Journal of Polymers and the Environment (2021) 29:219–229
https://doi.org/10.1007/s10924-020-01869-7

ORIGINAL PAPER

Preparation of Polymer Microparticles Through Non-aqueous Suspension Polycondensations: Part IV—Effect of the Continuous Phase on the Characteristics of Final Poly(Butylene Succinate) Particles

Luciana da Silva Dutra[1] · **Marcio Nele de Souza**[1,2] · **Jose Carlos Pinto**[1,2]

Published online: 3 September 2020
© Springer Science+Business Media, LLC, part of Springer Nature 2020

Abstract

Suspension polycondensations used to manufacture poly(butylene succinate) (PBS) can be regarded as a type of inverse heterogeneous polymerization technique, as the monomer phase is formed by polar reacting compounds (1,4-butanediol and succinic acid) that are partially soluble in water and require the use of a nonpolar continuous phase in order to form stable suspended droplets. In this context, the main objective of the present study was to investigate the influence of the continuous phase on the kinetic behavior of suspension PBS reactions and the morphological aspects of PBS particles produced through suspension polycondensations. Particularly, renewable soybean oil was used here for the first time as the continuous phase for preparation of PBS microparticles and results were compared to data obtained when paraffin was used as the continuous phase. It is shown that soybean oil can be used successfully as the continuous phase of polycondensations, allowing for production of microparticles with regular spherical morphology and leading to sustainable *greener* processes, as the constituents of both the continuous and discontinuous phases can be obtained from renewable materials.

Keywords Poly(butylene succinate) · Suspension polycondensation · Sustainable green process · Soybean oil

Introduction

The 21st century has been distinguished by the pursuit of new technologies and processes, which can generate closed carbon cycles and promote the circular economy [1]. Additionally, there has been growing concern for use of feedstocks derived from renewable sources and production of more sustainable and environmentally friendly materials [2, 3]. Within this very broad context, one must cite applications that require the manufacture of polymer microparticles intended for hygiene and personal care products [4]. Nowadays, these polymer microparticles are predominantly produced with oil-based monomers, so that the development of alternative sustainable materials is necessary [5].

When polycondensation resins are used as raw materials for manufacture of polymer microparticles, the final beads must usually be obtained with help of post-reaction techniques, including spray drying, solvent evaporation, coaxial electrospraying and microfluidic devices [6]. In all these cases, a polymer solution must be initially prepared and the solvent must be removed from droplets after some sort of atomization [7–10]. These procedures normally require the use of large amounts of solvents, leading to significant energy consumption and necessary recirculation of the residual solvent, which lead to increasing costs and high environmental impacts. Therefore, the removal of post-reaction treatments can be very beneficial for process intensification and development of cleaner polycondensation processes.

When polymerizations are performed in heterogeneous media, as in standard emulsion and suspension free-radical polymerizations, the polymer synthesis and the particle production steps occur simultaneously inside the reactor, simplifying the process [11]. However, very little is known about polycondensations performed in heterogeneous media. Recently, Dutra et al. [12–14] reported the successful development of a suspension polycondensation process that can be used for manufacture of microparticles in a single process

---

✉ Luciana da Silva Dutra
ldutra@eq.ufrj.br

[1] Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brazil

[2] Programa de Engenharia Química/COPPE, Universidade Federal do Rio de Janeiro, Cidade Universitária, CP: 68502, Rio de Janeiro, RJ 21941-972, Brazil

step. Particularly, Dutra et al. [12–14] showed that it is possible to produce poly(butylene succinate) (PBS) microparticles through suspension polycondensation of succinic acid (SA) and 1,4-butanediol (BD) [12] and studied the effects of different operation variables (such as reaction temperature, reaction time, monomer holdup, surfactant concentration and stirring speed) on the properties of the obtained PBS product (such as particle size distributions and molecular weight distributions) [13]. Dutra et al. also investigated the degradation of PBS microparticles in different aqueous media at different conditions of salinity, pH and temperature, showing that these materials can be hydrolyzed in aqueous media at distinct conditions and suitable time scales [14]. Other groups also reported the successful production of polycondensation polymers in suspension, including polybenzimidazole [15], polyimides [16, 17], polyurethane [18] and poly(p-phenylene terephthalamide) (PPTA) [19].

PBS suspension polycondensations can be regarded as a type of inverse heterogeneous polymerization technique, as the monomer phase is formed by polar reacting compounds (BD and SA) that are partially soluble in water and require the use of a nonpolar continuous phase in order to form stable suspended droplets. For this reason, Dutra et al. [13] originally proposed the use of paraffin as the continuous phase. Nevertheless, the use of paraffins can cause some process drawbacks. For instance, oil-based paraffins are not renewable and increase the environmental impact of the process. Besides, oil-based paraffins that are liquid at the required polymerization temperatures are solid at ambient temperatures, imposing the filtration and cleaning of the obtained microparticles at relatively high temperatures, which make the post-reaction treatment of the obtained products more complex and expensive and can cause modification of the morphological properties of the soft microparticles. Therefore, there are many incentives for replacement of paraffins for other nonpolar materials as the continuous phase of suspension polycondensations.

Arshady et al. [20] reported that vegetable oils can be used successfully as suspending media in some applications, leading to formation of stable droplets even in absence of surfactants. Surprisingly, these findings apparently have not impacted the field of suspension polycondensations.

Based on the previous remarks, the main objective of the present manuscript is to investigate the influence of the continuous phase on the kinetic behavior of PBS suspension polycondensation reactions and the morphological aspects of the PBS microparticles produced through suspension polycondensations. In order to do that, renewable soybean oil is used here for the first time as the continuous phase for preparation of PBS microparticles through suspension polycondensation of SA and BD and results are compared to data obtained when paraffin is used as the continuous phase at distinct reaction temperatures and stirring speeds. It is shown that soybean oil can be used successfully as the continuous phase of PBS polycondensations, allowing for production of microparticles with regular spherical morphology and leading to sustainable *greener* processes, as the constituents of both the continuous and discontinuous phases can be obtained from renewable materials.

