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Thermodynamic Study of Portland Cement Containing Multi-walled Carbon Nanotubes (MWCNT)

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The objective of this work is the thermodynamic study of portland cement containing multi-walled carbon nanotubes. The measurements of the thermal expansion coefficient of the two pure samples and its nanocomposite have the same shape. The dilatometric curves contain the same number of abnormalities. Their intensity differs from sample to sample. The calorimetric study reveals a similar character between the DSC curves of the two samples, the matrix and its nanocomposite. The thermogravimetry of the two materials shows the presence of several anomalies probably linked to the phenomena of dehydration. The insertion of the multi-walled carbon nanotubes into the cement made the nanocomposite stable over a wide temperature range compared to the cement matrix.

Keywords: Dilatometry, Anisotropy, Nanotubes, Calorimetry, Thermogravimetry, Cement.

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1. INTRODUCTION

Due to their high aspect ratio, low density [1, 2], superior mechanical [3], thermal[4] and electrical properties [5], multi-walled carbon nanotubes (MWCNTs) have been shown to be effective in enhancing the properties of polymers [6], metals [7], ceramics [8] and biomaterials [9]. The introduction of CNTs for the reinforcement of ceramic nanocomposites has not yet been well studied.

Unlike other important matrix materials, little work has been done on the use of cements reinforced with MWCNTs. Preliminary work has been reported [10, 11]. The majority of research work on composites containing CNTs has rather focused on metallic and ceramic matrices. The initial results were generally unattractive and often showed little or no improvement in the properties of composites compared to traditional materials. More recent results were much more promising [12]. Some researchers have shown significant improvements in toughness, hardness and strength [8, 13, 14].

Improving the properties of concrete through its interaction with admixtures has been the subject of much attention for years. In addition to steel rebars, various incorporated admixtures have been added to cement composites mainly to improve their mechanical performance [15]. Recently, nanomixes have also aroused the interest of researchers because of their ability not only to further improve several characteristics of cementitious materials, but also to provide new properties that can lead to a wide range of potential applications. These materials include concrete, mortar and cement paste, used in structural members, pavements, finishing and repair products [16, 17].

Portland cement, as the main binder in concrete, forms an important part of infrastructure built around the world. Since the material has low tensile strength, its reinforcement is generally obtained by inserting cement in the form of bars or macro or micro fibers. This can lead to a significant improvement in the mechanical properties of the resulting composite[18]. However, the availability of nanoscale materials, in particular CNTs, has opened up new avenues for modifying cement properties at the nanoscale [10].

Studies [19-21] on the role of CNTs used in ordinary Portland cement (OPC) have shown excellent properties, toughness and strengthening of the microstructure. Zou et al., [22], added 0.075 wt % MWCNTs in OPC pastes and improved flexural strength and modulus of elasticity by 63 % and 32 %. Xu et al, [23], determined that CNTs can fill nanoscale pores of calcium silicate hydrate and reduce the porosity of OPC pastes [24].

2. EXPERIMENTAL

Two samples were used in this study. The first is made from Portland cement, polycarboxylateas a plasticizer and water (S1).

The second contains Portland cement, polycarboxylate, water and 1 % multi-wall carbon nanotubes (S2).

The two samples underwent several thermophysical treatments to study the effect of the addition of MWCNT on the thermal and structural characteristics of the samples thus produced.

For dilatometry, we used the NETZSH DIL 402C

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dilatometer. The heating rate was 10 °C/min. Measurements of the coefficient of thermal expansion as a function of temperature were made in the temperature range 25-1000 °C.

The DSC measurements were performed using a NETZSH STA 409 PC/PG device coupled to a TG. The analysis conditions were the same as in dilatometry, namely a constant heating rate equal to 10 °C/min and the same temperature range.

The XRD was carried out by the difractometer XPERT-PRO.

