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Effect of Initiator on the Incorporation of Graphite into Polymer Matrix During Suspension Polymerization

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Summary: The incorporation of graphite into polystyrene (PS) particles produced by suspension polymerization was studied using a monofunctional and a bifunctional initiator, benzoyl peroxide (BPO) and 2,5-dimethyl-2,5-bis(2-ethyl hexanoyl peroxide) hexane (L256), respectively. The results showed that the polymerization rate was affected by graphite concentration when BPO was used as the initiator while no such effect was observed for L256. Results also showed that the incorporation of graphite in the PS particles was higher when using BPO than when using L256. Molecular weight distribution showed that during the reaction with BPO and graphite oligomers were formed indicating that the free radicals generated by the decomposition of BPO presented a very high reactivity with the functional groups present at the graphite surface while no significant effect was observed for the reaction with L256.

Keywords: benzoyl peroxide; bifunctional initiators; graphite; polystyrene; suspension polymerization

Introduction

Expandable polystyrene (EPS) consists of particles of polystyrene (PS) obtained by suspension polymerization swollen by an expandable agent (usually pentane). The applications of EPS extend to various areas being widely used for packaging electric-electronic devices protecting them from damage and as an isolating material due to its capacity to resist sound and heat conduction. These properties are obtained because 98% of EPS is composed of air and 2% of PS. Suspension polymerization is in principle the conversion, by free radical polymerization, of monomer(s) droplets dispersed in an aqueous medium by a combination of strong stirring and the use of small amounts of suspending agents into polymer particles. Monofunctional initiators, as benzoyl peroxide (BPO), are usually employed in the production of EPS. Nevertheless, the use of bifunctional initiators, as Luperox 256® (Luperox is a registered trademark of ATOFINA Chemicals, Inc.) allows the reduction of reaction time maintaining molecular weight distribution (MWD) of the final polymer in a desired range. This is very interesting since strategies to reduce reaction time by increasing reaction temperature or using higher initiator concentrations increase the rate of propagation and also the radical concentration. Therefore, both methods inevitably decrease the molecular weight of the polymer due to the higher radical concentration. Nevertheless, better polymer properties (impact strength, mechanical strength, etc.) are obtained with PS with high molecular weight.

Thermal conductivity may be modified by the incorporation of materials with low heat conductivity, as graphite, into the polymer. Therefore, the insulating property of EPS can be improved by the incorporation of graphite into the polymeric matrix. Nevertheless, the particles of

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EPS are produced during the suspension polymerization, which includes the incorporation of the expandable agent. Consequently, the incorporation of graphite should be done during the polymerization step. It is well known that graphite presents surface activity and low wet-ability by aqueous or organic phase and that would be a challenge to its incorporation into the organic phase in such heterogeneous medium as suspension polymerization. Some authors have already observed a strong evidence of inhibition caused by surface quinone groups of carbon blacks on the free radical thermal polymerization of styrene[1] and in the solution polymerization of styrene catalyzed by *n*-butyllithium in the presence of carbon black at 0 °C in toluene.[2]

In order to produce a PS particle with graphite incorporated into it that should be used in the production of EPS, it is necessary that the incorporation of graphite during the polymerization step should not have any deleterious effect on the polymer properties necessary to produce EPS (molecular weight and particle size should be at a certain range) and not reduce the productivity of the plant (not reducing the reaction rate would be desirable). Although, several aspects of the process of incorporating graphite still need to be better understood, among them the influence of graphite on the reaction kinetics and polymer properties since the incorporation must occur during the suspension polymerization reaction. Therefore, this study has an objective to investigate the effect of graphite concentration and type of initiator (monofunctional and bifunctional) upon the reaction kinetics and properties of the PS/graphite produced by suspension polymerization.

Experimental Part

Suspension polymerization reactions were carried out at 90 °C with stirrer speed of 600 rpm, with the following reagents being used: styrene (without the removal of the *p*-terc-butylcatechol inhibitor); graphite (Cia. Nacional de Grafite Ltda, with 99.92% carbon and a d_{50} of 6.20 μm); BPO (Elf Atochem Chemicals, analytical grade); 2,5-dimethyl-2,5-di(2-ethyl hexanoyl peroxide)hexane, Luperox 256® (Akzo Nobel); polyvinyl pyrrolidone, PVP K-90; distilled water; and dodecyl benzene sodium sulfonate (Sigma-Aldrich, analytical grade).