Experimental Section

Materials

Succinic acid (SA) was provided by VETEC (Rio de Janeiro, Brazil) and used as monomer. 1,4-butanediol (BD) was supplied by MERCK (Darmstadt, Germany) and used as monomer. SPAN 80 (sorbitan monooleate) was provided by FLUKA (Mexico City, Mexico) and used as surfactant. Paraffin (wax, a mixture of aliphatic chains with characteristic FTIR, Fourier transform infrared, spectrum shown in Fig. 1) was supplied by VETEC (Rio de Janeiro, Brazil) with melting point of 62 °C and used as the suspending medium in

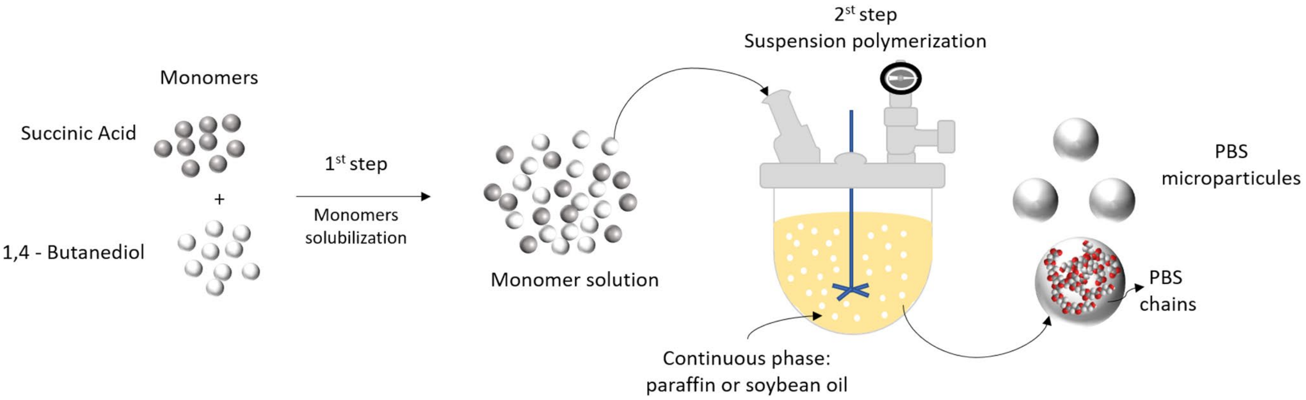


Fig. 1 Schematic representation of the suspension polycondensation reaction (adapted from [12, 23])

some of the polymerization trials, as described elsewhere [12, 13]. Soybean oil (with characteristic FTIR spectrum shown in Fig. 1) was supplied by Bunge Alimentos (Santa Catarina, Brazil) as a food grade material, with acidity of 0.3 wt% [21, 22], and used as the suspending medium in some of the polymerization trials. All reagents were supplied as analytical grades of high purity and used as received without further purification.

Production of PBS Microparticles Through Suspension Polycondensations

PBS particles were manufactured through inverse non-aqueous suspension polycondensations of BD and SA, as recommended by Dutra et al. [13], using paraffin or soybean oil as suspending media (70 wt% of the reacting system) and SPAN 80 (5 wt% and 10 wt% in respect to the suspended monomer phase) as suspending agent (surfactant). Reactions were performed in a 400 mL glass reactor that was initially heated to 70 °C, purged with nitrogen and filled with the suspending and dispersed phases. Succinic acid is solid and 1,4-butanediol is liquid at the ambient temperature. These two chemicals are miscible and form a homogeneous solution. The monomer solution was added into the reactor and mixed with a solution of soybean oil and SPAN 80 (solid surfactant) to form a liquid–liquid dispersion. Then, the reaction temperature was raised to the desired value (ranging from 160 to 180 °C) under continuous mechanical stirring (ranging from 600 to 800 rpm), as can be seen in Fig. 1. The reaction then took place inside the suspended monomer droplets, forming the viscous PBS particles, which became solid after cooling. The reaction time was equal to 5 h in all runs. After finishing the reaction, the produced polymer particles were separated by filtration and washed with acetone, in order to remove the residual stabilizer. After that, the PBS particles were dried in a circulation oven at 70 °C.

When paraffin is used as the continuous phase, filtration and washing of the obtained microparticles must be performed at 70 °C, due to the melting point of wax. On the other hand, as soybean oil is liquid at room temperature, filtration and washing of the obtained microparticles can be performed at room temperature, when soybean oil constitutes the suspending phase. The main practical consequence of this fact is that the morphological aspects of the obtained microparticles are less affected by the filtration and cleaning stages when soybean oil is used in the analyzed polycondensations. Besides, when soybean oil is used as the suspending medium, all materials employed in the proposed process are renewable, including the acetone used for removal of residual oil [24], rendering the process more sustainable and cleaner.

Reaction trials were performed as described in Table 1. Runs P1 and P2 were performed with paraffin and used as benchmarks. Runs O1 to O7 were performed with soybean oil containing 5 wt% of surfactant, while run O8 was performed with soybean oil containing 10 wt% of surfactant.

Table 1 Experimental conditions of the analyzed suspension polycondensation reactions

Reaction Batch	Continuous phase	Stirring speed (rpm)	Reaction Temperature (°C)
P1	Paraffin	800	160
P2	Paraffin	800	180
O1	Soybean oil	800	160
O2	Soybean oil	800	180
O3	Soybean oil	600	180
O4	Soybean oil	600	160
O5	Soybean oil	700	170
O6	Soybean oil	700	170
O7	Soybean oil	700	170
O8	Soybean oil	800	160

Characterization

Gel Permeation Chromatography (GPC)

Molar mass distributions of polymer samples were evaluated through gel permeation chromatography (GPC) at 30 °C, using a GPC MAX VE 2001 (Viscotek, Worcestershire, UK) equipped with a refractive index detector and using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) columns (KF-804L, KL-805L, Shodex, Tokyo, Japan). The flow rate of HFIP was equal to 1.0 mL/min. The calibration curve was built with PMMA standards (Polymer, USA) with average molar masses ranging from 450 to 1×10^6 g/gmol.

Particle Size Distribution (PSD)

Particle size distributions (PSDs) of particles with sizes smaller than 10^3 µm (samples P1 and P2) were measured through light scattering using a Mastersizer 2000 equipment (Malvern, Worcestershire, UK). The light source comprised a helium–neon laser, with wavelength of 632.8 nm, allowing for characterization of particle sizes ranging from 10 nm to 3000 µm. Samples were dispersed in distilled water and measurements were performed at room temperature.

Average particle diameters and PSDs of particles larger than 10^3 µm (samples O1 and O7) were measured by optical microscopy, using a Nikon SMZ800 stereomicroscope equipped with a Nikon Coolpix 995 digital camera (Nikon, Japan). The polymer particles were initially placed in a Petri dish in order to register the micrographs. At least 500 particles were considered in order to assure the accuracy of the measurements and reduce the experimental errors [25].

Scanning Electron Microscopy (SEM)

The morphology of the surfaces of the obtained polymer particles was examined through scanning electron microscopy (SEM), using the microscope provided by Tescan (model VEGA3, Kohoutovice, Czech Republic). Before the analyses, samples were covered with films of 5 nm of gold, using a deposition rate of 50 nm/min, with the metalizer provided by Emitech (East Sussex, United Kingdom).