3. RESULTS AND DISCUSSION

3.1 DSC

We begin with DSC, an interesting thermodynamic scalar quantity allowing highlighting the precipitation sequences and the appearance temperatures of phase transitions due to the introduction of impurities into the matrix. Calorimetric analysis shows a curve containing several anomalies related to changes in the structure of the matrix. There are several sequences appearing at different temperatures. The peak appearing at 150 °C is probably related to the dehydration of our material. From 200 °C, the DSC increases strongly to reach very high values exceeding 0.25 mw/mg, while in the low temperature range, the DSC was negative and was equal to – 0.35 mw/mg. As the temperature increases the intensity of the DSC is multiplied by a factor of 2. In the temperature range 300-600 °C, the DSC signal is very intense. The energy intake is very significant. From 650 °C, the DSC begins to decrease to reach average values. Relatively less heat is released. Structural rearrangement does not require a large amount of heat. Overall, the anomalies of the DSC curve can be related to the dehydration of the different groups (ettringite, calcium monosulfoaluminate, dehydroxylation of portlandite ($Ca(OH)_2$), dehydration of CH or dehydration of $C_{12}A_7H$) present in the cement[25, 26].The DSC curves of the two samples are shown in Fig. 1.

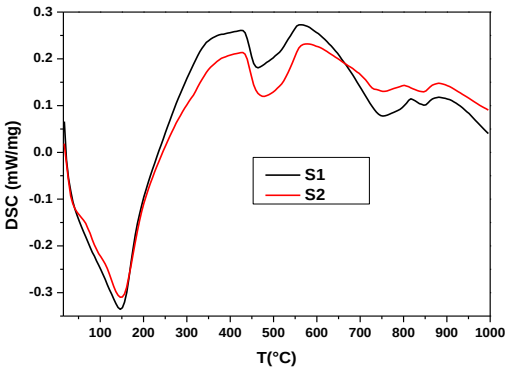

Fig. 1 – DSC of the two samples

The two curves have the same behavior. We notice that the intensities of the peaks have changed slightly.

The comparative study shows that the DSC curves of the two samples are similar. The two curves contain the same number of anomalies and they appear at the same temperatures. This can mean that only one mechanism is operational.

Overall the two curves overlap. We find that the calorimetric variations change depending on the temperature range. From ambient to 230 °C, the two curves are practically the same. The two materials behave in the same way. Apparently there is insufficient energy for a possible role of MWCNTs. From 200-660 °C, the DSC of the nanocomposite is lower than that of the matrix. Probably, the MWCNTs begin to move in the cement for a rearrangement of the particles. Beyond 675-1000 °C, it becomes higher. The effect of the dispersion of MWCNTs is intense.

3.2 Thermogravimetry

The TGhighlights the dependence of the mass change on the temperature.Fig. 2 represents the curves of the TG of of the matrix of the two samples.It shows a decreasing curve over the entire temperature interval. It contains several anomalies, the most important of which are located at temperatures 100, 200, 500, 650 and 800 °C. They are linked to changes in the structure. Their origin is probably due to the dehydration of the different groups. We believe that the decrease in TG is relatively substantial. At high temperatures, it exceeds 20 %. Probably, this large drop has a direct connection with the evaporation of water. In the temperature range 850-1000 °C, the TG changes the slope and becomes a line segment. It becomes stable and the weight loss is practically null.

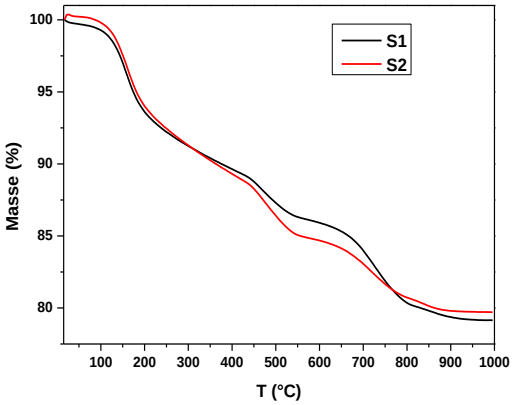

Fig. 2 – The TG of the two samples

We find that the TG curves of the two samples are the same (Fig. 2). They have the same shapes. They contain the same number of anomalies. In the high temperature range 800-1000 °C, the TG of the nanocomposite is less strong. The mass loss of the cement containing MWCNTs is small compared to that of the matrix.

