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Abstract: Conducting polypropylene composites containing graphite, carbon black and carbon nanotubes have been prepared and the effect of composition on the flexural modulus and electrical conductivity has been studied. Keeping the graphite content constant and varying only the ratio of carbon black and nanotubes within the mixture the conductivity varied according to an exponential, the flexural modulus according to a linear mixture rule. Flexural strength and impact strength depended less on the composition. The results were supported by optical micrographs.

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Electrical conductivity and mechanical properties of polypropylene composites containing hybrid carbon fillers

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Abstract

Conducting polypropylene composites containing graphite, carbon black and carbon nanotubes have been prepared and the effect of composition on the flexural modulus and electrical conductivity has been studied. Keeping the graphite content constant and varying only the ratio of carbon black and nanotubes within the mixture the conductivity varied according to an exponential, the flexural modulus according to a linear mixture rule. Flexural strength and impact strength depended less on the composition. The results were supported by optical micrographs.

1. Introduction

Development of conductive polymers is very promising and it is being studied more and more widely. Due to their corrosion resistance and low density they may replace metals in several applications, thus increasing the useful life of the equipments. Significant weight reduction can be achieved by their use, accompanied by cost reduction.

The conductivity of the polymer increases significantly if the conductive filler forms a continuous network in the matrix, a process called percolation that can be explained by percolation theory [1]. Below the so-called percolation threshold the material behaves as an insulator, while above the percolation threshold infinite

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conducting network is formed in the matrix, thus the material becomes conductive. The maximum conductivity is achieved in principle at the maximum (100%) loading, between the percolation threshold and the maximum the conductivity increases steeply.

Graphite (G) is one of the most widely used additive used to improve the conductivity of polymers [2-5]. Above the percolation threshold, in the case of polypropylene matrix it increases significantly the conductivity in the 30-80 vol% loading range, at 80 vol% 50-150 S/cm conductivity can be achieved [6,7].

Carbon black (CB) is a typically amorphous form of carbon of about 50 nm diameter, which tends to form aggregates of about 250 nm size [8]. If using carbon black in polypropylene matrix, above the percolation threshold an increasing conductivity value is observed in the 2-10 vol% range, above this value, however, no further significant improvement can be achieved. At about 10 vol% loading the maximum achievable conductivity is in the range of 0.001-0.005 S/cm [9,10]. Wang and coworkers [11] have shown that in the percolation range the distance between the CB aggregates decreases, but does not vanish. Therefore the electrons have to overcome this potential barrier in order to get through the network of CB aggregates. In this non-ohmic conduction range according to earlier studies [12,13] the probability of the electron transmission through this gap depends exponentially on the gap width. According to the Balberg-model [14] one may find products with both globular and acicular particles with low or high surface structure among the various CB grades. The closer the shape of the particle to spherical, the less structured it is, but the more structured the surface (i.e. the higher the specific surface) the lower is the percolation threshold value, as a tunnel effect arises between the adjacent particles, which is more intense between more structured particles [2]. Tunneling is possible, however, only between CB aggregates being very close to each other. In the high loading range the

conductivity becomes ohmic [11]. Based on the studies of Narkis et al. [10] the size and specific surface of the CB additives does influence the percolation threshold value but does not change substantially the achievable conductivity. It has been shown that the admixture of insulating glassfibers to the matrix decreases significantly the percolation threshold, due to the better dispersion of the CB.

In the case of carbon nanotube filled polypropylene (PP) composites the percolation threshold may vary considerably because of the strong aggregation tendency of the carbon nanotubes (CNT). Namely CNT tend to form bundles in the matrix because of the strong van der Waals interaction between them, therefore their dispersion in within the material will not be uniform, and the adhesion between the nanotubes and the matrix material will not be acceptable either. According to the experiments the percolation threshold value is in the range of 0.4-2.6 m% CNT content, depending on the processing method and its parameters [15-19]. The maximum, 0.5-2 S/cm conductivity value is achieved at a CNT loading level of 9-10 m% [20].

In hybrids filled with graphite and carbon black a significant amount (25-60 vol%) of graphite and less (3-12 vol%) CB is used [2,21]. Malaysian researchers [7] revealed the presence of synergetic effect when using these hybrids: the amount of G was changed in the composites with constant, 0, 5 and 25 m% CB content. When measuring the conductivity it was observed the composites containing more carbon black reach the percolation threshold at lower G contents and they also exhibit higher conductivity. The maximum value was measured at 25 m% CB content, a further increase of the filler loading resulted in decreasing conductivity.

Lia et al. [6] used G and CNT filler to increase the conductivity of PP. Increasing the CNT content gradually at a constant graphite content of 80 m% a steep increase was

observed up to 0.8 m% CNT content, thereafter a decreasing tendency was observed, which was explained by the agglomeration of the carbon nanotubes.

The goal of this study is to investigate the interactions of various conductive fillers in polypropylene matrix, from the viewpoints of conductivity and mechanical properties.

2. Experimental

2.1 Materials

Tipplen H949A polypropylene (TVK, Hungary) with an MFR value of 45g/10 min was used as a matrix material in the experiments. The graphite powder used to increase the conductivity (Carbosint Ltd. Hungary) was crystalline natural graphite. The carbon black used was Ketjenblack EC-600 JD (Akzo Nobel), the multiwall carbon nanotube was Baytubes C150P (Bayer). The properties of the fillers used are summarized in Table 1.

The various compositionss were mixed by a Brabender kneader at 240°C for 12 min at 25 rpm. From the melt-mixed materials 2 mm thick plates were compression molded at 250°C and 160 bar using a Collin P 200E mold.

2.2 Test methods used

The conductivity was measured using a four probe resistivity test using an Agilent 4333B type milliohmmeter.

Three point bending tests were performed on a Zwick Z020 type universal tester with 64 mm span length, at 5 mm/min deformation rate, at room temperature.

Impact strength tests were made using a CEAST Resil Impactor Junior equipment with 2 J hammer, at room temperature.

Cross sections of the test specimens were polished with a Buehler Beta twin polishing equipment. An Olympus PMG3 type optical microscope was used for optical microscopy, data evaluation was made by analySIS Steel Factory 5.0 software.

2.3 Results and discussion

2.3.1 Changes of the conductivity of PP composites containing only one filler

Before studying the polypropylene samples containing dual hybrid fillers, the conductivities of composite containing only one kind of filler were compared. As shown by Figure 1, in the case of the PP matrix carbon black increased the conductivity to the highest degree and graphite proved to be the least effective. The percolation threshold appeared at 1.6 vol% for carbon black, at 7.5 vol% for carbon nanotube and at 30 vol% for graphite. The reason for this is that CNT is prone to aggregation in PP during melt mixing, so the conductive network is formed only at higher loading in the matrix [24].

2.3.2 Changes of the conductivity of PP composites containing hybrid fillers

Figure 2 shows the changes of conductivity of composites containing 0, 20 and 40 vol% graphite and CB-CNT mixtures in various proportions. Figure 2/a plots the conductivity of polypropylene composites containing 5 vol% CNT-CB at various graphite loadings (the conductivity of the sample containing only carbon nanotube could not be measured). At high graphite content conductivity is high, it decreases with increasing nanotube fraction according to the exponential mixture rule (1) at all three graphite contents. Figure 2/b shows the changes of conductivity of composites with 10 vol% CB-CNT content, where again a decreasing tendency according to equation (1) can be observed as a function of the CNT loading.

$$\sigma_c = \sigma_{CB} \exp \left(V_{CNT} \ln \frac{\sigma_{CNT}}{\sigma_{CB}} \right), \quad (1)$$

where σ_c is the conductivity of the composite, σ_{CB} is the conductivity of the material containing carbon black alone, σ_{CNT} is that of the material containing nanotube alone, V_{CNT} is the volume fraction of the nanotube within the carbon black-nanotube mixture.

It can be observed that in comparison to samples containing graphite only (Fig. 1.) both CB and CNT, and various combinations thereof increased the conductivity, but no synergetic effect was observed for materials containing both CB and CNT.

The intensities of the conductivity enhancement vs. the CNT fraction at various graphite contents are different. This intensity value taken from Figure 2 is the apparent slope of the nearly linear curves (due to the logarithmic representation). It can be observed that the change of the conductivity is less intense with increasing graphite contents, i.e. its absolute value is decreasing (Figure 3). This trend indicates that with increasing graphite content the effect of the CB/CNT ratio within the CB-CNT mixture is less important on the conductivity.

2.3.3 Mechanical properties

The results of the bending tests are summarized in Figures 4 and 5. As shown by Figure 4, the flexural strength value is increased by 20 and 40 vol% graphite contents to a similar degree (with the exception of 100% CNT), independently of the fact whether 5 or 10 vol% CB-CNT mixture is present in the material.

