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The Effect of Halloysite Nanotubes Prepared from Iraqi Kaolin Clay in Improving Rubber Properties

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ABSTRACT

Nanotube halloysite prepared from Iraqi kaolin clay and kaolinite was used as a filler in the manufacture of styrene-butadiene rubber (SBR) to improve its properties. Halloysite and kaolinite ratios added to the SBR components ranged between 20 - 100 Phr. The physio-mechanical tests showed that SBR matrixes with the nano-halloysite filler were more effective than with the kaolinite clay alone as a filler. The increase in tensile strength and elongation of SBR using nano-halloysite filler was 89% and 91% compared to that using kaolinite alone which gave 83% and 87%. Results of the scanning electron microscope (SEM) of the nano-halloysite showed a regular distribution within the SBR, while it showed agglomerations and an irregular distribution of kaolinite within the SBR. These properties revealed weakness in the interfacial interaction between kaolinite and SBR. Thermogravimetric analysis (TGA) of the SBR sample filled with nano-halloysite of 40 Phr showed higher thermal stability than the SBR sample filled with 40 Phr kaolinite.

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تأثير الهالوسايت النانوي المحضر من اطيان الكاؤولين العراقية في تحسين خواص المطاط

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الملخص

استخدم الهالوسايت النانوي الانبوبي المحضر من اطيان الكاؤولين العراقي فضلا عن الكاؤولينايت كمادة مالئة في صناعة مركبات المطاط من نوع ستيرين – بوتادين SBR Styrene–butadiene rubber بهدف تحسين خواصه . وقد تراوحت نسبة الهالوسايت والكاؤولينايت المضاف الى مكونات المطاط بين 20- phr 100). اظهر (الاختبار الفيزيو-ميكانيكي (Physio-mechanical Test) لمركبات المطاط ان الهالوسايت النانوي كان اكثر فعالية من اطيان الكاؤولينايت وحده المستخدم كمادة مالئة، فقد احدث زيادة في مقاومة الشد والاستطالة بمقدار (91% و 89%) للهالوسايت النانوي مقارنة مع الكاؤولينايت (87% و 83 %). وقد أظهرت نتائج فحص المجهر الالكتروني الماسح SEM ان الهالوسايت النانوي اظهر توزيعا منتظما مع مطاط ستيرين – بوتادين SBRفي حين اظهر وجود تكتلات في مركبات الكاؤولينايت وانتشار غير منتظم وغير متجانس وهذا يدل على ضعف التداخل البيني ما بين الكاؤولينايت و مطاط ستيرين – بوتادين (SBR). واظهر التحليل الحراري الوزني TGA لعينة SBR المحشوة 40 Phrمن الهالوسايت اللنانوي ثباتًا حراريًا أعلى من عينة SBR المحشوة بـ 40 Phr من الكاؤولينايت.

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Introduction

Halloysite is a silicate clay mineral that belongs to the Phyllosilicate group, as a dioctahedral type (1:1) (Berthier, 1826; Joussein et al., 2005; Bauluz, 2015), where each layer is composed of a tetrahedral plate (Si-O). The Al-OH octahedral sheet is similar to that of kaolinite, while the halloysite has an overall higher water content and anisotropy in the interlayer voids. The presence of water between the layers at the time of formation reduces the electrostatic interaction with the neighboring layers and facilitates the bending of the layers to accommodate the incompatibility in the dimensions of the tetrahedral and the octahedral plates. As a result, halloysite usually crystallizes in a tubular shape with an inner sheet of Al-OH and an outer sheet of Si-O. In the case of kaolinite, and due to the lack of water between the layers, the mismatch between the octahedral plate and the tetrahedral plate is reduced by rotating the tetrahedral silica and the deformation in the tetrahedral plate gives a flat shape similar to the plate, (Pasbakhsh et al., 2013). Naturally occurring halloysite appears in a variety of shapes, either lamellar, spherical, or tubular, the tubular shape of halloysite is dominant (Yuan et al., 2015; Robertson and Eggleton, 1991; Singh and Mackinnon, 1996). The chemical formula for halloysite is AL2Si2O5 (OH) 4. nH2O when n = 0 for halloysite of type 7A° and n = 2 for halloysite of type 10A° (Joussein et al., 2005; Yuan et al., 2015; Ahmad and Kumar, 2020). In this paper, the terms halloysite (10A°) for the wet mineral, and halloysite (7A°) for the dry form are used as recommended by the AIPEA Nomenclature Committee (Joussein et al., 2005; Bauluz, 2015).