Viscosity

In order to characterize the viscosity of the continuous phase, analyses were performed for both the paraffin and vegetable oil on an Ofite Model 900 viscometer (Houston, Texas, USA) with coaxial cylinder geometry at 155 °C and 600 rpm.

Interfacial Tension

In order to evaluate the stability of the droplets, interfacial tensions between the suspended phase (comprising a liquid mixture of the two monomers) and the continuous phase were analyzed. Analyses were performed with a tensiometer (Kruss Process, model K100, Hamburg, Germany), using the Wilhelmy plate method [26] at 70 °C.

Thermogravimetric Analyses (TGA)

TGA analyses were performed with a TGA-7 Calorimeter (Perkin-Elmer, Massachusetts USA). Samples were heated from 20 to 650 °C at constant heating rate of 10 °C/min under nitrogen flow.

Fourier Transformed Infrared (FT-IR)

Fourier transformed infrared (FT-IR) spectra of continuous phase samples were collected and recorded with a Nicolet-6700 FT-IR spectrometer (Thermo Scientific, Massachusetts, USA) in the wavenumber range from 500 to 4000 cm^{-1} using a diffuse reflectance accessory, with a resolution of 4 cm^{-1}. Spectra were recorded as averages of 128 scans.

Results and Discussion

Continuous Phase Characterization

Soybean oil is a vegetable oil and is composed of triacylglycerols, which are esters of glycerol with fatty acids [27]. As a consequence, the mixture contains different components formed by polar and nonpolar molecular segments, while paraffin is predominantly nonpolar [3]. Figure 2 show the FTIR spectra of paraffin and soybean oil, respectively. As one can see in Fig. 2, characteristic peaks placed at 2962, 2853, 1455 and 729 cm^{-1}, corresponding to –CH$_3$ and –CH$_2$ stretching vibrations, could be detected in both analyzed continous phases. It is important to highlight the more intense peaks positioned at 2957 to 2849 cm^{-1} in the case of paraffin, which correspond to C–H vibrations of the alkane structure. The peaks located at 3008, 1651, 1746, and 1099 cm^{-1}, related to vibrations of CH=CH, –C=C–, –COOC– and –C–O–C– groups can be observed in soybean oil, indicating that the main difference between the analyzed suspending materials is related to these fatty acid peaks, which vary according to the type of vegetable oil and are not present in paraffin [28, 29].

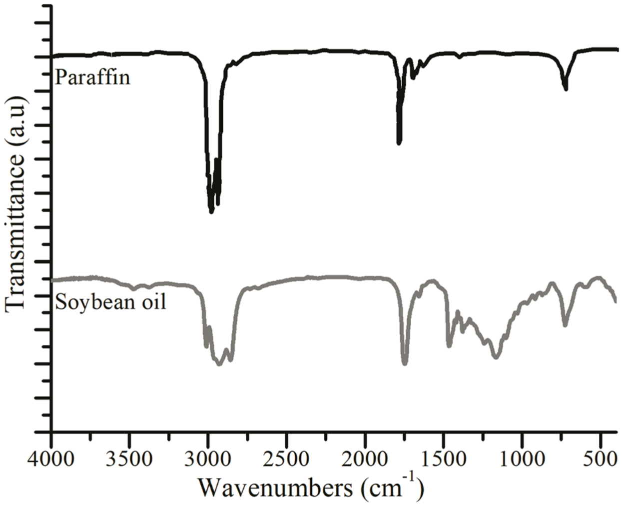


Fig. 2 FTIR spectra of paraffin and soybean oil used as suspending media

The nature of the diluent, including the viscosity and polarity, can affect the course of the suspension polycondensation reaction because they can affect the stability of the suspended droplets and the rates of particle coalescence and breakup. As a matter of fact, the FTIR spectra show the presence of polar fatty acid groups in the vegetable oil, as expected, which can affect the charge density on the particle surfaces, the stability of the suspended phase and the particle size distribution of the final product [30].

Moreover, as shown in the thermograms of Fig. 3, the temperature of maximum mass loss rate of soybean oil is close to 350 °C, while the temperature of maximum mass loss rate of paraffin is close to 225 °C, much closer to the desired reaction temperature. Consequently, the use of soybean oil can lead to more versatile processes that are less sensitive to variations of reaction temperatures. In the analyzed cases, the rates of mass loss are related to vaporization of the continuous phase and indicate that the use of soybean oil can be more appropriate for suspension