At the composition containing 5 vol% CB-CNT additive an increase is observed at 40% CNT fraction at all three graphite concentrations (Figure 4/a). As this trend can be observed also in materials without graphite, it is not the consequence of graphite

addition, but is caused by the variation of the CB-CNT proportion.

On Figure 4/b small setback can be observed at 80% CNT fraction for composites containing 0 and 20 vol% graphite, followed by an increase at 100% CNT fraction. At 40 vol% graphite content, however, further decrease appears at 100% CNT fraction too.

Figure 5 shows the changes of the flexural modulus as a function of the CNT fraction. The curves exhibit a linearly decreasing trend according to equation (2).

$$E_k = V_{CNT} (E_{CNT} - E_{CB}) + E_{CB}, \quad (2)$$

where E_C is the flexural modulus of elasticity of the composite, E_{CB} is that of the material containing carbon black, E_{CNT} is that containing nanotubes alone, while V_{CNT} is volume fraction of the carbon nanotube within the carbon black - nanotube mixture.

Figure 6 shows the changes of the slopes of the trend lines of Figure 5 vs. the graphite content. It can be observed that with increasing graphite content the flexural modulus exhibits more intense decrease if the CNT portion is increased within the CB-CNT mixture. This intensity variation is independent of the fact whether 5 or 10 vol% of (CB-CNT) mixture is used. Increasing graphite content helps to disperse the carbon black parts better, and more uniformly dispersed CB hinders the movement of molecular chains more effectively, thus increasing the rigidity of the material. This effect is not so important with CNT aggregates, this explains the change of $(E_{CNT} - E_{CB})$ plotted in Figure 6.

Results of the impact strength tests are shown in Figure 7. The trend of the curves resembles that of the flexural strength curves plotted on Figure 4, but, due to the low impact strength values the absolute differences are smaller, the results vary within the 1.5-2.5 kJ/m² range for all graphite contents.

2.3.4 Optical microscopic studies

Comparing the flexural and impact strength values of materials with 20 and 40 vol% graphite contents a significant difference can be observed between 100% CB and 100% CNT proportions. In order to understand the phenomenon optical microscopic studies were performed. Graphite aggregates observed on the polished cross sections (see Figure 8) were analyzed by image analysis software to characterize the distribution of graphite. Frequencies of graphite particles of different areas were compared, as shown in Figure 9. It can be observed that neither 5 nor 10 vol% added CB or CNT changes significantly the size distribution of the graphite particles, thus the changes in the mechanical properties and the electrical conductivity are not caused by dispersion differences of the graphite particles, but by those of CB and CNT particles.

3. Conclusions

Three kinds of fillers were studied: Combined effects of graphite, carbon black and carbon nanotube were studied on the electrical conductivity and on the mechanical properties for polypropylene matrix. The proportion of added carbon black and carbon nanotube was studied at various graphite contents. Conductivity decreased exponentially, the flexural modulus of elasticity according to the linear mixture rule with the CNT ratio at all graphite contents. The decrease of conductivity was less intense with increasing graphite contents, while the decrease of the flexural modulus became more intense, which can be explained by various dispersing effects of graphite on CB and CNT.

The flexural strength and impact strength values changed similarly with the variation of CNT proportion. In case of 5 vol% added CB-CNT mixture the values

increased somewhat at 40% CNT fraction, while at 10 vol% CB-CNT content not unambiguous trend can be observed when varying the CNT proportion. In the case of the studied hybrid composites the graphite content has less influence on these properties than on conductivity or rigidity.

Acknowledgements

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References

- [1] Stauffer D, Aharony A. Introduction to Percolation Theory. London: Taylor & Francis; 1994.
- [2] Antunes RA, de Oliveira MCL, Ett G, Ett V. Carbon materials in composite bipolar plates for polymer electrolyte membrane fuel cells: A review of the main challenges to improve electrical performance. J Power Sources 2011; 196():2945-61.
- [3] Kara S, Arda E, Dolastir F, Pekcan Ö. Electrical and optical percolations of polystyrene latex-multiwalled carbon nanotube composites. J Colloid Interface Sci 2010; 344():395-401.
- [4] Lee JH, Jang YK, Hong CE, Kim NH, Li P, Lee HK. Effect of carbon fillers on properties of polymer composite bipolar plates of fuel cells. J Power Sources 2009; 193():523-9.
- [5] Wissler M. Graphite and carbon powders for electrochemical applications. J Power Sources 2006; 156():142–50.
- [6] Liao SH, Yen CY, Weng CC, Lin YF, Ma CC, Yang CH, et al. Preparation and properties of carbon nanotube/polypropylene nanocomposite bipolar plates for polymer electrolyte membrane fuel cells. J Power Sources 2008; 185():1225–32.
- [7] Dweiri R, Sahari J. Electrical properties of carbon-based polypropylene composites for bipolar plates in polymer electrolyte membrane fuel cell (PEMFC). J Power Sources 2007; 171():424–32.
- [8] Dicks AL. The role of carbon in fuel cells. J Power Sources 2006; 156():128–41.
- [9] Kozłowski M, Frackowiak S. Chemical sensors based on polymer composites. Sensor Actuat B-Chem 2005; 109():141–5.

- [10] Narkis M, Lidor G, Vaxman A, Zuri L. New injection moldable electrostatic dissipative (ESD) composites based on very low carbon black loadings. *J Electrostat* 1999; 47(4):201-14.
- [11] Wang YJ, Pan Y, Zhang XW, Tan K. Impedance Spectra of Carbon Black Filled High-Density Polyethylene Composites. *J Appl Polym Sci* 2005; 98(3):1344–50.
- [12] Medalia AI. Electrical Conduction in Carbon Black Composites. *Rubber Chem Technol* 1986; 59(3):432.
- [13] Kimura T, Yoshimura N, Ogiso T, Maruyama K, Ikeda M. Effect of elongation on electric resistance of carbon-polymer systems I. *Polymer* 1999; 40(14):4149.
- [14] Rubin Z, Sunshine SA, Heaney MB, Bloom I, Balberg I. Critical behavior of the electrical transport properties in a tunneling-percolation system. *Phys Rev B* 1999; 59(19):12196-9.
- [15] Menzer K, Krause B, Boldt R, Kretzschmar B, Weidisch R, Pötschke P. Percolation behaviour of multiwalled carbon nanotubes of altered length and primary agglomerate morphology in melt mixed isotactic polypropylene-based composites. *Compos Sci Technol* 2011; 71(16):1936-43.
- [16] Yang L, Liu F, Xia H, Qian X, Shen K, Zhang J. Improving the electrical conductivity of a carbon nanotube/polypropylene composite by vibration during injection-moulding. *Carbon* 2011; 49(10):3274-83.
- [17] Aguilar JO, Bautista-Quijano JR, Avilés F. Influence of carbon nanotube clustering on the electrical conductivity of polymer composite films. *Express Polym Lett* 2010; 4(5):292-9.

- [18] Tjong SC. Editorial corner – a personal view, Carbon nanotubes – attractive nanofillers for forming bio-, functional and structural polymer composites. *Express Polym Lett* 2010; 4(9):516.
- [19] Bauhofer W, Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Compos Sci Technol* 2009; 69(10):1486-98.
- [20] Maheshwari PH, Mathur RB, Dhami TL. Fabrication of high strength and a low weight composite bipolar plate for fuel cell applications. *J Power Sources* 2007; 173(1):394-403.
- [21] Socher R, Krause B, Hermasch S, Wursche R, Pötschke P. Electrical and thermal properties of polyamide 12 composites with hybrid filler systems of multiwalled carbon nanotubes and carbon black. *Compos Sci Technol* 2011; 71(8):1053-59.
- [22] <http://www.akzonobel.com>
- [23] <http://www.baytube.com>
- [24] Zhang SM, Lin L, Deng H, Gao X, Bilotti E, Peijs T, et al. Synergistic effect in conductive networks constructed with carbon nanofillers in different dimensions. *eXPRESS Polymer Letters* 2012; 6(2):159-68.