Halloysite possesses a set of unique and multifunctional properties that attracted the interest of many researchers, in addition to being non-toxic and biologically compatible with life and the environment. These characteristics include its small diameter (40-70 nm outer diameter and 10-40 nm inner diameter), high flexibility (140 GPa), and large surface area. Mean surface area according to BET (22.1–81.6 m2/g) (Liu et al., 2007; Guimaraes et al., 2010; Lu et al., 2011; Lecouvet et al., 2013) in addition to a relatively high cation exchange capacity of approximately (8-60) cmol/kg compared to the kaolinite, which is characterized by its weak ability to exchange cations (1-15) cmol/kg, which is due to the possession of the mineral halloysite of water molecules in its composition (Singh and Gilkes, 1992; Bobos et al., 2001; Churchman et al., 2016). The low density of halloysite also contributes to the preparation of lightweight polymeric materials (Pasbakhsh et al., 2013; Liu et al., 2014; Roy et al., 2019), as well as filler which can be used in the manufacture of styrene-butadiene rubber (SBR), which is the aim of this study, in which halloysite was used. Styrene-butadiene rubber is one of the most widely used polymers in the rubber industry, and the manufacturing processes of polymeric materials depend largely on the fillers dispersed in the polymer filler material. To extend the usefulness of polymeric materials, especially reinforcing fillers must be added (Ismail et al., 2014; Gaca et al., 2020, Zirbstein et al., 2018).

Halloysite is added as a filler to polymers and rubbers, as it increases the mechanical properties and improved thermal stability. It is an effective and low-cost material in the manufacture of polymers, electronic components, drug preservatives, cosmetics, and in the manufacture of nanotubes (Kamble et al., 2012).

The current research includes the use of the prepared halloysite as a filler for styrene-butadiene rubber, it is the first comprehensive applied study in this field, while many previous studies were conducted on the natural halloysite. (Kausar, 2018) published a paper on polymer composites with a filler of nanoparticles of halloysite, and great efforts have been made by the author to explore the effect of nanotube halloysite as a filler in different types of polymers, such as polyethylene (PE), polyvinyl chloride (PVC), and polypropylene (PP). and polystyrene (PS) (Roy et al., 2019). In addition to the study of (Anyszka et al., 2015) on the use of nanoparticles of halloysite as a filler in the rubber industry. The research showed the possibility of obtaining high tensile strength for rubber due to the good surface area that these nanoparticles possess. (Ranasinghe et al., 2001) explained the effect of the surface chemistry of kaolinite as a filler on rubber compounds, where the physicomechanical tests of the rubber compounds showed that the surface properties of kaolinite are highly effective when used as a filler in the rubber matrix. The current study aims to use the nanotubular halloysite prepared in the laboratory from Iraqi kaolinite, as a filler in the matrix of SBR to improve their properties in terms of tensile strength, elongation, elasticity, and thermal stability.

Materials and Methods

The nanotubular halloysite mineral prepared in the laboratory by intercalation reaction of the kaolinite mineral with high-purity potassium acetate (Aladwane et al, 2023) and Iraqi kaolinite were applied as fillers in SBR compounding. Iraqi kaolin (which contains 85% kaolinite) is located in the Western Desert in Iraq, specifically in the Dwekhla region, and belongs to the Ga'ara formation (Permo Carboniferous). The raw kaolin was distinguished chemically by containing SiO2 (55.09%) and Al2O3 (32.75%), and other oxides.

SBR paste was prepared by adding the ratios of the components revealed in (tables 1, 2, and 3). All components were mixed in an open two-roll mill. SBR was prepared and tested in the Laboratory of Flexible Materials at the University of Babylon / College of Materials Engineering / Department of Polymers and Petrochemical Industries.

Table 1: Components of SBR paste with the proportions of halloysite added.

Sample name	(SBR) Phr	ZincOxide Phr	Stearic acid Phr	Oil Phr	TMTD Phr	Antioxidant (TMQ) Phr	Sulfur Phr	Halloysite Phr
Pure	100	3.5	1.25	1.75	1.75	1.75	1.75	0.0
H20	100	3.5	1.25	1.75	1.75	1.75	1.75	20
H40	100	3.5	1.25	1.75	1.75	1.75	1.75	40
H60	100	3.5	1.25	1.75	1.75	1.75	1.75	60
H80	100	3.5	1.25	1.75	1.75	1.75	1.75	80
H100	100	3.5	1.25	1.75	1.75	1.75	1.75	100

Table 2: Components of styrene-butadiene rubber (SBR) paste with the proportions of kaolinite added.

Sample name	(SBR) Phr	Zinc Oxide Phr	Stearic acid Phr	Oil Phr	TMTD Phr	Antioxidant (TMQ) Phr	Sulfur Phr	Kaolinite Phr
Pure	100	3.5	1.25	1.75	1.75	1.75	1.75	0.0
K20	100	3.5	1.25	1.75	1.75	1.75	1.75	20
K40	100	3.5	1.25	1.75	1.75	1.75	1.75	40
K60	100	3.5	1.25	1.75	1.75	1.75	1.75	60
K80	100	3.5	1.25	1.75	1.75	1.75	1.75	80
K100	100	3.5	1.25	1.75	1.75	1.75	1.75	100

Table 3: Stages of SBR matrix formation.