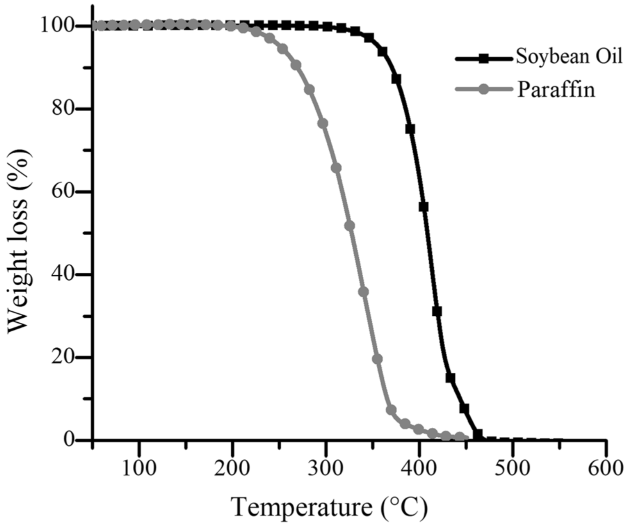


Fig. 3 TGA thermograms of paraffin and soybean oil used as suspending media

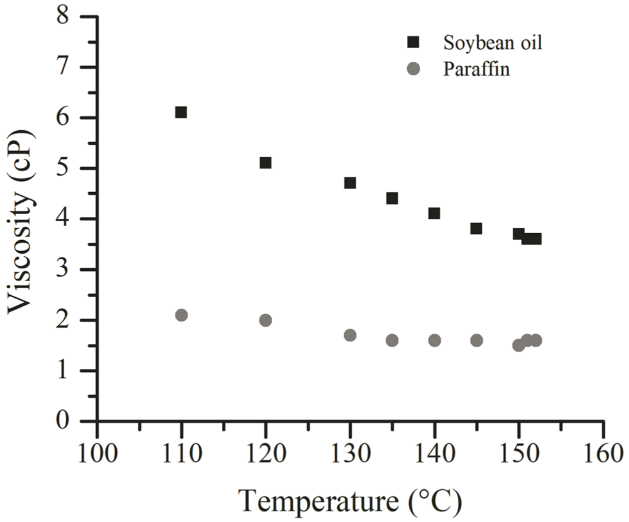


Fig. 4 Viscosities of paraffin and soybean oil used as suspending media

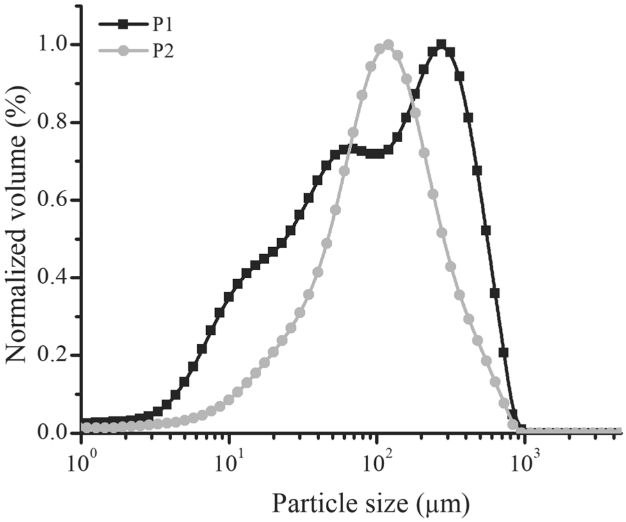


Fig. 5 Particle size distributions of PBS samples prepared when paraffin was used as the continuous phase

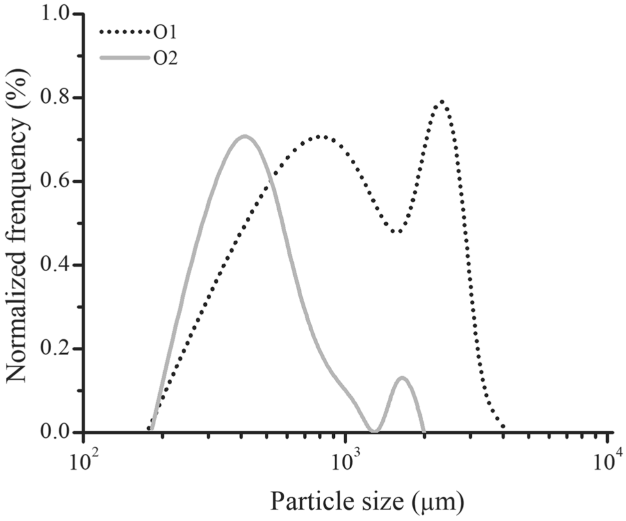


Fig. 6 Particle size distributions of PBS samples prepared when soybean oil was used as the continuous phase

polycondensations, given the much wider range of operating conditions that can be used for the manufacture of the beads and the lower volatility of the suspending phase.

Besides the higher thermal stability, the vegetable oil is also more viscous than paraffin in the entire analyzed temperature range, as one can see in Fig. 4. In particular, the analyzed soybean oil and paraffin have viscosities equal to 3.6 cP and 1.6 cP at 152 °C, respectively, which are not much different from the viscosity of water at room temperature, indicating that mixing does not constitute an operation problem at the analyzed reaction conditions. As a matter of fact, the viscosity of the continuous phase constitutes an important parameter for performance analyses of suspension polymerizations, affecting the rates of droplet breakage and coalescence and influencing the obtained particle size distributions [31].

Influence of the Continuous Phase on Obtained Particle Sizes

Figures 5 and 6 show the particle size distributions of microparticles produced when paraffin and soybean oil were used as the continuous phases. The use of paraffin led to average particle sizes of 207 and 112 μm, for reactions performed at 160 and 180 °C, respectively. The lower sizes at higher temperatures is related to the lower viscosity of the continuous phase, which can lead to higher rates of particle breakage e [32]. The particle size distribution of samples collected in run P2 (180 °C) was monomodal, while the particle size distribution of samples collected in run P1 (160 °C) was wider and multimodal, indicating the more complex evolution of rates of particle breakage and coalescence in the more viscous reaction environment.

When soybean oil was used as the continuous phase, the particle size distributions of final PBS samples were much wider and bimodal, as shown in Fig. 4, with sizes ranging from 200 to 4000 µm when the surfactant concentration was equal to 5 wt% in respect to the monomer phase. For reactions trials O1 (160 °C) and O2 (180 °C), the average particle sizes were equal to 1954 and 778 µm, respectively, indicating once more the strong effect of temperature on the evolution of particle size distributions. As observed in the previous case, higher temperatures favor the development of narrower distributions and shift distributions towards lower particle sizes, given the higher rates of particle breakage when the viscosity of the continuous phase becomes smaller.

According to the literature, when the viscosity of the continuous phase increases, the stability of the droplets increases, due to the lower frequencies of collisions between suspended droplets, generating narrower distributions and smaller sizes [33]. However, the increase of the viscosity of the continuous phase also leads to significant decrease of rates of particle breakage, which favor the formation of larger particles [34]. As mentioned before, the viscosity of the paraffin is smaller than the viscosity of the soybean oil, indicating that the breakup effect seems to control the evolution of particle sizes in this case.

The interfacial tensions between the continuous phase (oil and surfactant) and the dispersed phase (mixture of monomers) were also measured, indicating interfacial tensions of 2.50 ± 0.03 mN at 70 °C for the paraffin system and of 7.13 ± 0, 03 mN at 70 °C for the soybean oil system. The increase of the interfacial tension favors the formation of larger droplets [35, 36], which can also support the shifting of distributions towards larger particle sizes when soybean oil was used as the continuous phase. Therefore, based on viscosity and interfacial tension data, it is possible to explain why the obtained average particle sizes were higher in soybean oil than in wax. From a practical standpoint, this also means that the manufacture of small beads may require the combination of higher agitation speeds, higher surfactant concentrations and higher reaction temperatures when droplets are dispersed in soybean oil than when droplets are dispersed in wax.

Thus, an experimental design (corresponding to reactions O1 to O7 in Table 1) was proposed and executed to evaluate the influences of reaction temperature and stirring speed on average particle sizes and molar masses of PBS samples produced in soybean oil. The obtained results can be seen in Table 2.

Regarding the average particle sizes, Tables 2 and 3 show that the increase of the agitation speed leads to reduction of average particle sizes, as expected. It is interesting to observe that the analysis of average particle sizes of PBS samples produced in paraffin indicated that this property was not very sensitive to modification of the agitation speed and was significantly affected by the filtration and cleaning stages, given the higher temperatures required for operation [13]. Therefore, this can be regarded as an additional advantage of using soybean oil as the suspending phase, as this oil allows for better and simpler control of breakage and coalescence phenomena (and of average particle sizes) through manipulation of stirring speeds.