Figure Captions

Figure 1. Variation of the conductivity vs. the filler content for graphite, carbon black and carbon nanotube loaded systems

Figure 2. Changes of the conductivity of composites loaded with various conductive fillers

Figure 3. Intensity of the conductivity enhancement vs. the graphite content

Figure 4. Changes of the flexural strength in composites filled with conductive filler combinations of various compositions

Figure 5. Changes of the flexural modulus in composites filled with conductive filler combinations of various compositions

Figure 6. Intensity of the flexural modulus variation vs. the graphite content

Figure 7. Changes of the impact strength in composites filled with conductive filler combinations of various compositions

Figure 8. Optical micrographs of composites containing two kinds of fillers (a: 20G+5CNT; b: 20G+5CB; c: 20G+10CNT; d: 20G+10CB; e: 40G+5CNT; f: 40G+5CB; g: 40G+10CNT; h: 40G+10CB)

Figure 9. Frequency distribution of graphite particle areas for 5 vol% CNT or CB addition (a), or for 10 vol% CNT or CB addition (b)

Table1

	Graphite	Carbon black	Carbon nanotubes
	(G)	(CB)	(CNT)
Apparent bulk density			
(g/cm ³)	0.40	0.11	0.15
Density			
(g/cm ³)	2.24	1.80	1.50
Average particle size	diameter: 10-20		diameter: 0.015
(μm)	thickness: 0.1-1	0.035	length: 0,3 - 1
Specific surface			
(m ² /g)	6	1400	300

Table 1. Properties of the fillers used [22, 23]

Table2

Notation		PP	G	CB	CNT
Material group	Material	(vol%)	(vol%)	(vol%)	(vol%)
0G+5(CB+CNT)	95PP+5CB	95	0	5	0
	95PP+4CB+1CNT	95	0	4	1
	95PP+3CB+2CNT	95	0	3	2
	95PP+2CB+3CNT	95	0	2	3
	95PP+1CB+4CNT	95	0	1	4
	95PP+5CNT	95	0	0	5
0G+10(CB+CNT)	90PP+10CB	90	0	10	0
	90PP+8CB+2CNT	90	0	8	2
	90PP+6CB+4CNT	90	0	6	4
	90PP+4CB+6CNT	90	0	4	6
	90PP+2CB+8CNT	90	0	2	8
	90PP+10CNT	90	0	0	10
20G+5(CB+CNT)	75PP+20G+5CB	75	20	5	0
	75PP+20G+4CB+1CNT	75	20	4	1
	75PP+20G+3CB+2CNT	75	20	3	2
	75PP+20G+2CB+3CNT	75	20	2	3
	75PP+20G+1CB+4CNT	75	20	1	4
	75PP+20G+5CNT	75	20	0	5
20G+10(CB+CNT)	70PP+20G+10CB	70	20	10	0
	70PP+20G+8CB+2CNT	70	20	8	2
	70PP+20G+6CB+4CNT	70	20	6	4

40G+5(CB+CNT)	70PP+20G+4CB+6CNT	70	20	4	6
	70PP+20G+2CB+8CNT	70	20	2	8
	70PP+20G+10CNT	70	20	0	10
	55PP+40G+5CB	55	40	5	0
	55PP+40G+4CB+1CNT	55	40	4	1
	55PP+40G+3CB+2CNT	55	40	3	2
	55PP+40G+2CB+3CNT	55	40	2	3
40G+10(CB+CNT)	55PP+40G+1CB+4CNT	55	40	1	4
	55PP+40G+5CNT	55	40	0	5
	50PP+40G+10CB	50	40	10	0
	50PP+40G+8CB+2CNT	50	40	8	2
	50PP+40G+6CB+4CNT	50	40	6	4
	50PP+40G+4CB+6CNT	50	40	4	6
	50PP+40G+2CB+8CNT	50	40	2	8
	50PP+40G+10CNT	50	40	0	10

Table 2. Compositions and notation

Figure1
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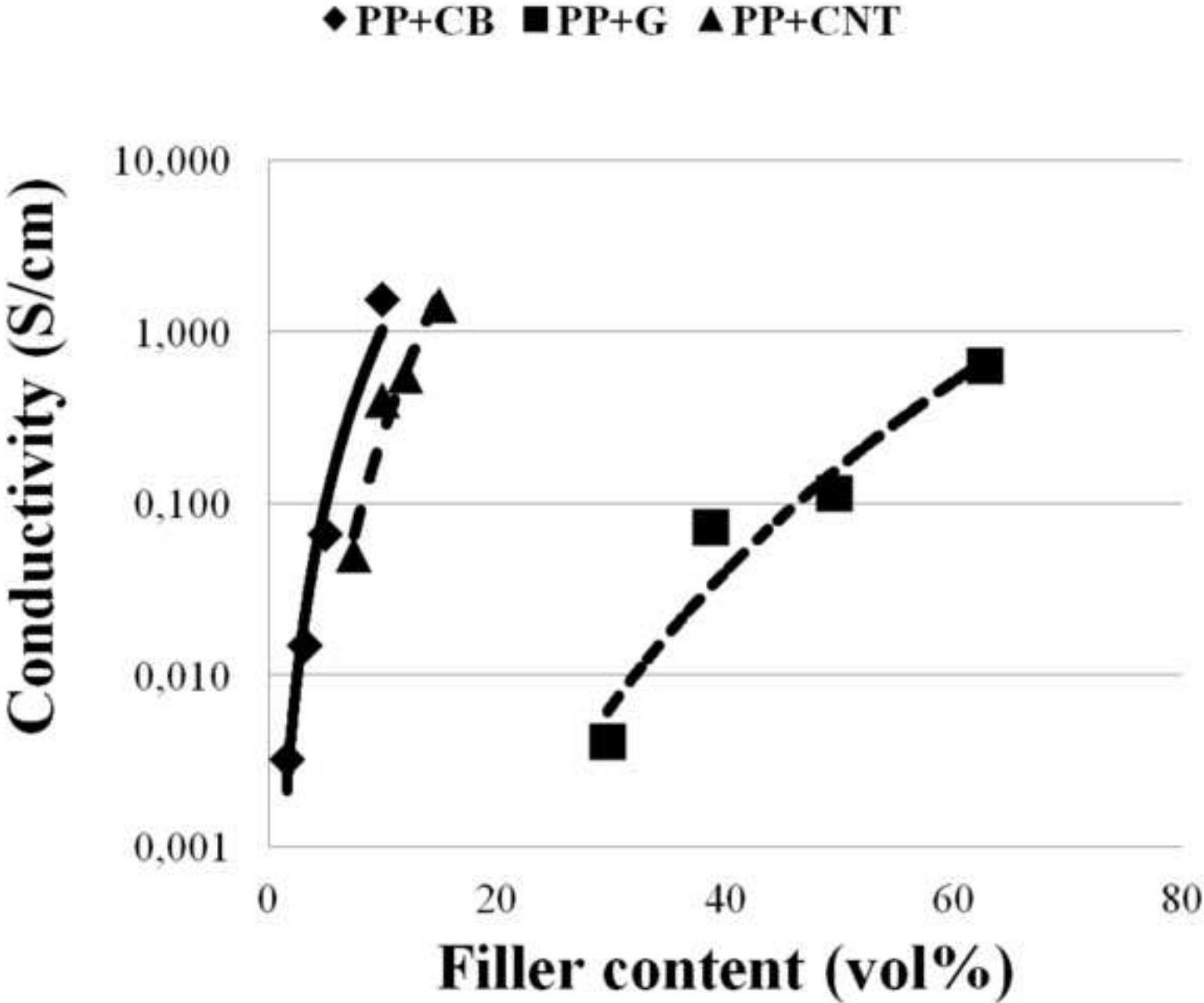


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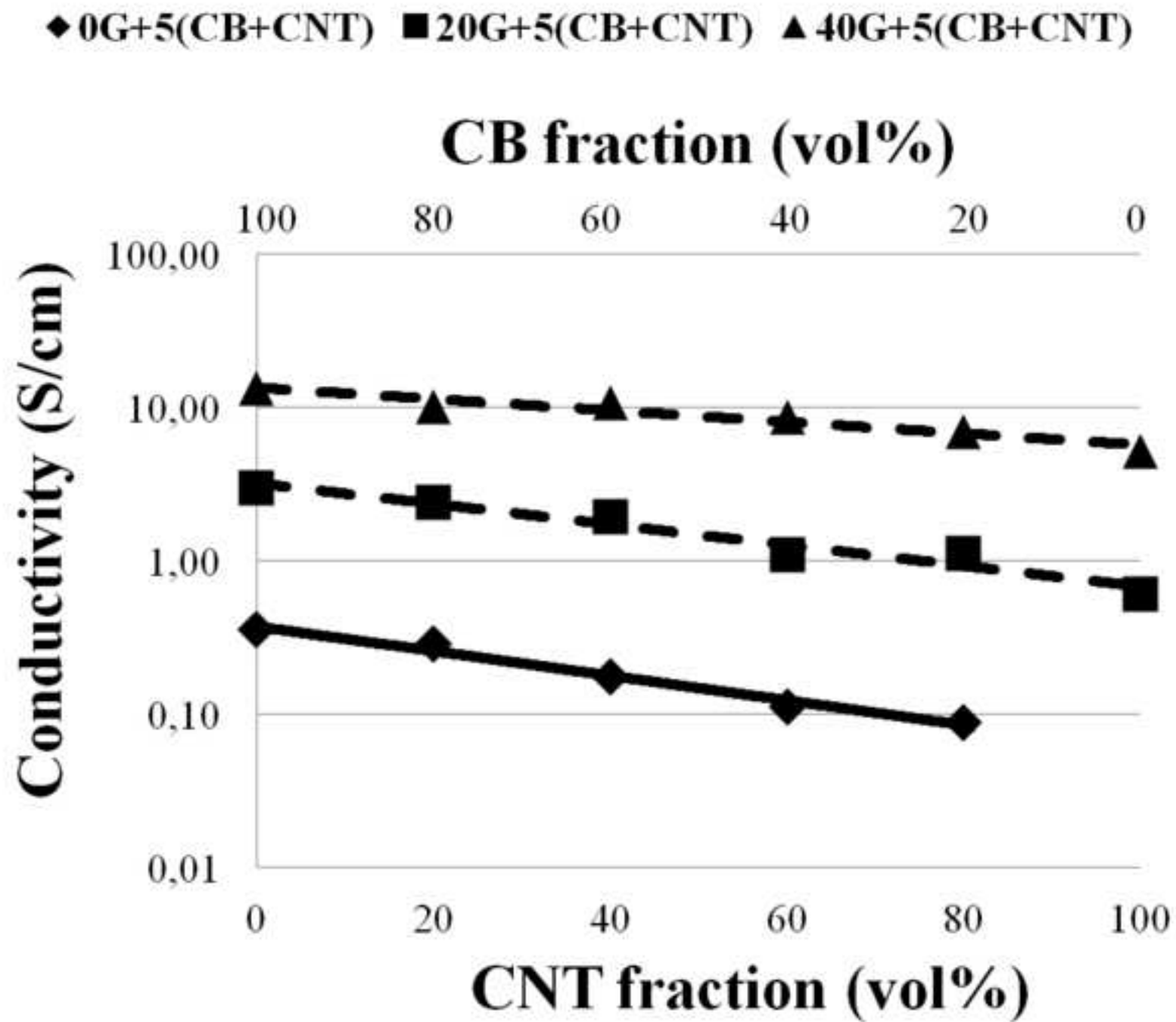