No.	mixing steps	Time in Minute
1	Passing the rubber between the two rolls, while reducing the distance, several times, at a temperature not exceeding 20-30 C°	5
2	Addition of zinc oxide followed by mixing to homogenize the materials	5
3	Adding citric acid followed by mixing to homogenize the materials	5
4	Add castor oil to several stages	10
5	Addition of antioxidant TMQ followed by mixing to homogenize the materials	5
6	Addition of the accelerator TMTD followed by mixing to homogenize the materials	5
7	Adding sulfur followed by mixing to homogenize the materials	5
8	Adding the filler Halloysite or kaolinite, while continuing the homogenization process for ten minutes, to obtain a homogeneous matrix.	10

The prepared SBR samples, which contain fillers of nano-halloysite and kaolinite, were subjected to tests shown in Table 4.

Table 4: Tests and devices used

No.	Test	Device	Origin
1	Tensile test ASTM D412-98	Universal Testing Machine Max. Load 5 KN	China
2	thermogravimetric analysis (TGA)	Mettler Toledo	Swiss
3	Field Emission Scanning Electron Microscopy	(Inspect f 50)	Germany
4	surface area and pore size Brunauere-Emmett-Teller (BET) method	MicroActive-TriStar II Plus 2.03	Italy

Result and Discussion

The following are the results of mechanical, thermal, and morphological studies of SBR with its different nanocomponents after adding halloysite and kaolinite as fillers.

1. Tensile Tests

The results of the tensile strength tests Fig. (1) and Table (5) for all samples of SBR containing nano-halloysite as a filler showed higher tensile and elongation forces than their counterparts of samples that contain Iraqi kaolinite filler, Fig. (2) and Table (6). The curves shown in Fig. (3) indicate that the improvement in the tensile strength properties resulted from the interaction between the SBR and the filler via the active functional sites found in the halloysite. To determine the optimal ratio of filler in the matrix of SBR, several experiments were conducted for matrixes containing the same components and in the same proportions, except for changing the proportion of the filler. Samples of SBR containing halloysite were prepared in varying proportions, as shown in table1, as well as similar samples under the same condition of preparation and proportions of kaolinite were prepared, as shown in table2.

A tensile test was conducted on all samples of SBR. The results through stress and tension curves as in Figure (3) and Tables (5 and 6) indicated that there is an improvement in the tensile strength properties of SBR. When increasing the proportions of halloysite added (20, 40, 60) Phr, the tensile strength will increase (115, 220, 375) MPa respectively, but it declined at 80 Phr under 263 MPa, then increased at 100 Phr (450) Mpa as is Shown in Figure 1. It was also observed that the same behavior in the properties of SBR occurred when kaolinite was added at the same proportions (20, 40, 60) Phr and the tensile strength will increase (40, 140, 125) Mpa respectively, but a decline occurs at 80 Phr (80) Mpa, then a greater improvement occurs at 100phr (300) Mpa, which represents the optimum proportion of filler in SBR.

A clear difference in the improvement achieved, as the ratio of increase in tensile strength, was 91% for halloysite compared to 87 % for kaolinite, as shown in figure1. It may be because the nanotubular halloysite has a nano-granular size and a tubular shape. This increase was expected due to the very fine particles which are an active agent as well as the nano size of halloysite which leads to an increase in the contact area and the interaction between halloysite and SBR, (Jia et al., 2014; Roy et al., 2019; Ahmad and Kumar, 2020).

Kaolinite has coarse grain size and lamellar shape which results in lower tensile strength compared to halloysite, since kaolinite particles lead to poor dispersion during the mixing process. Results of surface area measurement of nano-halloysite showed a large value compared to kaolinite, it was 68.7 m2/g for nano halloysite in comparison to 20.1 m2/g for kaolinite. Therefore, nano-halloysite has a clear superiority in strengthening and improvement of SBR, due to its morphology, relatively large surface area, and favorable surface activity. On the other hand, the pore diameter (average pore size) of kaolin was 10.9 nm., while the pore diameter of the prepared nano-halloysite was 8.1 nm. The smaller the pore diameter, the greater the surface area, as pore diameter is a key factor in improving mechanical properties.

Table 5: Mechanical properties of SBR with different halloysite ratios.

Halloysite Phr	Tensile Strength (Mpa)	Elongation at Break (%)	Modulus of elasticity (Gpa)
20	115	1.8	32.6
40	220	3.2	36
60	375	5.3	35.7
80	263	6.6	28.8
100	450	6.5	41.6

Table 6: Mechanical properties of SBR with different kaolinite ratios.

Kaolinite Phr	Tensile Strength (Mpa)	Elongation at Break (%)	Modulus of elasticity (Gpa)
20	40	1.4	20
40	140	2.75	30.7
60	125	2.5	16.3
80	80	1.75	31.2
100	300	4.25	43.5

Clear improvement in the properties of SBR was observed with the addition of halloysite and Iraqi kaolinite compared to pure SBR, whereas halloysite gave better elasticity for SBR (elongation, tensile strength, and flexibility), as shown in figure 1 and 2.