Therefore, MWCNTs stabilize the matrix better. This behavior has been observed in metallic [7]and polymer matrices in which multi-walled carbon nanotubes have been added.

3.3 Dilatometry

The third part of this work is reserved for dilatometric analysis where we study the relative linear dimensional variations and the coefficient of thermal expansion as a function of temperature. This important thermodynamic tensorial quantity allows us to high-

light the anisotropic character of the samples, the presence of phase transitions, their temperature of onset and the changes in interactions due to the introduction of nanometric additions.

The $\Delta L/L$ variations of the sample without MWCNTs (Fig. 3) change depending on the direction of measurement. This implies the presence of an anisotropy.

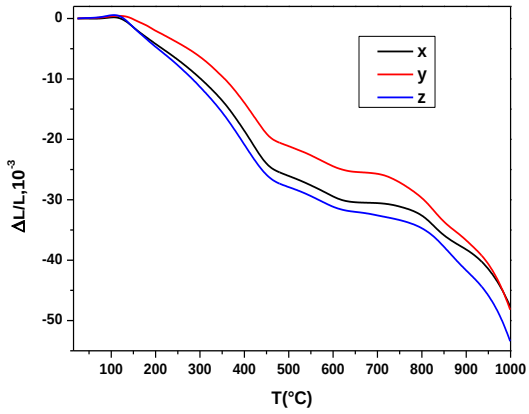

Fig. 3 – Relative variation $\Delta L/L$ according to the three directions of S1

From 100 °C, $\Delta L/L_z$ is lower than $\Delta L/L_x$ and $\Delta L/L_y$ over the entire temperature range. $\Delta L/L_x$ is intermediate. $\Delta L/L_y$ contracts the least over the whole temperature range.

When adding multi-walled carbon nanotubes, $\Delta L/L$ changes shape slightly and contains bearings (Fig. 4).

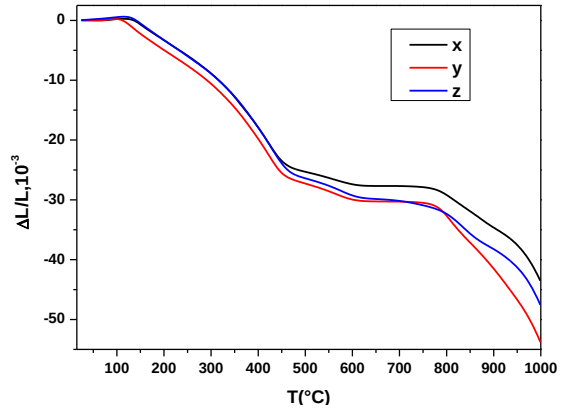

Fig. 4 – Relative variation $\Delta L/L$ according to the three directions of S2

From ambient to 450 °C, $\Delta L/L_x$ and $\Delta L/L_z$ are combined. At 500 °C, $\Delta L/L_x$ stands out from the other two. From 800 °C, the difference between the three curves becomes significant. The anisotropy becomes more pronounced involving strong interactions.

The relative variation $\Delta L/L$ along the z direction of the two samples is shown in Fig. 5.

The comparative study of the two samples following the z direction shows an appreciable difference. The gaits are similar and they have the same shape. The sample containing the MWCNTs shrinks the least up to 1000 °C.

3.3.1. Coefficient of Thermal Expansion

The study of the coefficient of thermal expansion as a function of temperature of the two materials reveals the following information.