Table 1.
Reaction conditions that were kept constant throughout the reactions.

T	Holdup	PVP[a)]	DBSS[a)]
°C		wt.-%	wt.-%
90.0	0.300	0.152	0.046

[a)] Wt.-% in relation to total water weight.

The experimental set-up comprisis a 1 000 ml jacketed glass reactor connected to a condenser to avoid monomer losses due to evaporation during the reaction. The start-up procedure in all reactions comprised filling the reactor with the initial charge and heating until the reaction temperature is reached. In order to remove traces of dissolved oxygen, the reactor was continuously purged with nitrogen. After 30 min of purging the initial charge the initiator solution was fed to the reactor. Table 1 and 2 present the experimental conditions of each reaction.

Analysis

The evolution of monomer conversion during the reaction was determined by

Table 2.
Graphite and initiator type and concentration for each reaction.

Run	Graphite[a)]	Initiator mol · L^{-1} Sty	
		BPO	L256
BG0	0	2.15	-
BG1	1.0	2.15	-
BG3	3.0	2.15	-
BG6	6.0	2.15	-
BmG0	0	0.03	-
BmG3	3.0	0.03	-
LmG0	0	-	0.03
LmG3	3.0	-	0.03

[a)] Wt.-% in relation to total monomer weight.

gravimetry according to the procedure described elsewhere.[3] The particle size distribution (PSD) was determined by sieving since particle size range is situated between 40 and 2 000 μm. MWD was measured in a gel permeation chromatography (GPC) apparatus from Waters with three Waters ultrastyragel columns (10^3, 10^4, and 10^6 Å). Tetrahydrofuran (THF) was used as carried fluid at 0.3 mL · min^{-1} at 35 °C.

To quantitate the amount of graphite incorporated at the end of the reaction, 10 g of PS/graphite was dissolved in 100 ml of toluene at 30 °C under continuous agitation. After complete dissolution of the polymer, it was centrifuged at 600 rpm and the graphite separated. The procedure described above was repeated one more time in order to ensure that the graphite was completely separated from the polymer. The mass of graphite was measured on a GEHACA analytical scale (model BG-200). The solution of toluene was dried and the residual polymer was analyzed by GPC in order to determine the MWD.

The graphite provided by Nacional de Grafite Ltda. was analyzed by several methods (FTIR, X-ray photoelectron spectroscopy (XPS), BOEHM method) in order to determine the presence of functional groups on the graphite particle surface that may interact with the free radical generated by the initiator decomposition. The analysis by FTIR and XPS detected the presence of such groups and by BOEHM method it was determined that the main functional group was the carboxylic acid at 492.24 meq per 100 g. The graphite was also analyzed by BET to obtain its specific area (13.78 $\text{m}^2 \cdot \text{g}^{-1}$).

Results and Discussion

Aiming to evaluate the influence of the initiator on the reaction kinetics, some reactions were carried out using BPO with different concentrations of graphite. Later, reactions utilizing the same concentration of BPO, with and without graphite, were compared with the same concentration in moles of L256 for both reactions.

Figure 1 shows the evolution of conversion, determined by gravimetry, in the reactions with BPO with different graphite concentrations and without any graphite. Observing Figure 1, it can be seen that with an increase in graphite concentration, a reduction in the reaction rate occurs and the reaction with 6% of graphite stopped before reaching 80% of conversion demonstrating that the free radicals generated by BPO decomposition reacted with the graphite. A possible explanation for this type of behavior may be associated with the fact that graphite has different functional groups at its surface which exert a

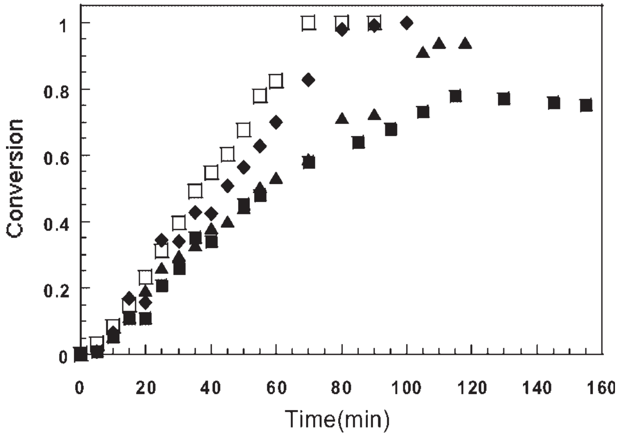


Figure 1.
Conversion in the reactions with BPO for different amounts of graphite. BG0 (□); BG1 (◆); BG3 (▲); BG6 (■).