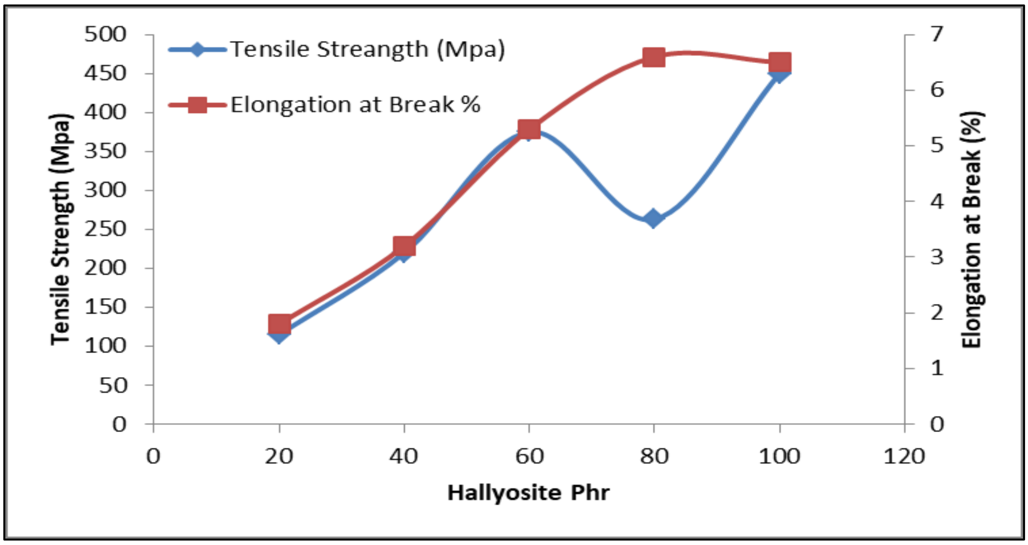

Fig. 1. Tensile strength test of a matrix of SBR with different ratios of halloysite.

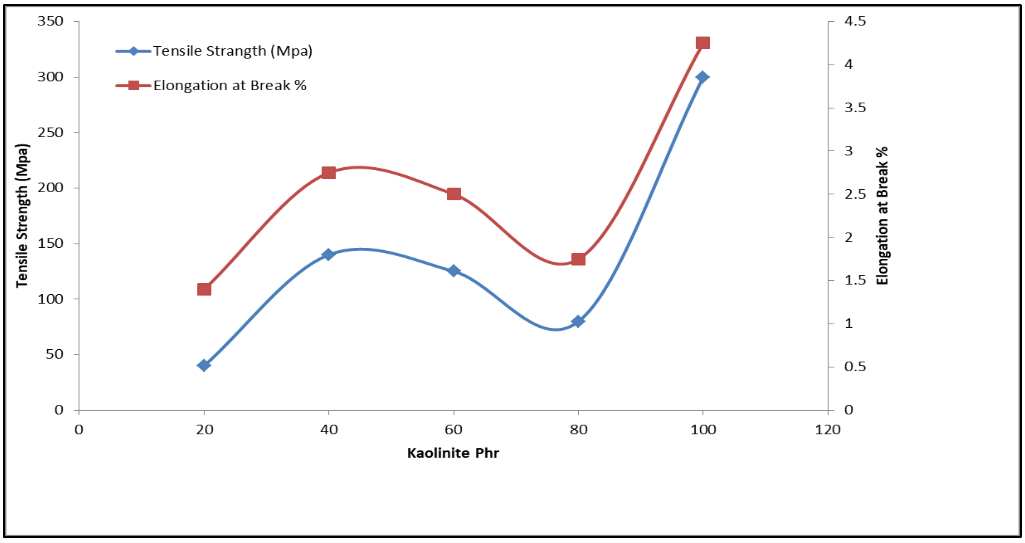

Fig. 2. Tensile strength test of a matrix of SBR with different ratios of kaolinite.

There is an improvement in the SBR elongation with increasing the proportions of halloysite in the SBR matrix of (20, 40, 60, 80, 100) Phr, as in Figure 1. The same behavior in the elongation of SBR also occurred with kaolinite at proportions (20, 40, 60) Phr, then decreased at 80 Phr, and improved at 100 phr (table 5). A clear difference in the improvement of the elongation ratio was observed. It was 89% with halloysite compared to 83% with kaolinite, because of the strong interfacial interaction between nano-halloysite and SBR and the porosity of halloysite, which ultimately leads to great resistance to fracture, where fine particles of halloysite are responsible for stabilizing SBR chains that give high elongation, as shown in figure 1. Results of comparing the use of halloysite and kaolinite as a filler for SBR showed that halloysite was the best at all ratios.

2. Scanning Electron Microscopy (SEM)

SEM analysis was carried out for samples of SBR containing halloysite and samples containing kaolinite as fillers with ratios of 20,40,100 Phr. Morphological characteristics indicated compatibility between halloysite and SBR, due to the uniform distribution of halloysite, especially with the sample of 40 Phr filler, as in Figure 4. (e, f, g). On the other hand, it was evident the presence of agglomerations in the SBR matrix with the kaolinite, as well as the irregular distribution of kaolinite at most proportions with SBR which indicates the weak compatibility between kaolinite and SBR, as in Figure 4 (b, c, d).