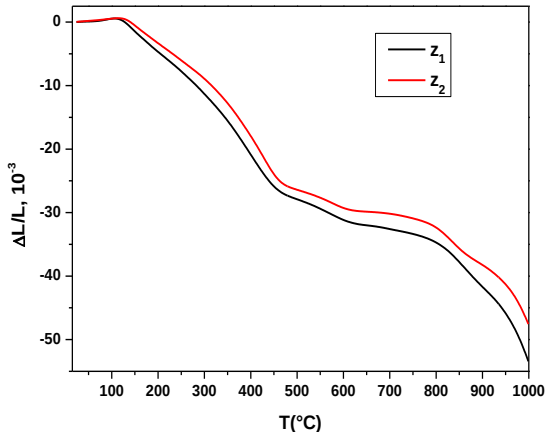

Fig. 5 – Relative variation $\Delta L/L$ according to the z direction of the two samples

Concerning the sample without MWCNTs (Fig. 6), the measurements of α along the three directions confirm the anisotropic nature of the material.

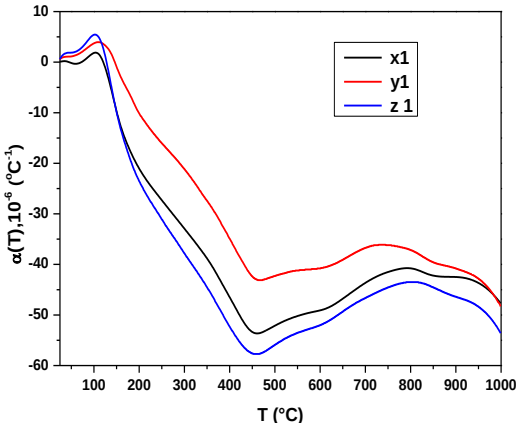

Fig. 6 – Coefficient of thermal expansion α of S1

The three curves have the same behavior and contain the same number of anomalies appearing at the same temperatures, but their intensity varies depending on the direction of measurement. According to the z direction, the expansion is the most accentuated compared to that following the y direction which is the weakest.

When the MWCNTs are injected (Fig. 7), the shape of the dilatometric curves remains practically unchanged.

The number of anomalies and the temperatures of their occurrence did not change. On the other hand, their intensities have increased or decreased depending on the temperature range.

Fig. 8 and Fig. 9 represent the variations of thermal expansioncoefficient in throw x and y directions of the two samples.

According to x, the two curves have the same shape but α_{x2} is greater than α_{x1} over the entire temperature range. The difference between the curves varies depending on the temperature range.

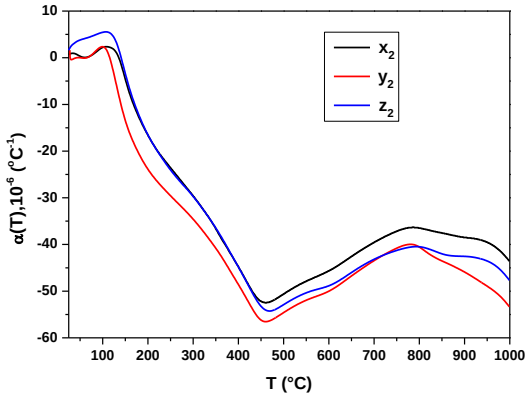

Fig. 7 – Thermal expansion coefficient α of S2

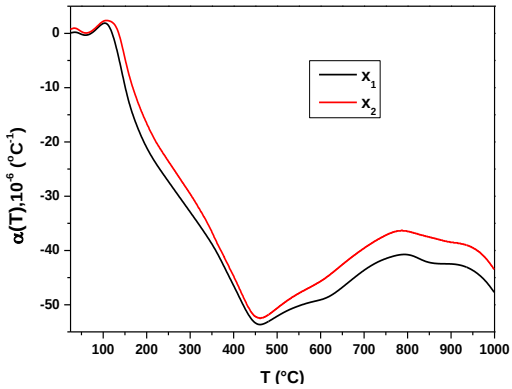

Fig. 8 – Coefficient of thermal expansion α according to the direction x for the two samples

It becomes important at temperatures where MWCNTs have sufficient energy to allow them some mobility. This is in agreement with the experimental results and the theoretical predictions concerning the role of the MWCNTs on the decrease in the expansion of materials containing nanometric fillers of the MWCNT type. As for the y direction, the effect of MWCNTs is more pronounced.