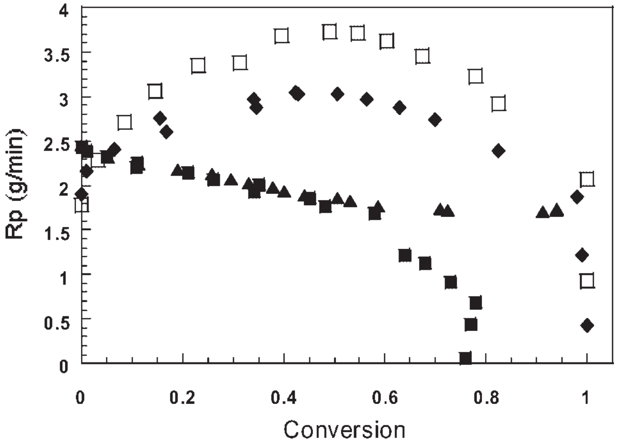
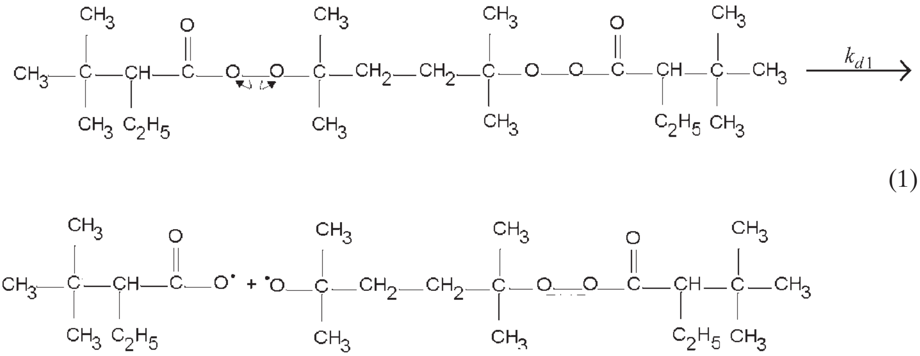


Figure 2.
Polymerization rate (R_p) in the reactions with BPO for different amounts of graphite. BG0 (□); BG1 (◆); BG3 (▲); BG6 (■).

pronounced effect on the surface properties of the carbons, since they constitute active sites which may react with the free radicals generated by the initiator decomposition.[4]

The polymerization rate (R_p) of the reaction without any graphite showed the expected behavior for the styrene suspension polymerization where the polymerization rate increases until 50% of conversion as the gel effect reduces the termination rate due to the lower mobility of the radicals with the increasing viscosity of the reaction medium. The conversion then decreases as the monomer concentration decreases. Figure 2 shows that on increasing the amount of a graphite R_p decreases. With 1% of graphite R_p is lower than without any graphite; nevertheless, both reactions presented the same behavior. The reactions with 3 and 6% presented a different behavior as R_p decreased during the whole reaction demonstrating that the gel effect was less significant for these reactions than the decrease of free radical concentration in the reaction medium.

However, for the reactions with and without graphite utilizing the bifunctional initiator L256 no changes in the kinetics was observed, as can be seen in Figure 3. When using the same concentration in moles of BPO and L256, the reaction rate for the bifunctional initiator is faster since the number of radicals generated per mol of initiator is higher. According to Gao et al.,[5] bifunctional initiators have the following general chemical structure: R_1–O–O–R_2–O–O–R_1, where R_1 and R_2 are hydrocarbon ligands. The oxygen bonds O–O can thermally break up and generate, for the L256 molecule, the following free radicals:



(1)