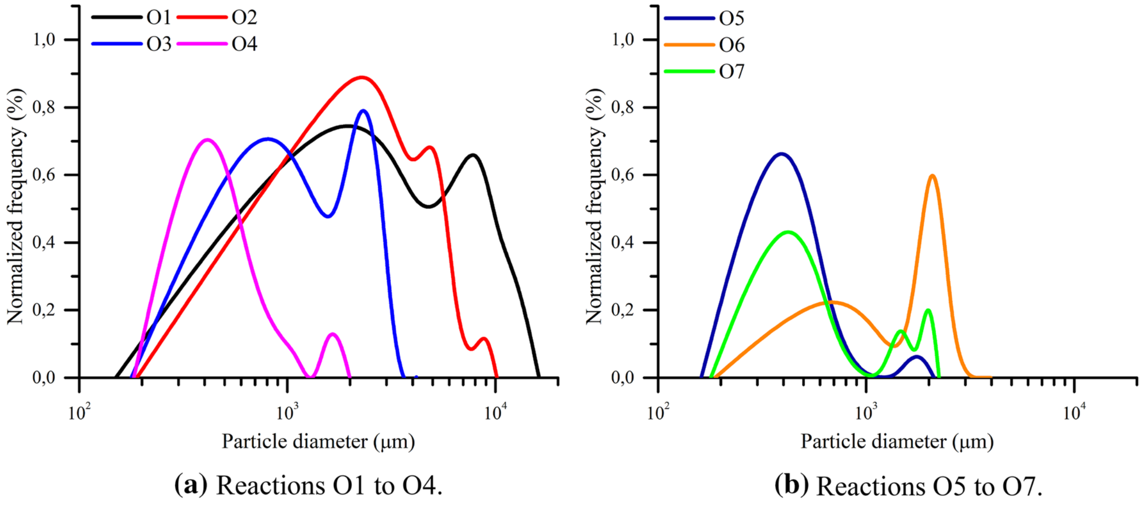
Figure 7 shows particle size distributions of PBS samples produced in runs O1 to O7. It is possible to observe the occurrence of multimodal distributions. As already

Table 3 Correlation matrix for design and response variables in runs O1 to O7 (95% significant correlation coefficients are displayed in bold)

	T	A	Mn	Mw	Dp
T	1.00	0.00	**0.84**	**0.89**	– 0.39
A	0.00	1.00	0.00	– 0.01	**– 0.75**
Mn	0.84	0.00	1.00	0.99	– 0.23
Mw	**0.89**	– 0.01	0.99	1.00	– 0.33
Dp	– 0.39	**– 0.75**	– 0.23	– 0.33	1.00

Table 2 Effects of reaction temperature and stirring speed on average particle sizes and molar masses of PBS samples produced in soybean oil

Reaction	Temperature (°C)	Stirring (RPM)	Mn (10^3 Da)	Mw (10^3 Da)	Dp (10^3 µm)
O1	160	800	6.3	8.0	2.04
O2	180	800	8.4	10.7	0.78
O3	160	600	6.6	8.3	6.80
O4	180	600	8.1	10.4	3.90
O5	170	700	6.4	8.5	0.91
O6	170	700	7.3	9.6	2.13
O7	170	700	7.9	10.2	1.32



(a) Reactions O1 to O4. **(b)** Reactions O5 to O7.

Fig. 7 Particle size distributions of PBS samples obtained in reactions O1 to O7 conducted in vegetable oil

said, runs O1 and O2 conducted with lower agitation speeds (600 rpm) resulted in size distributions that were displaced towards larger sizes, while runs O3 and O4 conducted with higher agitation speeds (800 rpm) resulted in size distributions displaced towards smaller sizes, as expected. Figure 7 also shows that particle size distributions were somewhat distinct at the central point, although qualitatively similar, with bimodalities placed in similar size ranges. This lose control of average size distributions may be linked to the stirring and cooling protocols at the end of the reaction, given the relatively low glass transition temperature (− 23 °C) and crystallization temperature (63 °C) of PBS [12]. Despite that, Fig. 7 and Table 3 show that the effects of the analyzed operation conditions on size distributions were more significant than the fluctuations observed in Fig. 7b.

Reaction run O8 was then performed with 10 wt% of surfactant in respect to the monomer phase and the obtained size distribution is shown in Fig. 8. In this case, the interfacial tension was equal to 2.53 ± 0.03 mN at 70 °C, indicating that the increase of the surfactant concentration caused the reduction of the interfacial tension, as expected. Consequently, Fig. 8 shows that size distributions were shifted towards lower diameters and became much more uniform. This clearly indicates that the particle size distribution can be manipulated more easily in soybean oil than in paraffin through modification of the analyzed operation variables.

Influence of the Continuous Phase on Average Molar Masses

Figure 9 shows the molar mass distributions of PBS samples produced when paraffin and soybean oil were used as the suspending phase. The obtained molar mass distributions were somewhat similar in all cases, indicating similar kinetic dynamics, as shown in Fig. 10. At 160 °C, obtained Mn and Mw values were equal to 7.1×10^3 Da and 9.1×10^3 Da for P1 and 6.3×10^3 Da and 7.9×10^3 Da for O1, respectively; at 180 °C, Mn and Mw values were equal to 7.6×10^3 Da and 10.0×10^3 Da for P2 and 8.4×10^3 Da and 11.0×10^3 Da for O2. The obtained results (see Table 3) confirm that the reaction temperature exerts the most significant influence on the evolution of conversions and molar mass distributions, as reported by Dutra et al. [13]. It is interesting to observe that the molar mass distributions were shifted towards lower molar masses when soybean oil was used as the suspending medium. This is probably related to the larger particle sizes, which

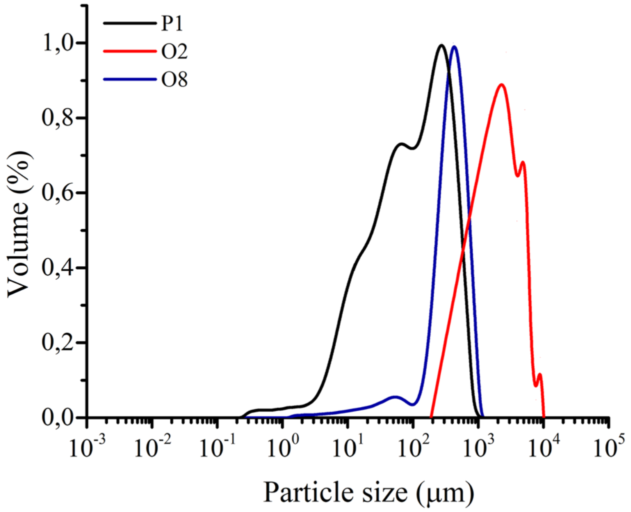


Fig. 8 Particle size distributions of PBS samples prepared in soybean oil and paraffin with different surfactant concentrations