The compatibility between the rubber and the filler has a major role in the homogeneous distribution of the filler in the rubber. It is weak with most types of fillers due to the difference in polarity. On the other hand, the main obstacle to improving the properties of rubber by fillers lies in the poor dispersion of the hydrophilic filler in the hydrophobic rubber filler, therefore, the dispersion of organic clays is weak in non-polar rubbers such as SBR (Roy et al., 2019). It was proved that the nano-filler in the polymer is a major factor in improving the mechanical properties as a result of directing the stress on the entire polymer matrix (Rooj et al, 2010).

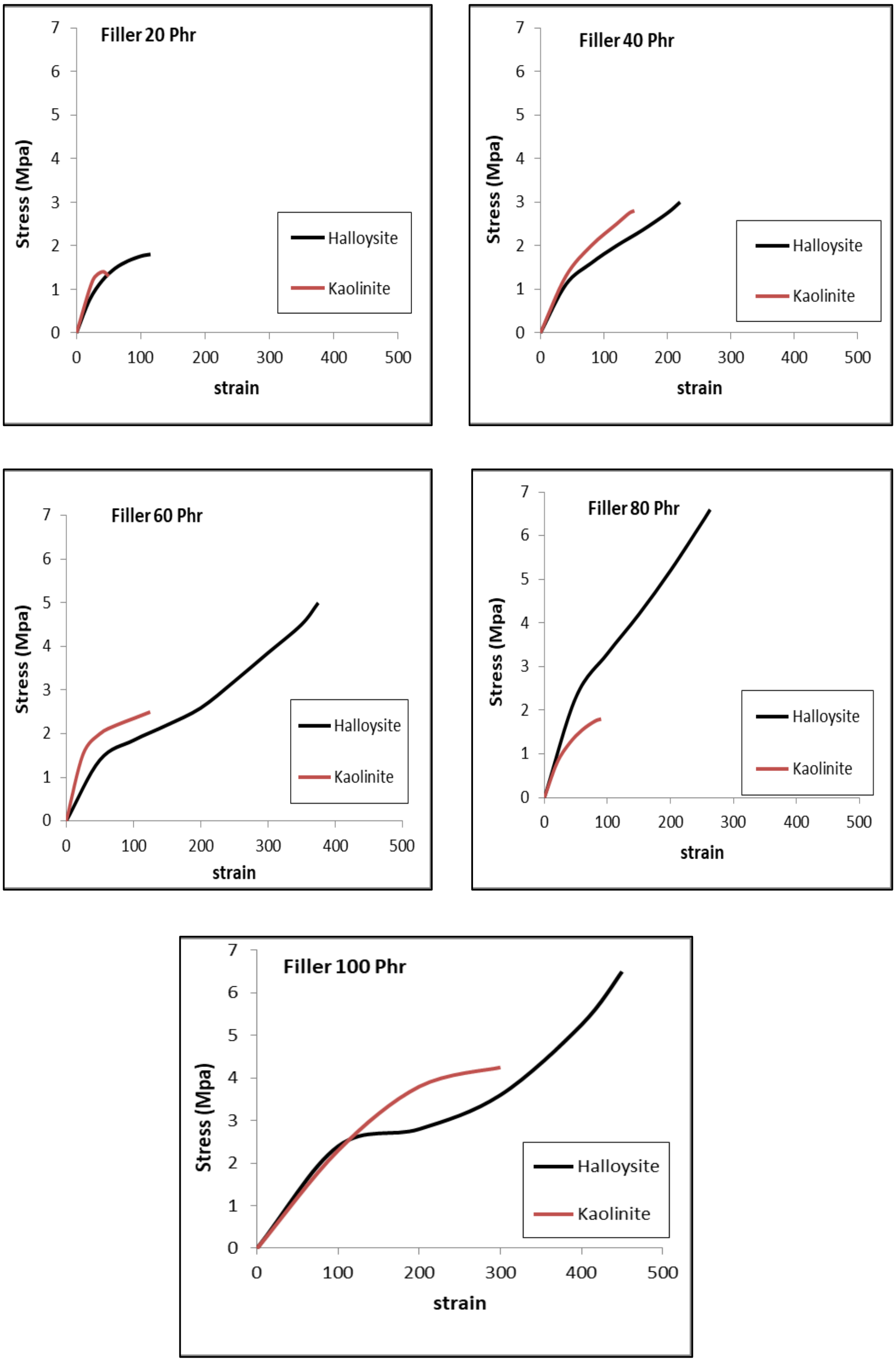

Fig. 3. Curves of tensile strength tests at different ratios of halloysite and kaolinite.