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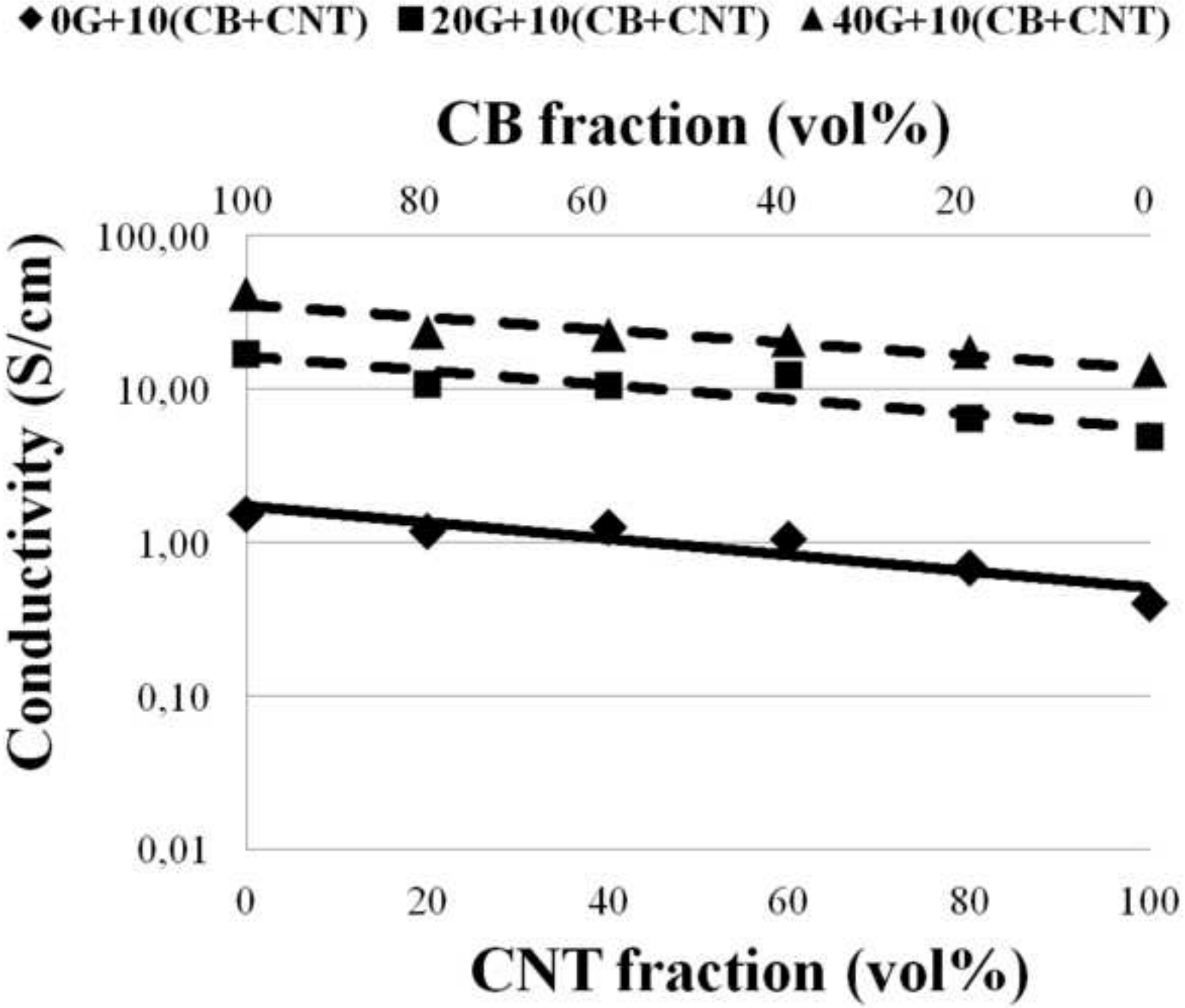


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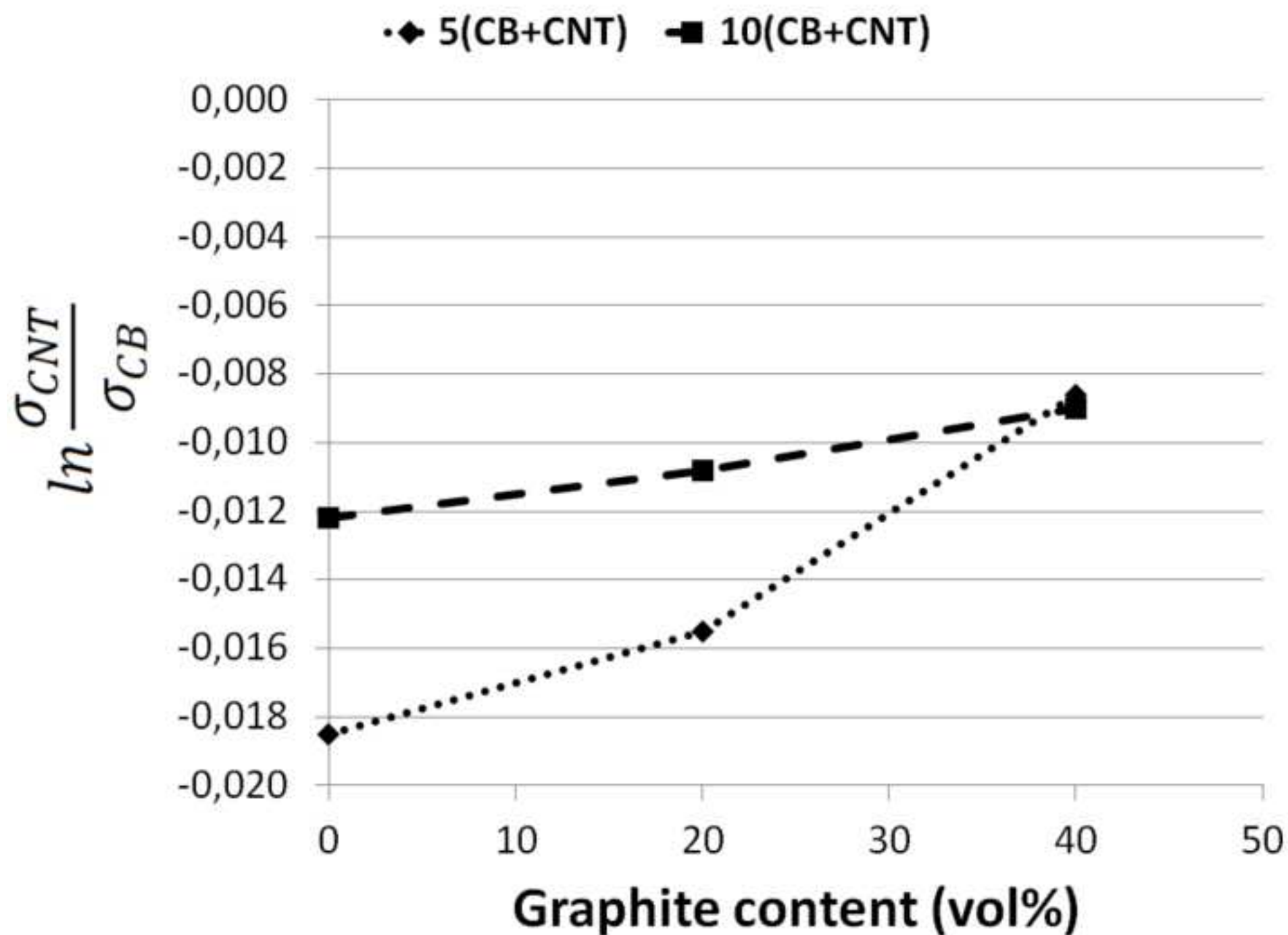