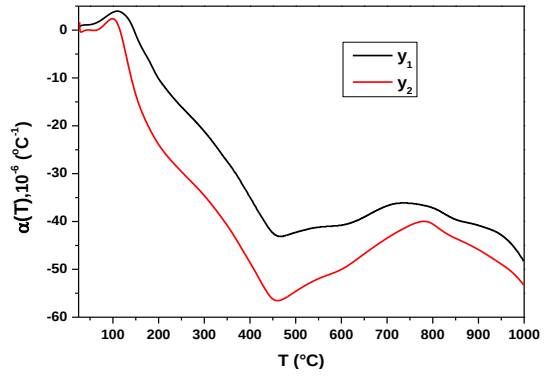

Fig. 9 – Coefficient of expansion α following the y direction for the two samples

The values α_{y2} of the nanocomposite are clearly lower than those of the matrix over the entire temperature range. In this case, the roles are reversed compared to the previous situation.

MWCNTs manifest their presence by playing strongly on the decrease in the coefficient of thermal expansion as a function of temperature. The intensities of the two important peaks, located around 450 °C, are $-43\times10^{-6}\,°C^{-1}$ and $-57\times10^{-6}\,°C^{-1}$ leading to an order of 130 %. In this direction, the agglomeration of MWCNTs blocks the matrix to expand which can lead to contraction and occupation of different types of defects. Apparently, the contribution of MWCNTs does not affect the structural characteristics of the material since we observe similar and superimposable curves containing the same anomalies except that their intensities are markedly different. This assumes that the same mechanisms interact in the two samples.

The study following the z direction shows that the situation is intermediate between the x and y directions (Fig. 10).

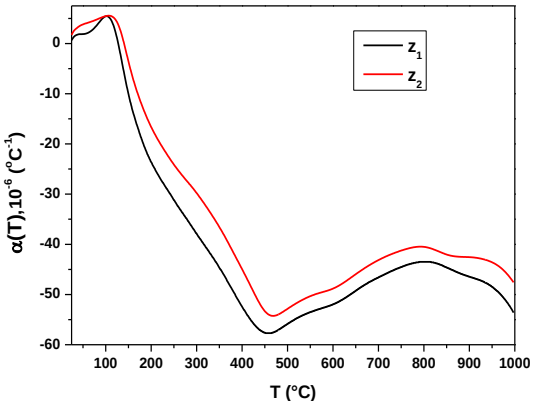

Fig. 10 – Coefficient of thermal expansion α along the z direction for the two samples

In this case, the MWCNTs resume their role by minimizing expansion. In addition, the presence of oxides, themselves having low thermal expansion coefficients, block the contribution of the matrix in the expansion of the nanocomposite. In addition, the various thermomechanical treatments can promote the dispersion of CNTs in the xy plane. Regarding the shape of the curves, it is comparable to the other two cases. They contain the same anomalies but with different intensities.

Therefore, according to the three directions, the dilatometric curves have similar behaviors and comparable shapes. All the peaks appear at the same temperatures except that their intensities are different.

Regarding the origin of the various anomalies observed on the dilatometric curves regardless of the direction of measurement, it can only be linked to the dehydration of the groups, mentioned above, present in the matrix and the nanocomposite.

3.4 XRD

The last part of this work is reserved to the XRD characterization. The spectrum of the composite without MWCNT (S1), and the spectrum of (S2) with 0.1 % of MWCNT of portland-polycarboxylate cementis shown in Fig. 11.