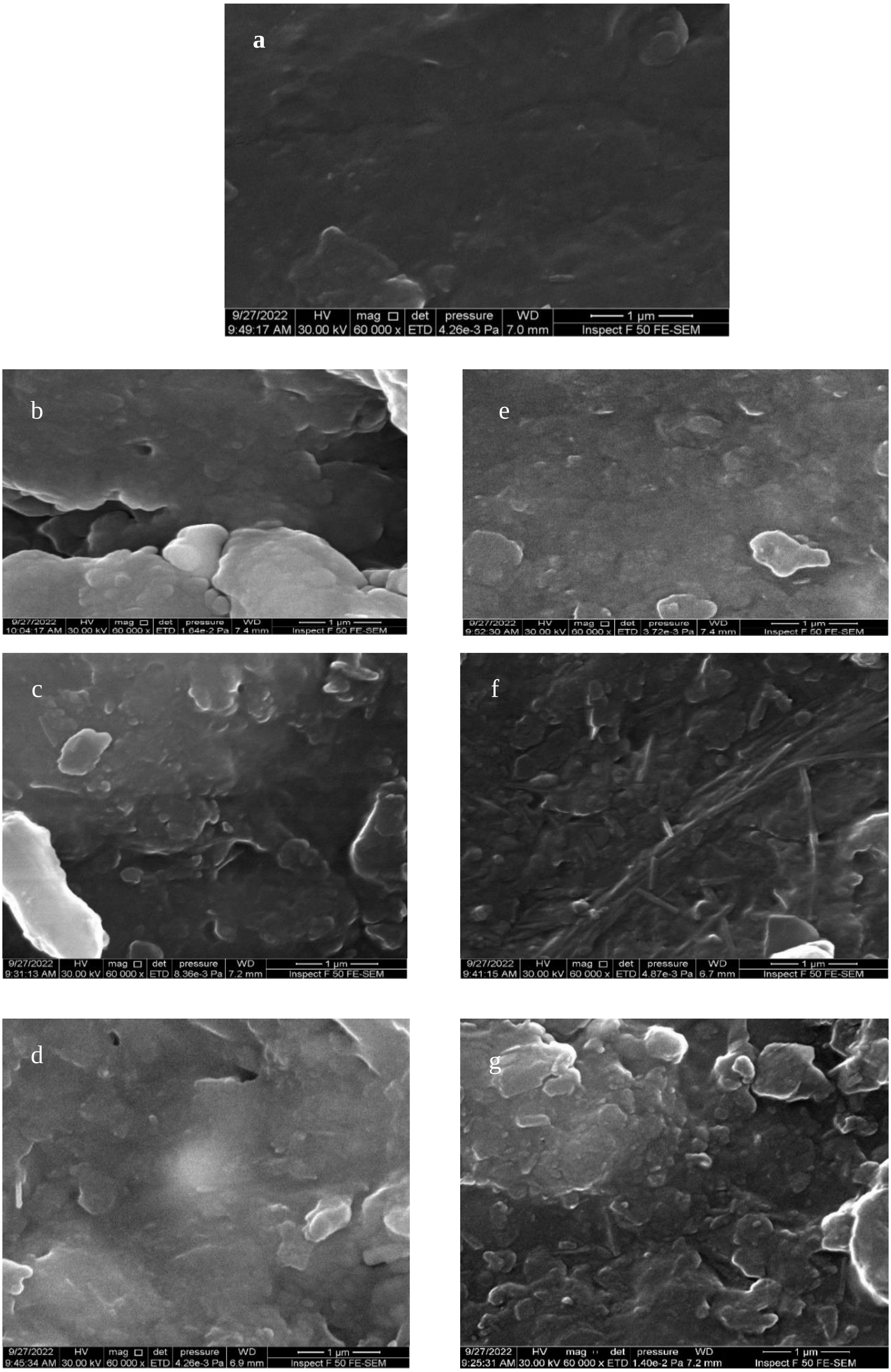

Fig. 4. SEM micrograph (a) of Pure SBR (e, f, g) for the halloysite samples, with the filler ratio of 20, 40, and 100 Phr, respectively, and (b, c, d) of the kaolinite samples with the filler ratio of 20, 40, and 100 Phr, respectively.

3. Thermogravimetric analysis (TGA).

Graph (5) of the thermogravimetric analysis shows the TGA curve of SBR samples containing halloysite and kaolinite as fillers at 20, 40, and 100 Phr. All samples have good thermal stability up to 350 C°, except for the two SBR samples that contain kaolinite at a ratio of 20 and 40 Phr. There is a weight loss of not more than 5%, which is mostly attributed to moisture absorption. After a temperature of 350 C°, a slight weight loss (2-3%) begins, which is attributed to the thermal decomposition of some unstable rubber components (decomposition of unstable chemicals). At the temperature of 400-600 C°, a large and uneven weight loss phase begins as a result of the thermal cracking of the SBR material, and then the thermal cracking of the fillers, and this is consistent with a study by (Ahmad and Kumar, 2020).

SBR samples containing kaolinite of 20 and 100 Phr showed higher thermal stability with less weight loss of 45% and 50%, respectively, followed by an SBR sample of 40 Phr of halloysite with a weight loss of up to 60%. The percentage of loss in weight is up to 70% in the SBR sample containing 40 Phr of kaolinite. Samples containing 20 and 100 Phr halloysite have had weight loss of up to 75%. On the other hand, it was noted that the SBR sample devoid of the filler suffers severe thermal cracking and the weight loss at 600 C° is more than 90%. Results of the thermogravimetric analysis showed an improvement in the thermal stability of SBR samples with the addition of the fillers. A decrease in the thermal stability showed irregular variation, as it is related to the proportions of kaolinite of 20 and 100 Phr compared to 40 Phr of halloysite. This may be attributed to the nature of the structure of the added clays. In some cases, kaolinite showed better thermal stability than halloysite contrary to what was expected.

