is expected to be higher for spherical reactor since the initiator/monomer ratio of spherical reactor (6.5) was higher than cylindrical reactor (4.3). However, the deviation from uniformity is higher in spherical reactor. Besides, number average molecular weight is much smaller than cylindrical reactor values. For both cases, molecular weight is smaller than literature in which Machado and Bolzan [32] reported 289000 for the PS-water system they carried out in a 9.2 L reactor. The L/D ratio and also impeller details were not mentioned in the study but a major difference from this work is they used baffles. Besides, the TCP amount that they used was much higher which might provide the styrene droplets not interfere with each other and the polymerization process going on within those styrene droplets.

Another outcome of this GPC analysis is even if geometry and agitation conditions are different, during suspension polymerization, PDI is not as broad as observed in thermally initiated polymerization reactions which may vary between 1.2-1.8 [43]. Hence, it is much easier to control polymerization rate in a suspension intermediate that provides heat and mass transfer instead of a bulk mixing of polymer itself.

For cylindrical geometry, the fast (2000 rpm) and slow (1600 rpm) agitation conditions were compared in means of impeller number. When impeller number is decreased but agitation speed is increased, M_n and M_w don't change much. This result shows that the mass and heat transfer can be balanced in such cylindrical geometry in terms of impeller design. The decrease in agitation speed will also provide energy saving in scale-up processes. By addition of extra impeller an effective axial flow pattern was provided. It should be noted that of course for scale-up processes not only the impeller design but the L/D ratio and the baffles must be selected in coordination. For this case, this result was a consequence of laboratory scale system whose volume was enough to have good mixing conditions. All in all it can be concluded that in cylindrical geometry, if a successful agitation change is provided, without changing the amount of additives, it is still possible to control the heat and mass transfer effect successfully.

Table 3. Molecular weight distribution results as a function of agitation conditions

Reactor Geometry	**Impeller Number**	**Agitation Speed (rpm)**	**Number Average Molecular Weight (M_n)**	**Weight Average Molecular Weight (M_w)**	**Polydisp. Index (PDI) (M_w/M_n)**
Cylindirical	1x3	2000	220000	225000	1.023
	2x3	1600	220000	223000	1.014
Spherical	2x3	1600	194000	216000	1.113

In a 2 L styrene-toluene system Erdogan et al. [26] tracked the effect of agitation speed and heat transfer coefficient with the help of conversion. The conversion was found to increase up to 500 rpm while above this speed, conversion rate seems decrease. However, as stirring speed was increased, the heat transfer coefficient was found to increase. This shows that even if heat transfer is good at higher stirring rates, still the related polymerization kinetics are not provided after a critical stirring conditions. As discussed by Nienow et al. [42] the shift in mass transfer boundary between reactants and the mixing intensity in suspension polymerization reactions may cause increase in number average molecular weight. However, in this study, it looks like the increase in impeller number provides only an effective breakage mechanism for polymer particles rather than an effective mass and heat transfer. On the other hand, when the reactor geometry is changed from cylindrical to spherical, a decrease in number and weight average molecular weight was observed. This is attributed to the decrease in effective mixing area due to the non-homogenous changes of the distance between reactor walls and impellers as can be seen in Figure 2. This geometry change obviously causes diminishing in mass transfer of initiators and additives resulting in the shortening of polymer chains. In addition, a slight increase in polydispersity index was obtained for spherical geometry related to this decrease in M_n and M_w. Tosun [44] suggested that polydispersity can rise greatly as mixing becomes increasingly non-ideal for a semi-batch stirred tank-reactors with the help of "partially segregated feed" model. In this case, both geometries can be said not dominated by partially segregated feed model as PDI was not rise greatly. Even if the spherical reactor has a more homogeneous particle size distribution as a result of effective drop breakage mechanism during stirring, the lower M_n and M_w values suggest that a better mixing pattern can be obtained in cylindrical geometry due to the created axial flow pattern in terms of heat and mass transfer. As a summary, GPC analysis showed that even if the narrowest particle size distribution was obtained for spherical reactor at 1600 rpm, the polymerization was not completed due to non-homogeneous agitation resulting in poor heat and mass transfer. Therefore, not only bead size distribution but also polymer properties must be tracked during reactor design for similar processes.

In theory, if M_n and M_w range is acceptable around 200000, in order to have a homogenous PSD, spherical geometry might be economical due to slower agitation conditions for laboratory experiments. However, during practical use, spherical geometries are not preferable for scale-up applications. All in all at higher agitations in spherical reactor, the increase in non-ideal mixing can be understood in terms of non-spherical particles. This was attributed in literature [9,10,13,14,25] due to the domination of coagulation rate of droplets rather than the drop breakage mechanism.

5. CONCLUSION

In cylindrical reactor, particle size deviations and vortex formation was obtained with single impeller agitation. This shows that the axial flow pattern and a homogeneous mixing couldn't be achieved with single-impeller. However, in means of molecular weight analysis, the heat and mass transfer seems enough for a similar polymerization rate when compared to double impeller agitation whose mixing was already the most homogenous among all other experiments. Since all the experiments were carried out without baffles, the particle size distribution can be improved with the addition of baffles when single impeller agitator is used. By this way, the coagulation of particles due vortex formation will be eliminated. On the other hand, by changing the reactor geometry from cylindrical to spherical, very narrow particle size distribution could be achieved at lower agitation speed. However, unlike cylindrical reactor, as the agitation speed was increased, a broadening in the particle size distribution was recorded.

Furthermore, the tendency of particles to agglomerate was greater than in cylindrical reactor. This was considered as the loss of effective mixing area due to the varying distance of reactor walls and agitator throughout the spherical geometry. This could also be observed in molecular weight distributions. The M_n decreased when the geometry was changed to spherical reactor.

6. ACKNOWLEDGEMENTS

This research has been funded by Çukurova University B.A.P. ID 6979. Endless support of Prof. Dr. Bilgehan GÜZEL is acknowledged.

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