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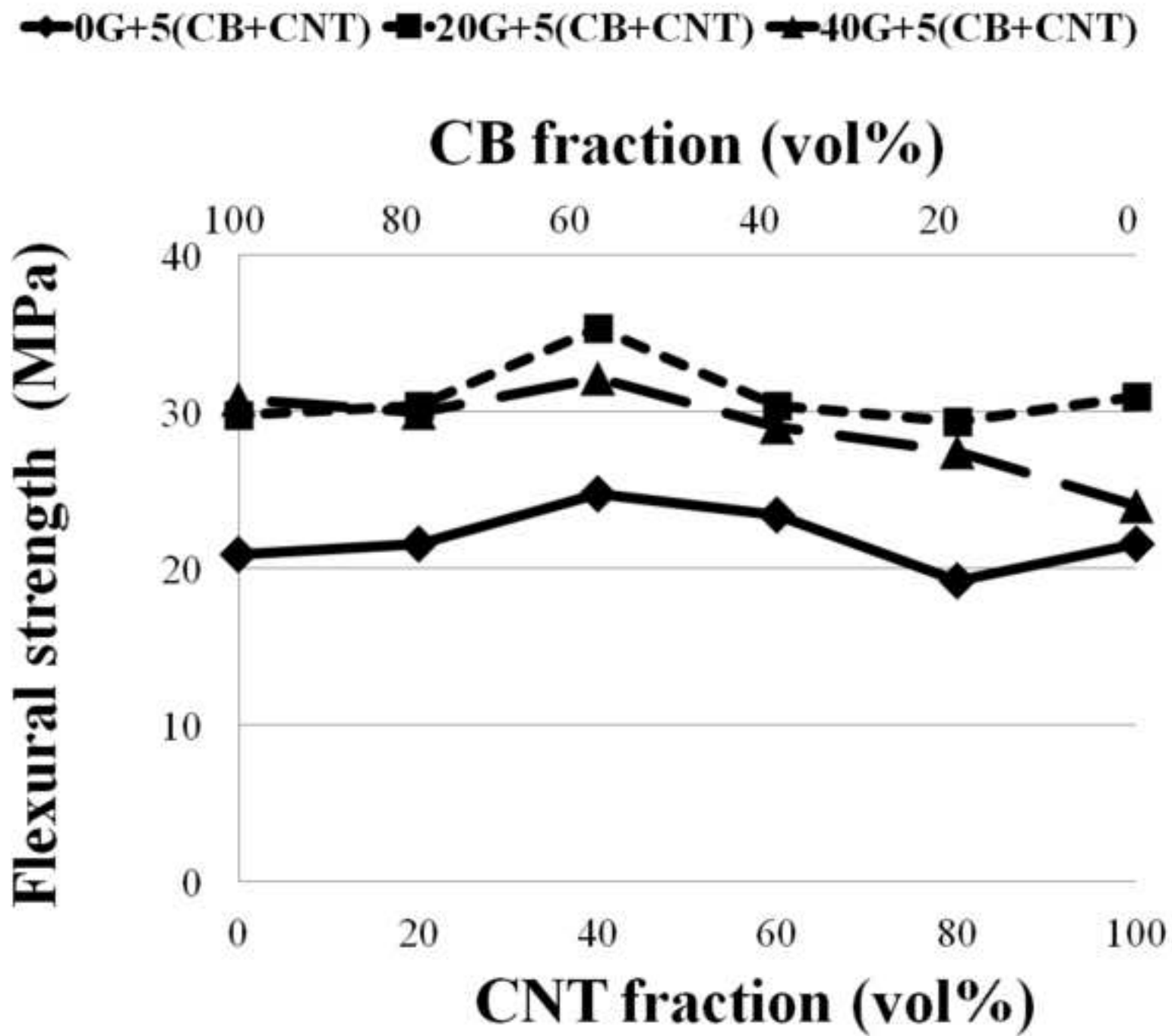


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◆ 0G+10(CB+CNT) ■ 20G+10(CB+CNT) ▲ 40G+10(CB+CNT)