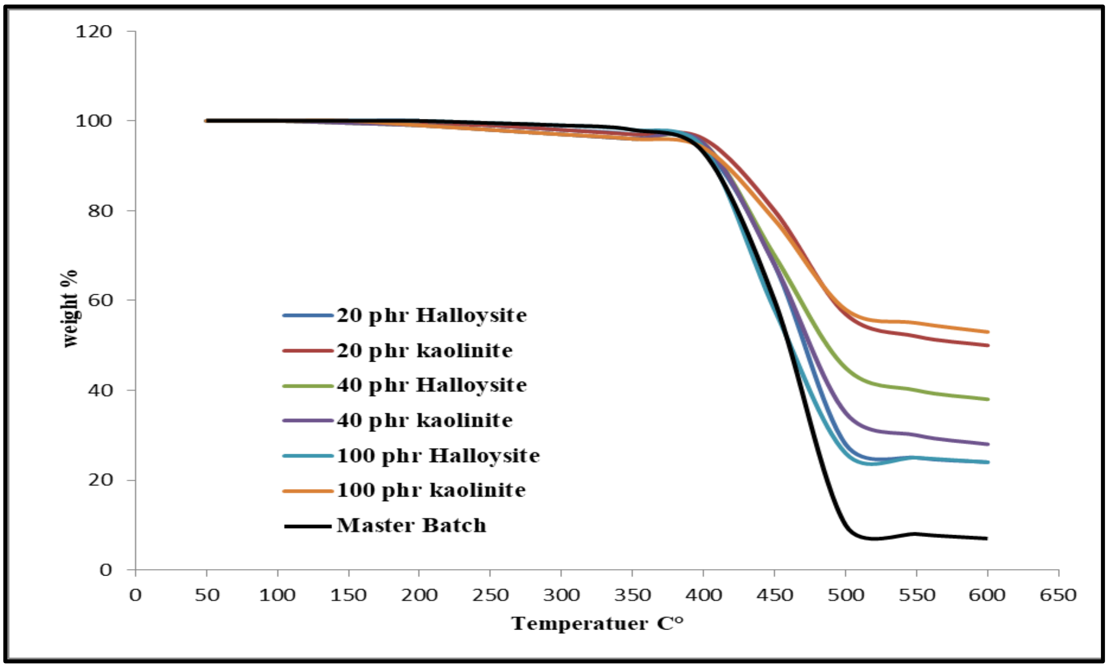

Fig. 5. Thermogravimetric analysis graph of SBR with and without fillers

Conclusion

Nanotube halloysite prepared from Iraqi kaolin clay and kaolinite was used as a filler in the manufacture of styrene-butadiene rubber (SBR) to improve its properties. The results showed that nano-halloysite filler was better than kaolinite for improving the mechanical properties of SBR in terms of tensile strength by 91% and elongation by 89%. This improvement is due to the tubular shape and the monocrystalline structure of the nano-halloysite as well as the interaction between the SBR and the filler material via the active functional sites found in the halloysite. Morphological characteristics through scanning electron microscope indicated a compatibility between halloysite and SBR, due to the uniform distribution of halloysite. On the other hand, it was evident the presence of agglomerations in the SBR matrix with the kaolinite, as well as the irregular distribution of kaolinite at most proportions with SBR which indicates the weak compatibility between kaolinite and SBR. Results of the thermogravimetric analysis showed an improvement in the thermal stability of SBR samples with the addition of the fillers, especially with the nano-halloysite. A decrease in the thermal stability showed irregular variation, as it is related to the proportions of kaolinite, and may be attributed to the nature of the structure of the added clays.

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Reference

Ahamad, A., Kumar P., 2020. Effect of Reinforcing Ability of Halloysite Nanotubes in Styrene-Butadiene Rubber Nanocomposites. Composites Communications, pp. 22 – 100440. DOI: https://doi.org/10.1016/j.coco.2020.100440

Al-adwane, O.E., Al-Mallah, A. Y. and Hussien, A. K., 2023. Transform of Kaolinite in Iraqi Kaolin Clay to Halloysite by Intercalation Reaction. Iraqi Geological Journal 56 (1D), pp. 260-271. DOI: https://doi.org/10.46717/igj.56.1D.19ms-2023-4-28

Anyszka, R., Bielinski, D., Kleczewska, J., Imiela M., 2015. Application of Halloysite Nano-Fillers in Rubber Industry. Elastomers 2015 16th Conference on Elaboration, Characterisation, Recycling and Durability 3-5 November 2015, Tours (France). DOI:10.13140/RG.2.1.2602.6641

Bauluz, B., 2015. Halloysite and Kaolin: Tow Clay Minerals with Geological and Technological Importance, Real Academia de Ciencias. Zaragoza, Vol.70, pp. 1- 33.