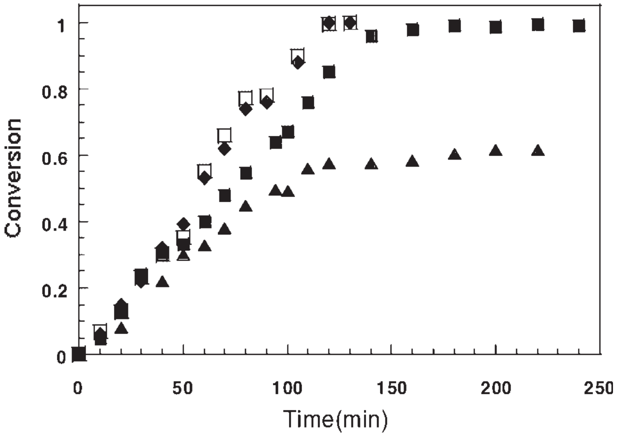
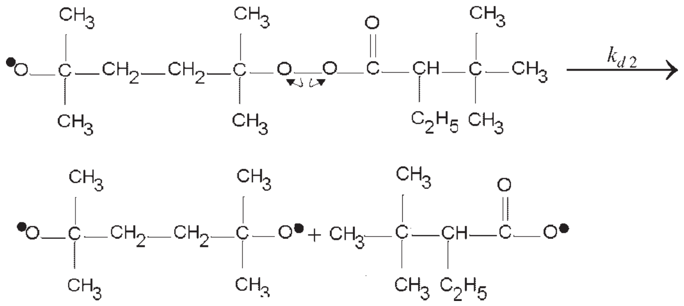


Figure 3.
Conversion in the reactions with BPO and L 256 for different amounts of graphite. BmG0 (■); BmG3 (▲); LmG0 (◆); LmG3 (□).

The radical $\bullet R_2–O–O–R_1$ contains an undecomposed peroxide radical that may further decompose like an initiator and is called "macro" peroxide:



$$\bullet O-C(CH_3)_2-CH_2-CH_2-C(CH_3)_2-O-O-C(=O)-CH(C_2H_5)-C(CH_3)_2-CH_3 \xrightarrow{k_{d2}} \bullet O-C(CH_3)_2-CH_2-CH_2-C(CH_3)_2-O\bullet + CH_3-C(CH_3)_2-CH(C_2H_5)-C(=O)-O\bullet \qquad (2)$$

where k_{d1} and k_{d2} present different values. For the L256 at 90 °C k_{d1} is equal to 0.013860 s^{-1} and k_{d2} is equal to 0.002952 s^{-1}. It means that the first reaction is almost five times faster than the second one.

One possible explanation for the different behavior observed when using BPO and L256 is the different reactivity of the radicals generated by both initiators, where the radicals present at the macro peroxide would have a lower reactivity when compared to the radicals generated by the decomposition of BPO due to the methyl groups attached to the last carbon that is bonded to the oxygen that contains the free radical. Ohkita et al.[6] observed, during the styrene polymerization in the presence of carbon black utilizing AIBN and BPO as initiators, that benzoate radicals generated during the decomposition of BPO, when reacting with the material surface, remove hydrogen atoms from the benzene ring of functional groups generating active sites that capture the free radicals originated from the dissociation of the initiator as in living polymer chains. However, this behavior was not observed for the reactions in which the AIBN was utilized, since the 2-cyano-2-propyl radical presents low

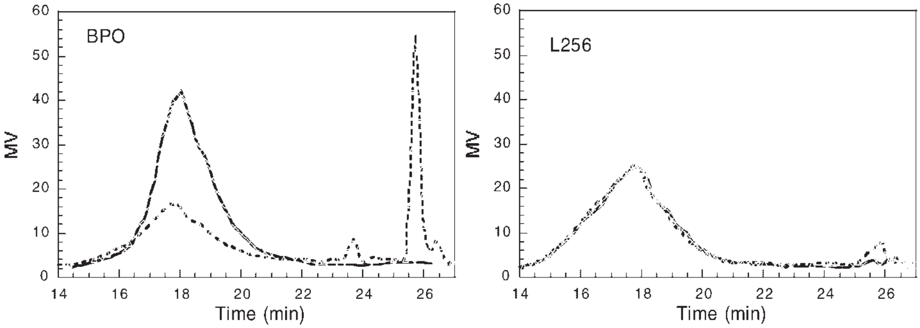


Figure 4.
Chromatograms obtained by GPC of the reactions: BmG0; BmG3; LmG0; LmG3. 0% (—) and 3% (- - -) of graphite wt.-% in relation to total monomer weight.

reactivity in relation to the carbon black. It is therefore probable that the radicals generated by the dissociation of the bifunctional initiator L256 have a low reactivity in relation to the functional groups present in the graphite.