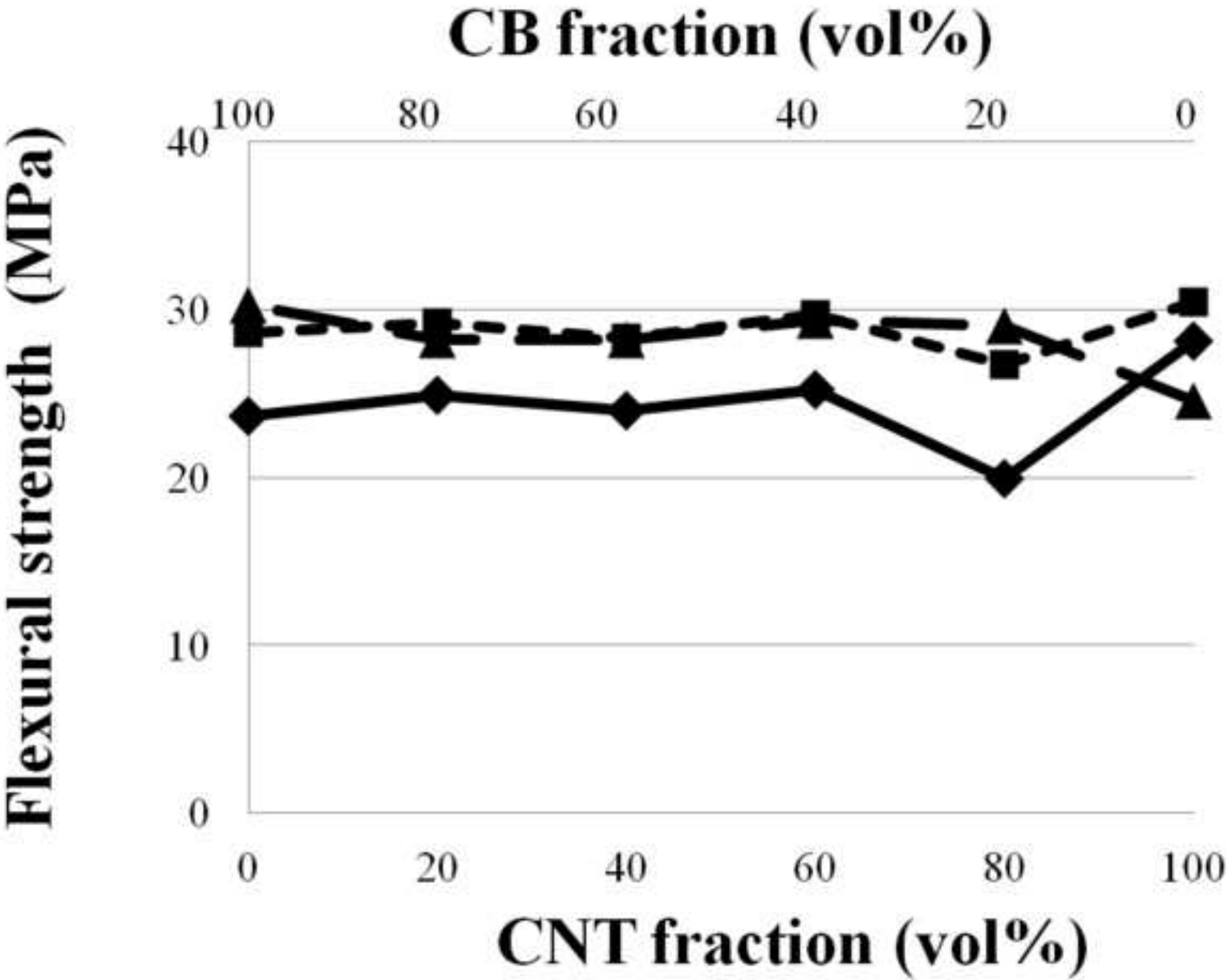


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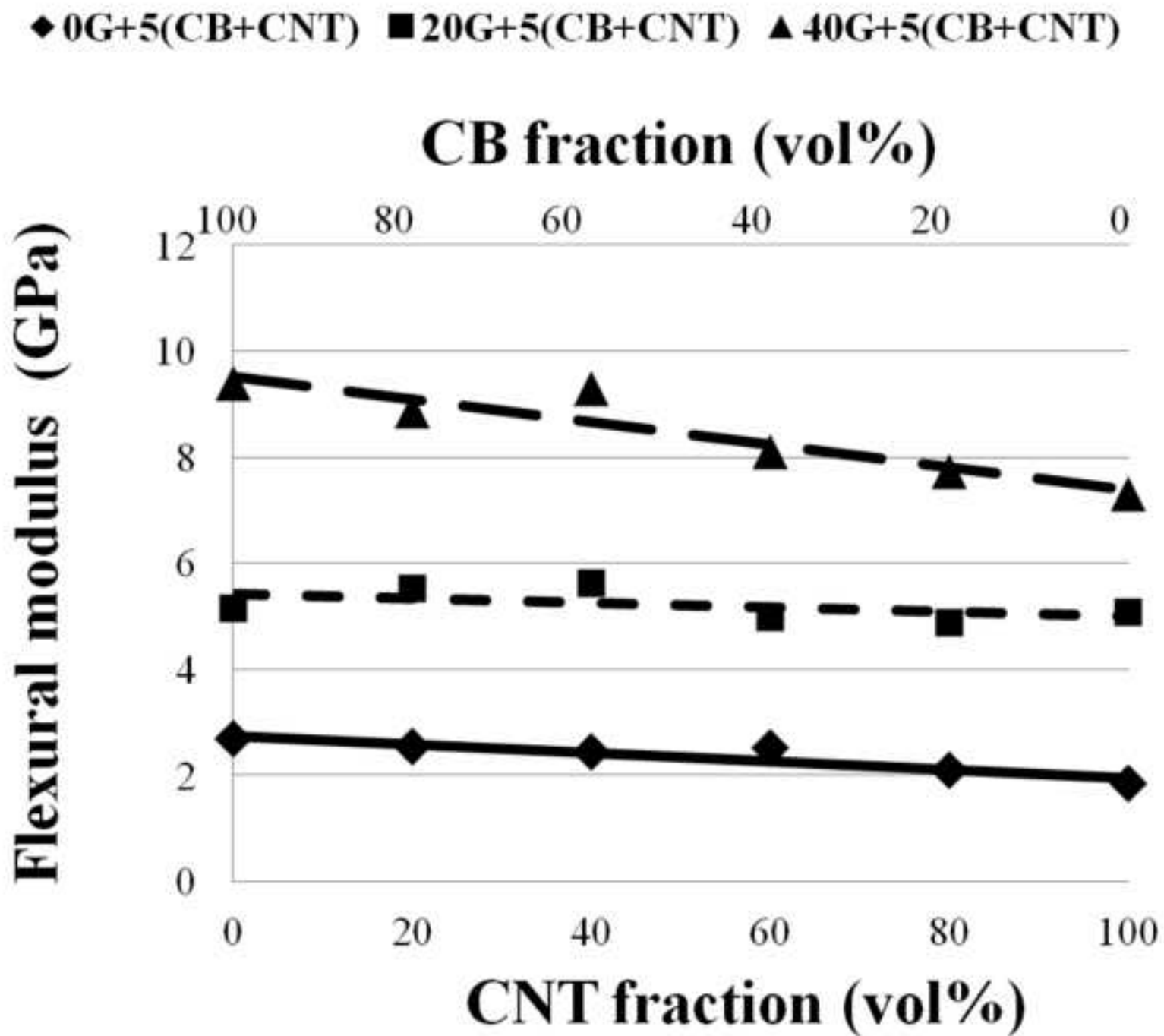


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◆ 0G+10(CB+CNT) ■ 20G+10(CB+CNT) ▲ 40G+10(CB+CNT)