The two spectra have the same shape; the peaks are in practically the same angles, but we see a remarkable increase in intensity in the characteristic peaks for S2. This increase could be related to the increase in the degree of crystallinity of the CH formed and/or to the

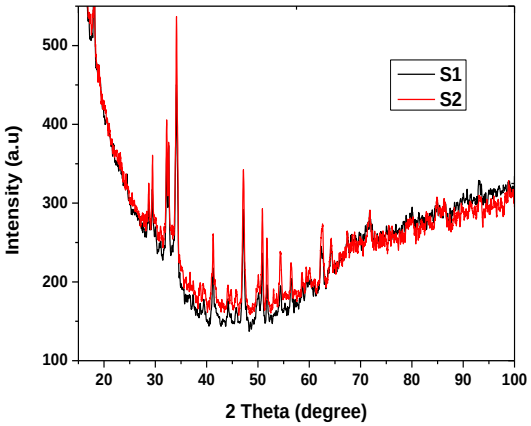

Fig. 11 – The XRD spectra of the two samples

increase in the rate of its formation [26]. While the addition of MWCNT increases the degree of crystallinity in our nanocomposite.

4. CONCLUSION

The comparative study has shown that the DSC curves of the two samples are similar. This can mean that only one mechanism is operational. The effect of the dispersion of MWCNTs plays a significant role.

The mass loss of the sample containing MWCNTs was small compared to that of the matrix. This implies that the MWCNTs stabilize the matrix better. This behavior has been observed in metallic and polymer matrices in which multi-walled carbon nanotubes have been added.

Following the y direction, the agglomeration of MWCNTs blocks the matrix to expand which can lead to contraction and occupation of different types of defects. Apparently, the contribution of MWCNTs did not affect the structural characteristics of the material since we have observed similar and overlapping curves containing the same anomalies except that their intensities were different. This assumes that the same mechanisms had interacted in the two samples.

According to the three directions, the dilatometric curves had similar behaviors and comparable shapes. All the peaks have appeared at the same temperatures except that their intensity differs from one direction to another. This means that there is anisotropy.

Regarding the origin of the various anomalies observed on the dilatometric curves whatever the direction of measurement, it can only be linked to the dehydration of the groups (ettringite, calcium monosulfoaluminate, dehydroxylation of portlandite ($Ca(OH)_2$), dehydration of CH or dehydration of $C_{12}A_7H$) present in the matrix and even the nanocomposite.

The XRD spectra have shown that the characteristic peaks are at almost the same angles, but there was a remarkable increase in intensity in the peaks for sample 2. This increase could be related to the increase in the degree of crystallinity. CH formed and/or an increase in the rate of its formation. So, the addition of MWCNT increases the degree of crystallinity of our nanocomposite.