Molecular Weight Distribution

Samples of the final polymer were collected to obtain the MWD. Observing Figure 4, it is interesting to note that a very high peak corresponding to very low molecular weight appeared for the reaction with BPO and graphite at 25 min of elution time and a smaller one appeared between 23.5 and 24 min. The highest peak was out of the calibration curve; therefore, its molecular weight was not quantitated. Nevertheless, its value must correspond to molecular weights lower than 1 000. The other peak corresponded to M_w of about 1 400. The reaction with L256 and graphite presented a small peak after 24 min of elution time but it was not as significant as for the reaction with BPO. It means that the reduction of free radical concentration, when compared to the reaction without graphite, was probably due to the termination of oligomeric radicals recently formed by the decomposition of BPO with the functional groups present at the graphite surface.

To obtain the MWD, the range considered for each sample was situated between 14 and 23 min of elution time. The chromatograms obtained by GPC of the reactions with and without graphite initiated by BPO showed that the MWD with graphite was displaced to higher values and was broader than the peak of the reaction without any graphite (Figure 5). Table 3 shows that the weight average molecular weight (M_w) remained the same

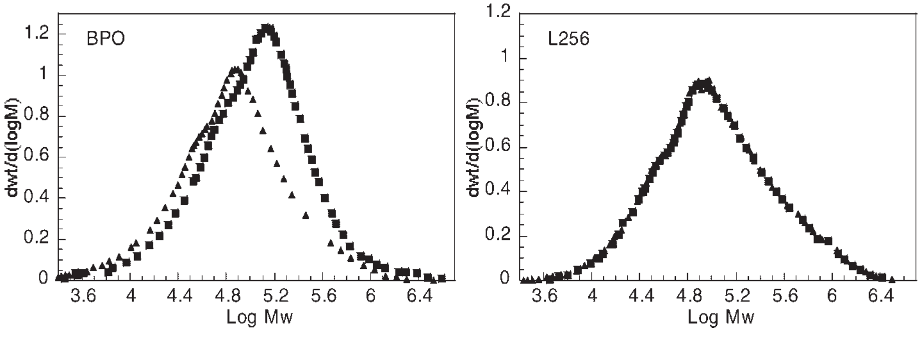


Figure 5.
MWD of the reactions: BmG0; BmG3; LmG0; LmG3. 0% (▲) and 3% (■) of graphite wt.-% in relation to total monomer weight.

Table 3.
Average weight molecular weight (M_w) and polydispersity index (PI).

Run	Initiator	Graphite[a)]	M_w	PI
G0	BPO	0	87 103	2.28
G3b	BPO	3.0	130 398	3.29
G0′	L256	0	194 243	3.07
G3c	L256	3.0	199 774	3.63

[a)] Wt.-% in relation to total monomer weight.

for the reactions with L256 and, as expected, the M_w was higher than those obtained in the reactions with BPO. For the reactions with BPO M_w increased (without taking into account the oligomers formed during the reaction) with the incorporation of graphite showing that the free radical concentration decreased at the reaction medium.

Percentage of Graphite Incorporated

In relation to the quantity of graphite incorporated, it was found that when utilizing BPO, a higher percentage of graphite was incorporated into the polymeric matrix (62%) in relation to the L256 (33%). This behavior may be associated with the fact that the benzoate radicals formed during the decomposition of the initiator react with the graphite surface producing a new pair of unpaired electrons which capture the growing polymeric radicals,[6] favoring the incorporation of graphite into the polymer. Furthermore, the functional groups present at the graphite surface may act as grafting sites which allow the addition of the growing polymer chains to the material surface.[2] The lower concentration of graphite incorporated in the reaction with L256 means that the graphite concentration at the reaction medium was lower than the concentration in the reaction with BPO. Therefore, the reaction rate of free radicals with functional groups present at the graphite surface should be lower than the reaction rate with BPO.

Particle Size Distribution

With the increase of graphite concentration in the reactions with BPO a displacement of the PSD for higher diameters was observed (Figure 6). Nevertheless, the behavior of the PSD for the reaction with L256 showed a complete different behavior, as the PSD was much broader and decreased with the incorporation of graphite. The PSD, among many other reaction parameters, is affected by the viscosity of the particles that depends on the MWD and conversion, as it affects the breakage and coalescence of the particles. As MWD and conversion changed in all reactions it is very difficult to take any conclusion about the effect of graphite in the PSD.

Conclusion

A decrease in polymerization rate was observed for the styrene suspension polymerization with BPO as initiator when graphite was added to the reaction. On increasing the graphite concentration, more pronounced was the effect that may be associated with the fact that graphite has different functional groups at its surface which exert a pronounced effect on the surface properties and may react with the oligomeric radicals recently formed by the decomposition of BPO. This hypothesis is corroborated by the analysis of GPC which shows a peak corresponding to a high concentration of oligomers formed at the reaction with BPO and graphite. Without taking into account the oligomers, M_w increased when graphite was added demonstrating that radical concentration decreased at the reaction medium due to the reaction with the functional groups present at the graphite.