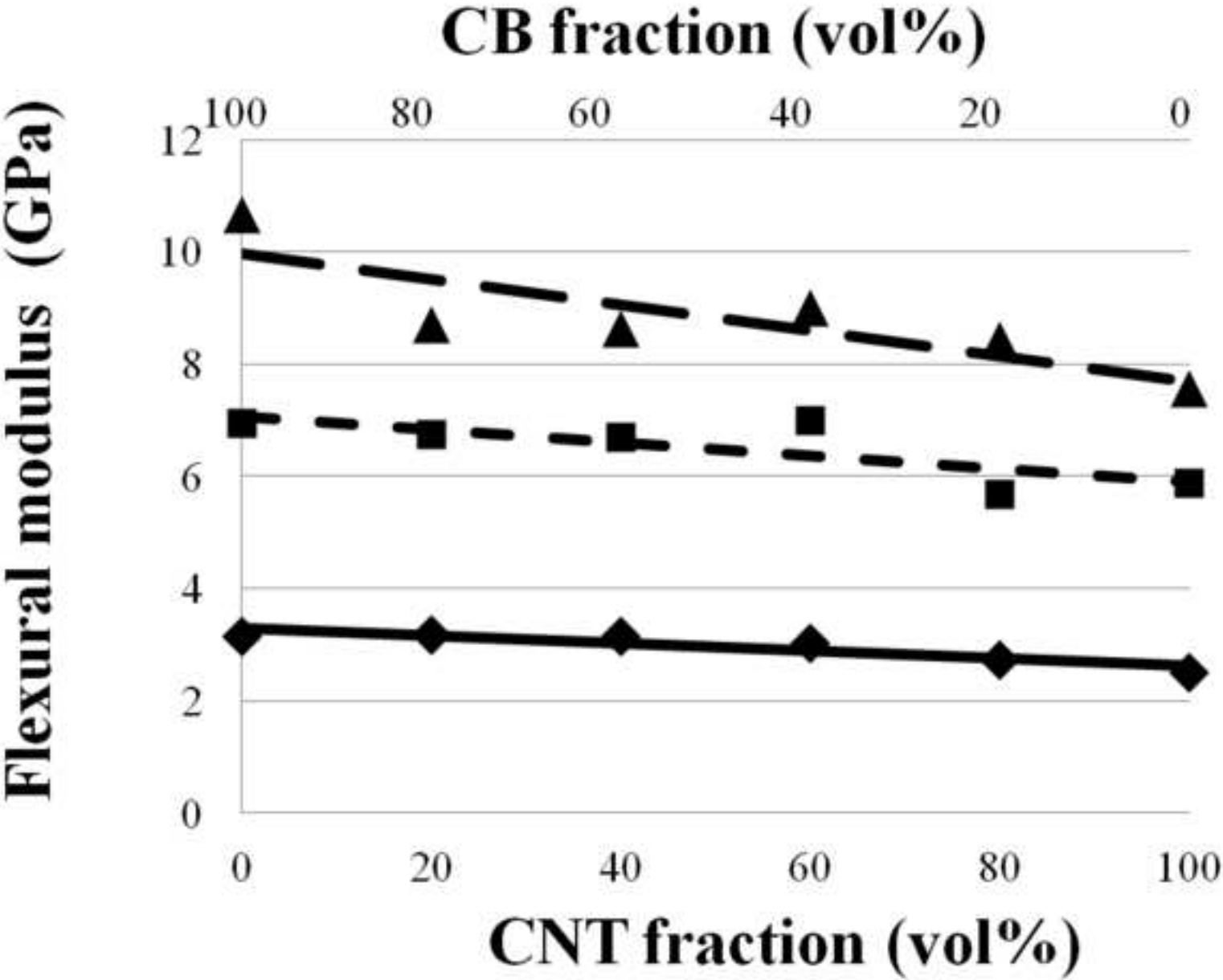


Figure6

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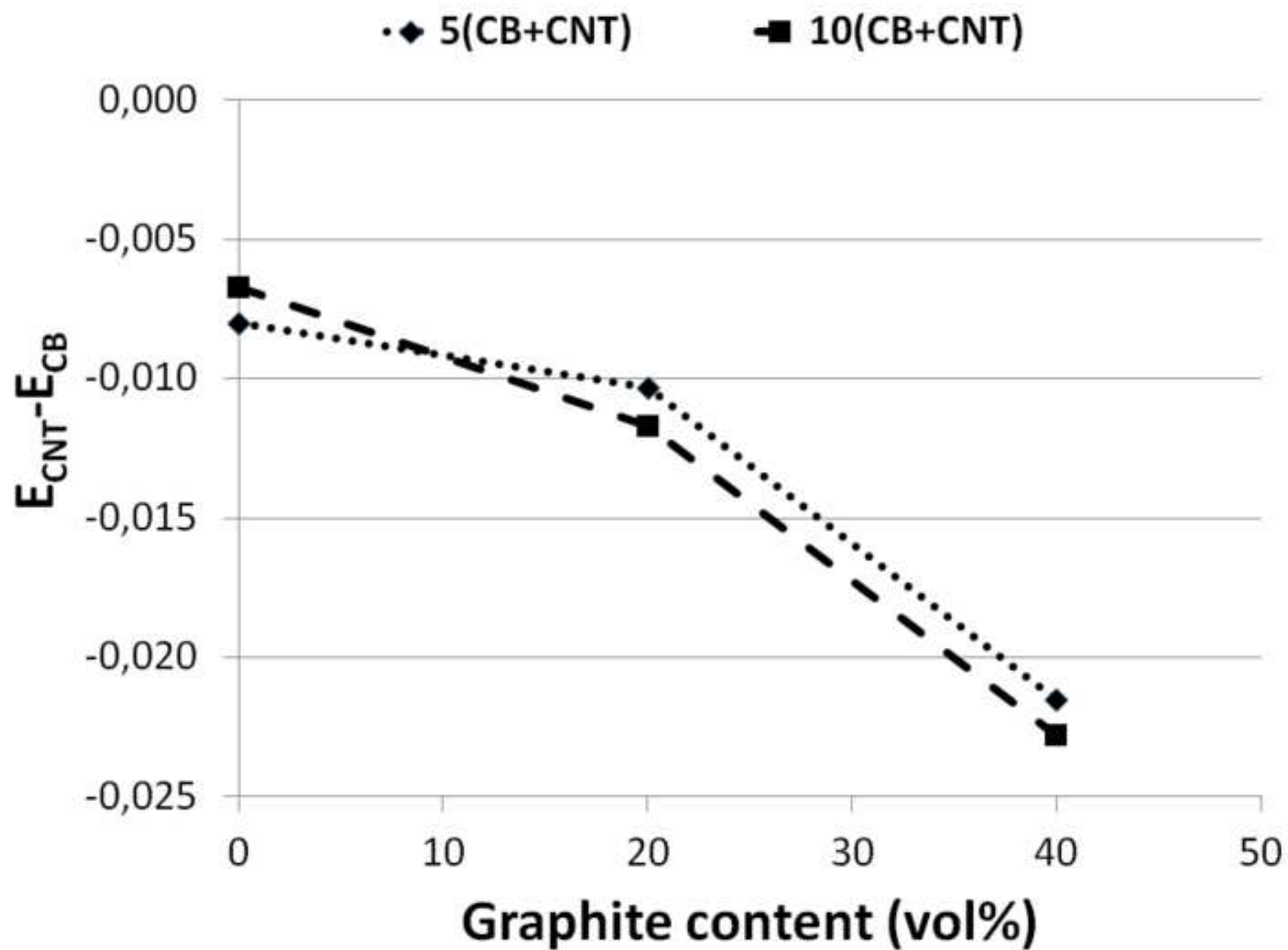


Figure7a

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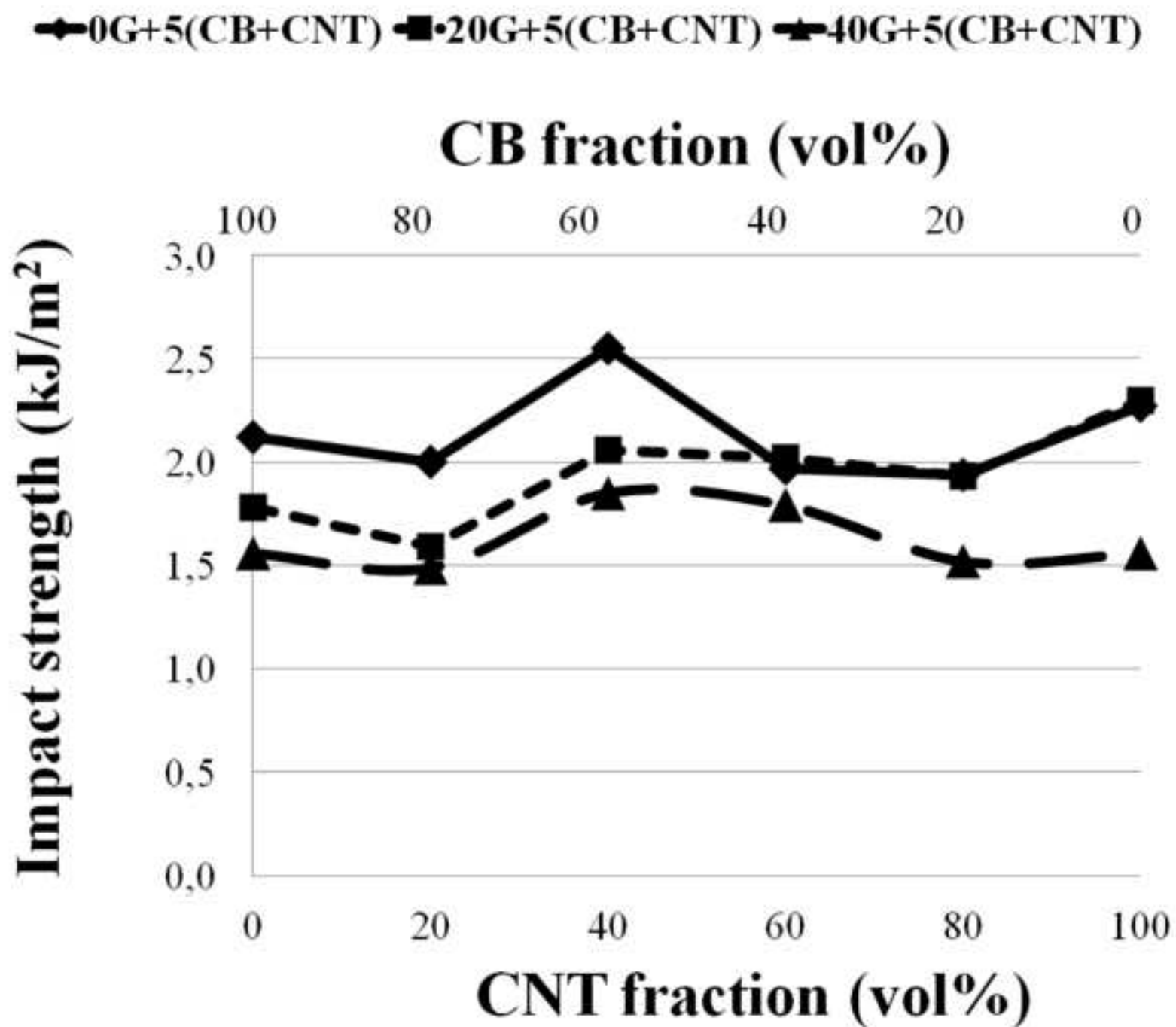


Figure7b
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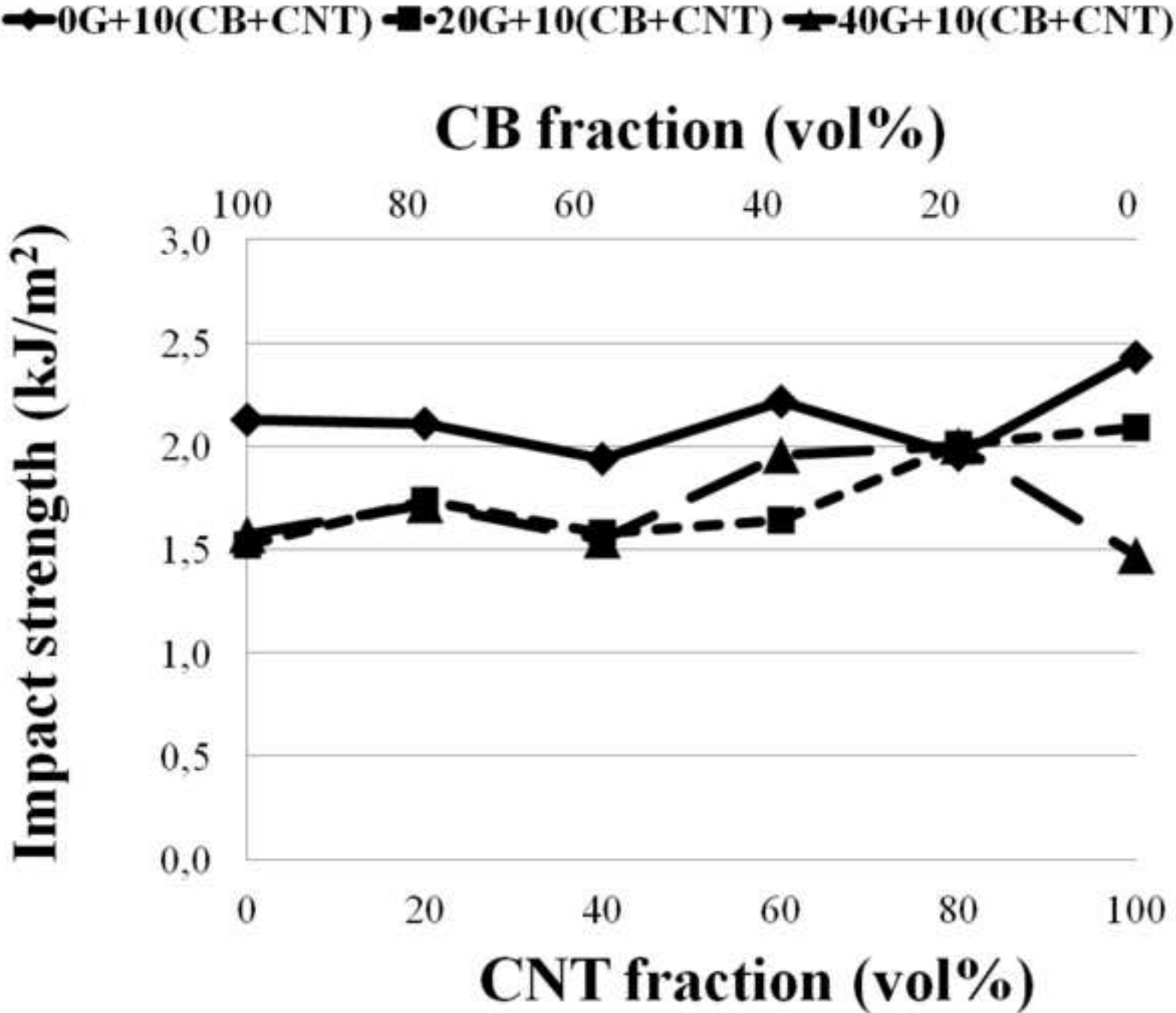