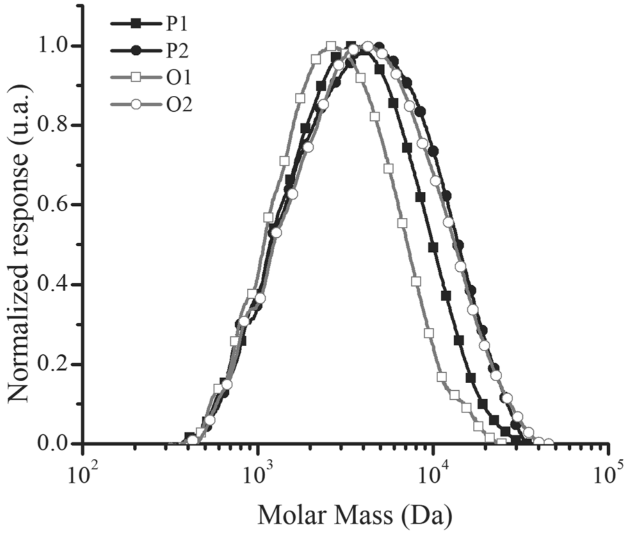


Fig. 9 Molar mass distributions of PBS samples prepared in soybean oil and paraffin

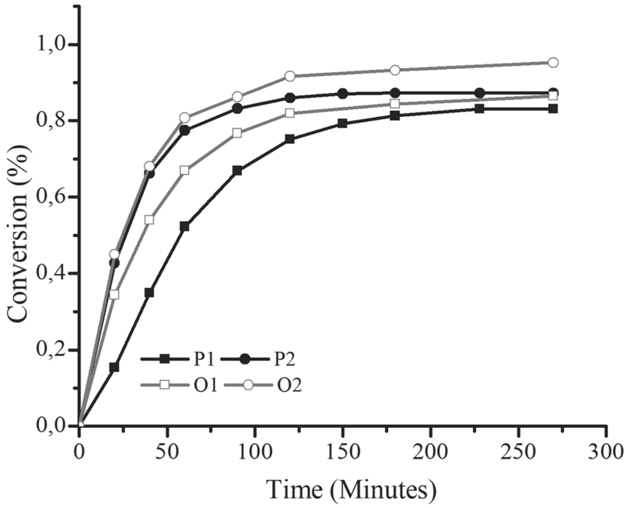


Fig. 10 Hydroxyl conversion profiles in reactions conducted in paraffin and soybean oil

can affect the rate of removal of the water byproduct from the suspended droplets, as discussed by Dutra et al. [13].

As expected, the increase of the reaction temperature caused the increase of the average molar masses of obtained PBS samples, as confirmed by the high and significant correlation coefficients observed between the design and response variables shown in Table 3. This was due to the higher rates of removal of the water byproduct at higher temperatures. In addition, as expected, the agitation speed did not exert any significant statistical influence on the analyzed average molar masses. This indicates that reaction rates control the chain growth, as modification of the agitation speed can affect the rates of removal of the water byproduct, due to modification of mass transfer rate coefficients. It is also important to note that the obtained average molar masses were higher in vegetable oil than in paraffin, indicating the more efficient removal of water in these cases, as shown in Fig. 10. This is probably due to the higher solubility of water in the polar soybean oil, which favors the removal of the water byproduct by the gaseous nitrogen stream.

Figure 11 shows the molar mass distributions of the obtained PBS samples. It is possible to observe graphically that the reaction temperature exerts higher influence than the agitation since on the observed molar masses. Figure 11 also illustrates the good reproducibility and control of molar masses in the analyzed system.

Although the average particle diameter is not significantly correlated with the average molar masses, it is possible to observe in Fig. 12 that particles with smaller average sizes tend to present larger average molar masses, probably due to the lower resistance for removal of the byproduct, which can promote the formation of larger chains.

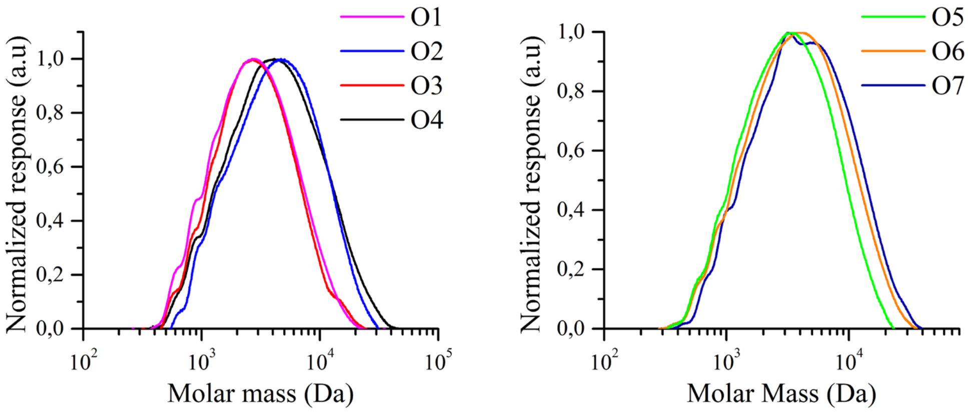
Influence of the Continuous Phase on Particle Morphology

Figure 13 presents SEM micrographs of particles produced when paraffin and soybean oil were used as the suspending media. One can clearly observe that particles produced with soybean oil were spherical and regular, while particles produced with paraffin lost the characteristic spherical morphology of suspension powders [32]. As already explained, this is due to the fact that particle filtration and cleaning must be performed at 70 °C when paraffin is the continuous phase, which leads to modification of the morphological features of the soft PBS microparticles. Figure 14 presents optical micrographs of particles produced with soybean oil, reinforcing the good morphological properties of the obtained polymer powder.

Conclusions

The present work investigated the influence of the continuous phase on the final properties of poly(butylene succinate) (PBS) particles produced through suspension polycondensations, using paraffin and soybean oil as suspending media. Particularly, it was shown that the reaction temperature exerted the most significant effect on the molar mass distributions and that the agitation speed and surfactant content exerted the most significant effects on the particle size distributions of the final PBS microparticles. Besides, particles produced in soybean oil were spherical and presented more regular morphological features than particles produced in paraffin, which is probably related to the easier filtration

Fig. 11 Molar mass distributions of PBS samples obtained in reactions O1 to O7 conducted in vegetable oil



(a) Reactions O1 to O4.