However, using the bifunctional initiator, L256, any significant change in the kinetics or in the weight average molecular weight was observed for the reactions with and without graphite probably due to the lower radical reactivity of the free radicals generated by the decomposition of L256 with the functional groups present at the graphite surface.

In relation to the amount of graphite incorporated, it was found that a higher

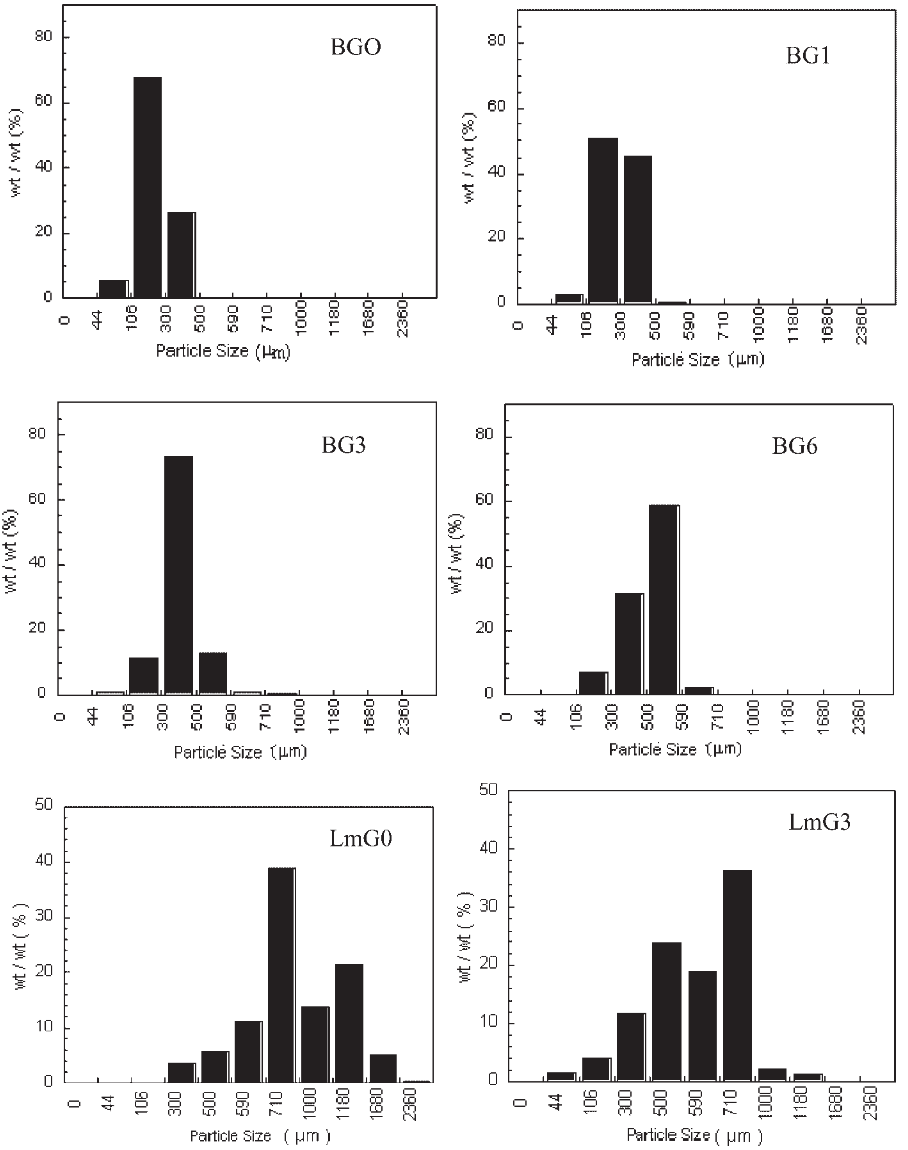


Figure 6.
PSD of the reactions with BPO and L256.

percentage of graphite was incorporated into the polymeric matrix when BPO is used as initiator instead of L256. It possibly is due to the higher interaction of the radicals generated by BPO and the functional groups present at the graphite surface that may generate grafting sites at the graphite surface.

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