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REFERENCES

1. S. Iijima, *Nature* **354**, 56 (1991).
2. M.F. De Volder, S. Tawfick, R. Baughman, A. Hart, *Science* **339**, 535 (2013).
3. M.F. Yu, O. Lourie, M.J. Dyer, K. Moloni, T.F. Kelly, R.S. Ruoff, *Science* **287**, 637 (2000).
4. R.S. Ruoff, D.C. Lorents, *Carbon* **33**, 925 (1995).
5. T.W. Ebbesen, H.J. Lezec, H. Hiura, J.W. Bennett, H.F. Ghaemi, T. Thio, *Nature* **382**, 54 (1996).
6. F.H. Gojny, M.H.G. Wichmann, B. Fiedler, K. Schulte, *Compos. Sci. Technol.* **65**, 2300 (2005).
7. Y. Naoui, A. Settar, K. Chetehouna, M.C. Bouleklab, S. Revo, S. Hamamda, *Appl. Phys. A* **126**, 283 (2020).
8. Z. Xia, L. Riester, W.A. Curtin, H. Li, B.W. Sheldon, J. Liang, B. Chang, J.M. Xu, *Acta Mater.* **52**, 931 (2004).
9. B.S. Harrison, A. Atala, *Biomaterials* **28**, 344 (2007).
10. J.M. Makar, J.J. Beaudoin, *Proceedings of the first international symposium on nanotechnology in construction*, 23 (Paisley: Scotland: 2003).
11. I. Campillo, J.S. Dolado, A. Porro, *Royal Soc. Chem.* 215 (2004).
12. P.M. Ajayan, O.Z. Zhou, *Applications of Carbon Nanotubes BT - Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, 391 (Eds by M.S. Dresselhaus, G. Dresselhaus, P. Avouris) (Springer Berlin Heidelberg: Berlin, Heidelberg: 2001).
13. G.D. Zhan, J.D. Kuntz, J. Wan, A.K. Mukherjee, *Nat. Mater.* **2**, 38 (2003).
14. J.K.W. Sandler, S. Pegel, M. Cadek, F. Gojny, M. van Es, J. Lohmar, W.J. Blau, K. Schulte, A.H. Windle, M.S.P. Shaffer, *Polymer (Guildf).* **45**, 2001 (2004).
15. P.-C. AÏtcin, *High-performance concrete* (Taylor & Francis: London: 2007).
16. A. Brandt, *Cement-Based Composites: Materials, Mechanical Properties and Performance, 2nd ed.* (Routledge: Abingdon, UK: 2009).
17. D.D. Chung, *Composite Materials. Science and Applications, 2nd ed.* (Springer: London, UK: 2010).
18. A. Yilmaz, S.S. P, A. Bruce, *J. Eng. Mech.* **127**, 311 (2001).
19. J.N. Coleman, M. Cadek, R. Blake, V. Nicolosi, K.P. Ryan, C. Belton, A. Fonseca, J.B. Nagy, Y.K. Gun'ko, W.J. Blau, *Adv. Funct. Mater.* **14**, 791 (2004).
20. J.F. Wang, L.W. Zhang, K.M. Liew, *Comput. Meth. Appl. Mech. Eng.* **309**, 411 (2016).
21. M. Szelag, *Nanomaterials* **7**, 267 (2017).
22. B. Zou, S.J. Chen, A.H. Korayem, F. Collins, C.M. Wang, W.H. Duan, *Carbon* **85**, 212 (2015).
23. S. Xu, J. Liu, Q. Li, *Constr. Build. Mater.* **76**, 16 (2015).
24. O. Mendoza-Reales, G. Sierra-Gallego, J. Tobón, *DYNA* **83**, 136 (2016).
25. N.C. Collier, *Ceramics-Silikáty* **60**, 338 (2016).
26. S.M.A. El-Gamal, F.S. Hashem, M.S. Amin, *Constr. Build. Mater.* **146**, 531 (2017).

Термодинамічне дослідження портландцементу, що містить багатостінні вуглецеві нанотрубки

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Мета даної роботи полягала в термодинамічному дослідженні властивостей потрландцементу, що містить багатошарові вуглецеві нанотрубки. Вимірювання коефіцієнта теплового розширення двох чистих зразків і його нанокомпозиту мають однакову форму. Дилатометричні криві містять однакову кількість аномалій. Їх інтенсивність у різних зразків відрізняється. Калориметричне дослідження показує подібний характер між кривими цифрового сигнального контролера (DSC) двох зразків, матриці та її нанокомпозиту. Термогравіметрія двох матеріалів показує наявність кількох аномалій, ймовірно, пов'язаних із явищем дегідратації. Впровадження багатошарових вуглецевих нанотрубок в цемент зробило нанокомпозит стабільним у широкому діапазоні температур порівняно з цементною матрицею.

Ключові слова: Дилатометрія, Анізотропія, Нанотрубки, Калориметрія, Термогравіметрія, Цемент.