Figure8
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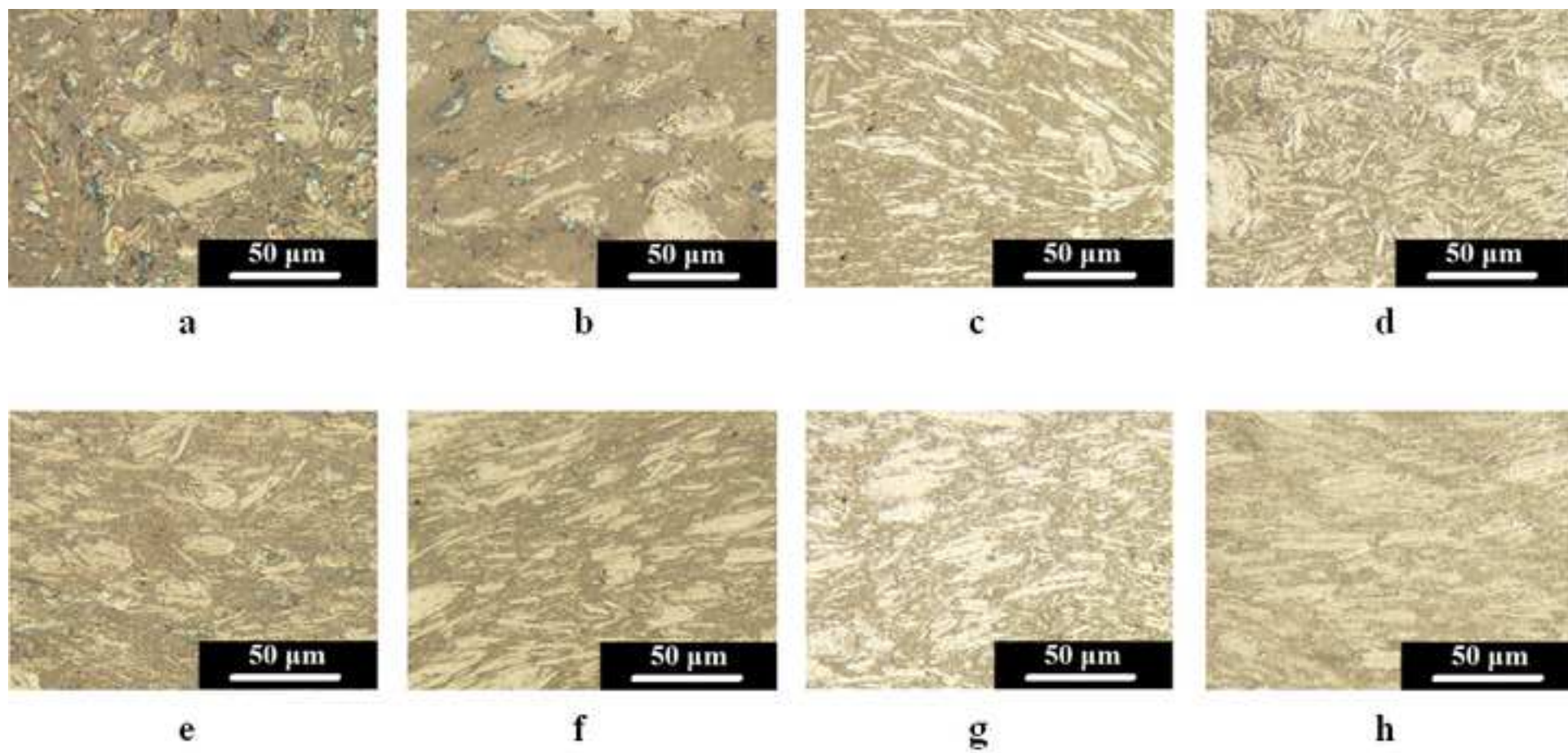


Figure9a

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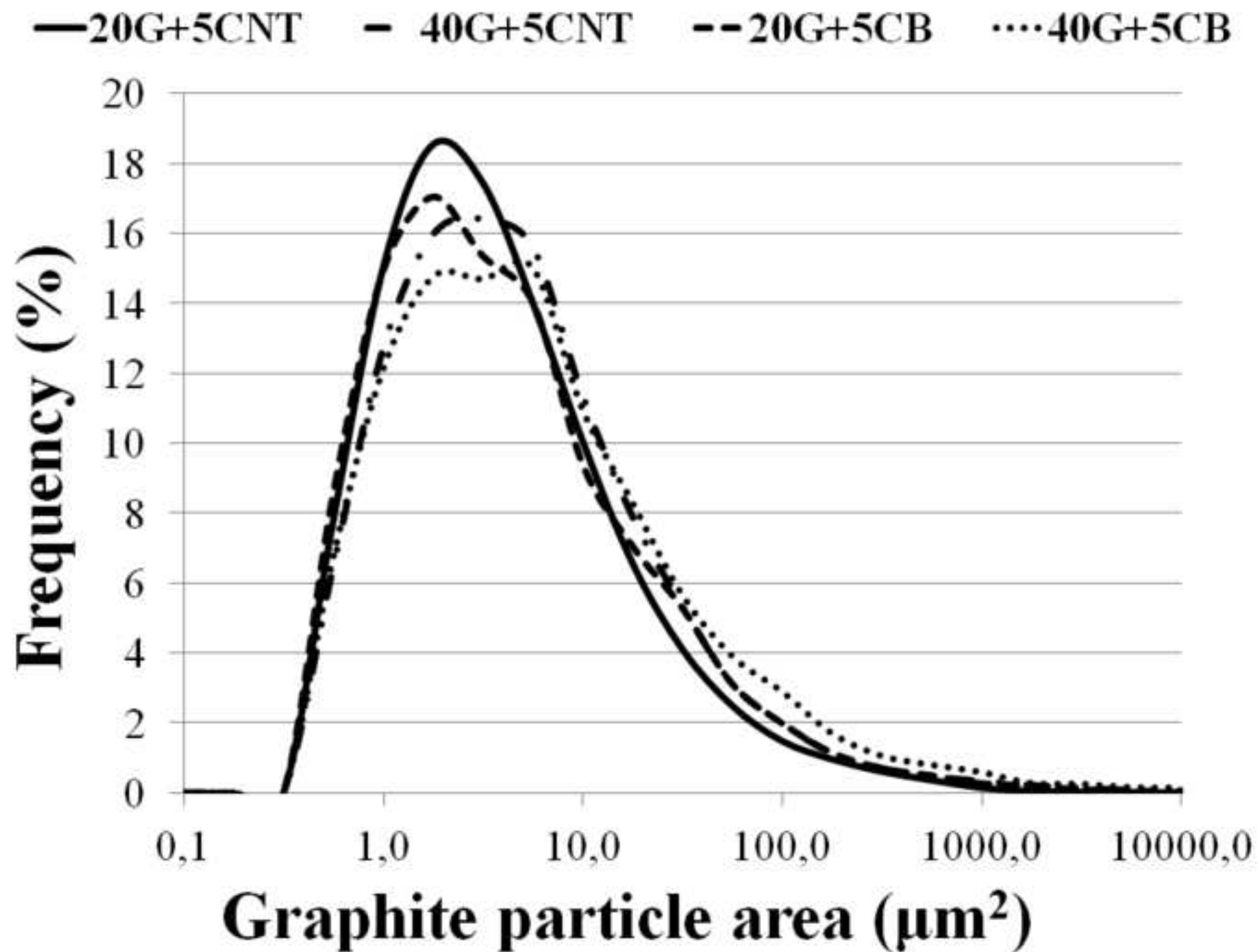


Figure9b

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