(b) Reactions O5 to O7.

and cleaning operations in soybean oil, which can be performed at room temperature. Additionally, average particle sizes were higher in soybean oil than in paraffin, due to the higher viscosities and interfacial tensions of the vegetable oil, and average molar masses were higher in soybean oil than in paraffin, due to the higher solubility of water in the polar medium and easier removal of the water byproduct from suspended PBS particles. Finally, it can be concluded that soybean oil can be used successfully as the continuous phase of PBS polycondensations, allowing for production of microparticles with regular spherical morphology and leading to sustainable *greener* processes, as the constituents of both the continuous and discontinuous phases can be obtained from renewable materials.

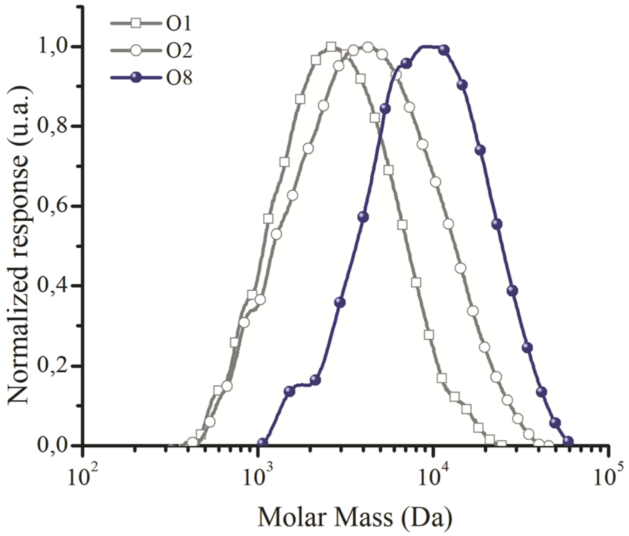
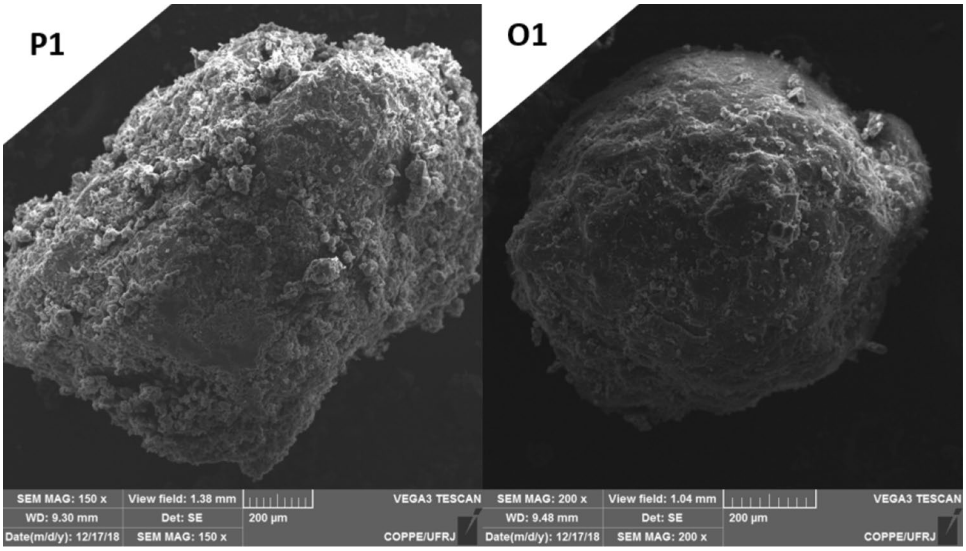


Fig. 12 Molar mass distributions of PBS samples prepared in soybean oil

Fig. 13 SEM micrographs of PBS particles obtained in paraffin (P1) and soybean oil (O1)



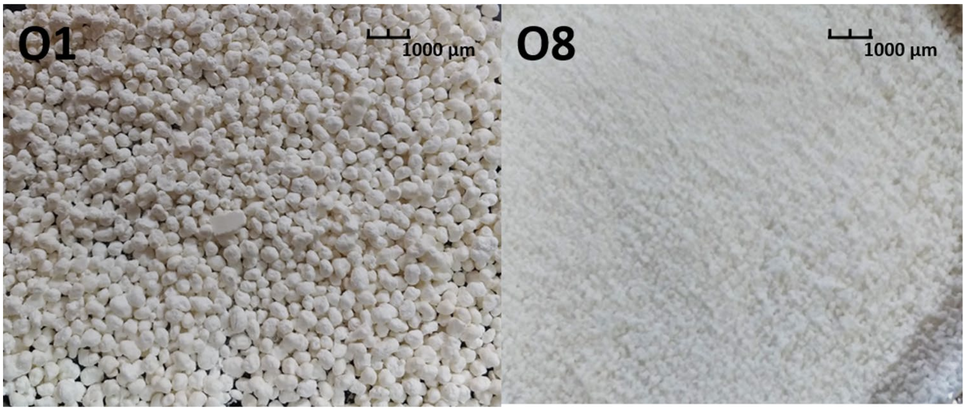


Fig. 14 Optical micrographs of PBS particles produced in soybean oil at different conditions

Acknowledgements The authors thank CNPq (Conselho Nacional de Pesquisa e Desenvolvimento Científico e Tecnológico) and FAPERJ (Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro) for providing funds and scholarships.

Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

References

1. Scott JL, Buchard A (2019) Polymers from plants: biomass fixed carbon dioxide as a resource. Managing global warming. Elsevier, Amsterdam, pp 503–525
2. Huo B, Gu M, Wang Z (2019) Green or lean? A supply chain approach to sustainable performance. J Clean Prod 216:152–166. https://doi.org/10.1016/j.jclepro.2019.01.141
3. John G, Nagarajan S, Vemula PK et al (2019) Natural monomers: a mine for functional and sustainable materials—occurrence, chemical modification and polymerization. Prog Polym Sci 92:158–209. https://doi.org/10.1016/j.progpolymsci.2019.02.008
4. Costa R, Santos L (2017) Delivery systems for cosmetics—from manufacturing to the skin of natural antioxidants. Powder Technol 322:402–416. https://doi.org/10.1016/j.powtec.2017.07.086
5. Napper IE, Bakir A, Rowland SJ, Thompson RC (2015) Characterisation, quantity and sorptive properties of microplastics extracted from cosmetics. Mar Pollut Bull 99:178–185. https://doi.org/10.1016/j.marpolbul.2015.07.029
6. Guan J, Chakrapani A, Hansford DJ (2005) Polymer microparticles fabricated by soft lithography. Chem Mater 17:6227–6229
7. Joye IJ, McClements DJ (2014) Biopolymer-based nanoparticles and microparticles: fabrication, characterization, and application. Curr Opin Colloid Interface Sci 19:417–427. https://doi.org/10.1016/j.cocis.2014.07.002
8. Jiang W, Gupta RK, Deshpande MC, Schwendeman SP (2005) Biodegradable poly (lactic-co-glycolic acid) microparticles for injectable delivery of vaccine antigens. Adv Drug Deliv 57:391–410. https://doi.org/10.1016/j.addr.2004.09.003
9. Murillo M, Gamazo C, Irache JM, Gon MM (2002) Polyester microparticles as a vaccine delivery system for brucellosis: influence of the polymer on release. Phagocytosis Toxic 10:211–219. https://doi.org/10.1080/10611860290022642
10. Obayemi JD, Danyuo Y, Dozie-nwachukwu S et al (2016) PLGA-based microparticles loaded with bacterial-synthesized prodigiosin for anticancer drug release: effects of particle size on drug release kinetics and cell viability. Mater Sci Eng 66:51–65. https://doi.org/10.1016/j.msec.2016.04.071
11. Machado F, Lima EL, Pinto JC (2007) Uma revisão sobre os processos de polimerização em suspensão. Polímeros 17:166–179. https://doi.org/10.1590/S0104-14282007000200016
12. Dutra L, Nele M, Pinto JC (2018) A novel approach for the preparation of poly(butylene succinate) microparticles. Macromol Symp 381:1800118. https://doi.org/10.1002/masy.201800118
13. Dutra L, Souza MN, Pinto JC (2018) Preparation of polymer microparticles through nonaqueous suspension polycondensations. Part II—effects of operating variables on properties of poly(butylene succinate). Macromol React Eng 12:1800039. https://doi.org/10.1002/mren.201800039
14. da Silva DL, de Souza Belan Coasta T, Lobo VTV et al (2019) Preparation of polymer microparticles through non-aqueous suspension polycondensations: Part III—degradation of PBS microparticles in different aqueous environments. J Polym Environ 27:176–188. https://doi.org/10.1007/s10924-018-1329-x
15. Brock T, Sherrington DC (1992) Preparation of spherical polybenzimidazole particulates using a non-aqueous suspension methodology. Polymer (Guildf) 33:1773–1777. https://doi.org/10.1016/0032-3861(92)91082-D
16. Brock T, Sherrington DC, Swindell J (1994) Synthesis and characterisation of porous particulate polyimides. J Mater Chem 4:229. https://doi.org/10.1039/jm9940400229
17. Ahn J-H, Sherrington DC (1996) Synthesis of functional polyimide beads and use as Mo VI epoxidation catalyst supports. Chem Commun. https://doi.org/10.1039/cc9960000643
18. Jabbari E, Khakpour M (2000) Preparation of aqueous suspension of porous polyurethane microspheres by suspension polycondensation. Sci Iran 7:102–110. https://doi.org/10.1016/j.jconhyd.2010.08.009
19. Wang P, Wang K, Zhang J, Luo G (2015) Non-aqueous suspension polycondensation in NMP-$CaCl_2$/paraffin system—a new approach for the preparation of poly(p-phenylene terephthalamide). Chinese J Polym Sci 33:564–575. https://doi.org/10.1007/s10118-015-1607-1
20. Arshady R (1989) Microspheres and microcapsules: a survey of manufacturing techniques. Part 1: suspension cross-linking. Polym Eng Sci 29:1746–1758. https://doi.org/10.1002/pen.760292404
21. Bunge (2012) Soya. https://www.soya.com.br/produtos/oleos/oleo-de-soja-soya
22. ANVISA (2005) Agência Nacional de Vigilância Sanitária. https://bvsms.saude.gov.br/bvs/saudelegis/anvisa/2005/rdc0270_22_09_2005.html

23. da Silva Dutra L, Nele M, Pinto JC (2020) Preparation of polymer microparticles through non-aqueous suspension polycondensations: Part IV—effect of the continuous phase on the characteristics of final poly(butylene succinate) particles. J Polym Environ
24. Li W, Ghosh A, Bbosa D et al (2018) Comparative techno-economic, uncertainty and life cycle analysis of lignocellulosic biomass solvent liquefaction and sugar fermentation to ethanol. ACS Sustain Chem Eng 6:16515–16524. https://doi.org/10.1021/acssuschemeng.8b03622
25. Schwaab M, Pinto JC (2007) Análise de Dados experimentais I Fundamentos de Estatistica e Estimação de Paramêtros. Editora E-papers, Rio de Janeiro
26. Ebnesajjad S (2006) Surface tension and its measurement. Surface treatment of materials for adhesion bonding. Elsevier, Amsterdam, pp 9–28
27. December NO (2011) Vegetable oils in food technology. Wiley-Blackwell, Oxford
28. Bao L, Bian L, Zhao M et al (2014) Synthesis and self-assembly behavior of a biodegradable and sustainable soybean oil-based copolymer nanomicelle. Nanoscale Res Lett 9:1–6. https://doi.org/10.1186/1556-276X-9-391
29. Khanifah L, Widodo S, Widarto W et al (2018) Characteristics of Paraffin Shielding of Kartini Reactor, Yogyakarta. ASEAN J Sci Technol Dev 35:195–198. https://doi.org/10.29037/ajstd.526
30. Thakur N, Weatherly CA, Wimalasinghe RM, Armstrong DW (2019) Fabrication of interconnected macroporosity in geopolymers via inverse suspension polymerization. J Am Ceram Soc 102:4405–4409. https://doi.org/10.1111/jace.16437
31. Jahanzad F, Sajjadi S, Brooks BW (2005) Comparative study of particle size in suspension polymerization and corresponding monomer−water dispersion. Ind Eng Chem Res 44:4112–4119. https://doi.org/10.1021/ie048827f
32. Brooks B (2010) Suspension polymerization processes. Chem Eng Technol 33:1737–1744. https://doi.org/10.1002/ceat.201000210
33. Dowding PJ, Vincent B (2000) Suspension polymerisation to form polymer beads. Colloids Surf 161:259–269. https://doi.org/10.1016/S0927-7757(99)00375-1
34. Azevedo GD, da Silva Pinto JCC (2019) Particle size distributions of P(VAc-co-MMA) beads produced through nonconventional suspension copolymerizations. Powder Technol 355:727–737. https://doi.org/10.1016/j.powtec.2019.07.097
35. Saien J, Fadaei V (2018) The study of interfacial tension of kerosene-water under influence of CTAB surfactant and different size silica nanoparticles. J Mol Liq 255:439–446. https://doi.org/10.1016/j.molliq.2018.01.120
36. Rosen MJ, Kunjappu JT (2012) Phenomena surfactants and phenomena. Wiley, Hoboken

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.