Berthier, P., 1826. Analyse de l'halloysite. Annales de Chimie et de Physique, 32, pp. 332−335.

Bobos, I., Duplay, J., Rocha, J. and Gomes, C., 2001. Kaolin to Halloysite-7A° Transformation in the Kaolinite, Deposit of Sao Vicente de Pereira, Portugal. Clays Clay Minerals,49, pp.596–607. DOI:10.1346/CCMN.2001.0490609

Churchman, G. J., Pasbakhsh, P., Lowe, D.J and Theng B.K. G., 2016. Unique but Diverse: some Observations on The Formation, Structure and Morphology of Halloysite. Clay Minerals, 51, pp. 395–416. DOI: 10.1180/claymin.2016.051.3.14

Gaca, M., Vaulot, C., Maciejewska, M., Lipinska, M., 2020. Preparation and Properties of SBR Composites Containing Graphene Nanoplatelets Modified with Pyridinium Derivative. Journal Materails 13(23),5407. DOI: https://doi.org/10.3390/ma13235407

Guimaraes, L., Enyashin, A.N., Seifert, G., Duarte, H.A., 2010. Structural, Electronic, and Mechanical Properties of Single-walled Halloysite Nanotube Models. J. Phys. Chem. C114, pp. 11358–11363. DOI:10.1021/jp100902e

Ismail, H., Ahmad, H.S., 2014. Effect of Halloysite Nanotubes on Curing Behavior, Mechanical and Microstructural Properties of Acrylonitrile-butadiene Rubber Nanocomposites, J. Elastomers Plast. 46, pp. 483–498. DOI:10.1177/0095244312469963

Jia, Z., Guo, B., Jia, D., 2014. Advances in Rubber/Halloysite Nanotubes Nanocomposites, Journal of Nanoscience and Nanotechnology Vol. 14, pp. 1758–1771. DOI:10.1166/jnn.2014.9124

Joussein, E., Pett, S., churchman, J., Theng, B., Righi and Delvaux., 2005. Halloysite Clay Mineral: A Review Clay Mineral 40, pp. 383-426. DOI: 10.1180/0009855054040180

Kamble, R., Ghag, M., Gaikawad, S. and Panda, B.K., 2012. Halloysite Nanotubes and Applications: A Review. Jour. Adv. Sci. Res., 32, pp. 25–29.

Kausar, A., 2018. Review on Polymer/Halloysite Nanotube Nanocomposite. Polym. -Plast. Technol. Eng. 57, pp. 548–564. DOI:10.1080/03602559.2017.1329436

Lecouvet, B., Horion, J., Haese, C.D., Bailly, C., Nysten, B., 2013. Elastic Modulus of Halloysite Nanotubes. Nanotechnology 24, 105704. DOI 10.1088/0957-4484/24/10/105704

Liu, M.X., Guo, B.C., Du, M.L., Cai, X.J., Jia, D.M., 2007. Properties of Halloysite Nanotube–epoxy Resin Hybrids and the Interfacial Reactions in the Systems. Nanotechnology 18, 455703. DOI: 10.1088/0957-4484/18/45/455703

Liu, M., Jia, Z., Jia, D., Zhou, C., 2014. Recent Advance in Research on Halloysite Nanotubes-polymer Nanocomposite. Prog. Polym. Sci. 39, pp. 1498–1525. DOI: https://doi.org/10.1016/j.progpolymsci.2014.04.004

Lu, D., Chen, H., Wu, J., Chan, C.M., 2011. Direct Measurements of the Young's Modulus of a Single Halloysite Nanotube Using a Transmission Electron Microscope with Abending Stage. J. Nanosci. Nanotechnol. 11, pp. 7789–7793. DOI:10.1166/jnn.2011.4720

Pasbakhsh, P., Churchman, G.J., Keeling, J.L., 2013. Characterisation of Properties of Various Halloysites Relevant to their Use as Nanotubes and Microfibre Fillers. Appl. Clay Sci. 74, pp. 47–57. DOI:10.1016/j.clay.2012.06.014

Ranasinghe, A., Gunapaia, O., Gunapala, PY 2001. Effect of the Surface Chemistry of Kaolinite, on the Properties of Filled Rubber Compounds. Moratuwa Engineering Research Conference (MERCon), pp. D37-D44.

Robertson, IDM., Eggleton, RA., 1991. Weathering of Granitic Muscovite to Kaolin and Halloysite and of Plagioclase−derived Kaolin to Halloysite. Clays Clay Miner 39, pp.113-126. DOI: https://doi.org/10.1346/CCMN.1991.0390201

Roy, K., Debnath, S. C., Potiyaraj.P., 2019. A Critical Review on the Utilization of Various Reinforcement Modifiers in Filled Rubber Composites, Journal of Elastomers and Plastics, pp. 1–27. DOI: 10.1177/0095244319835869

Roy, K., Debnathb , S. C., Pongwisuthiruchtea.A., Potiyaraj , P., 2019. Up-To-Date Review on the Development of High-Performance Rubber Composites Based on Halloysite Nanotube; Applied Clay Science 183, 105300. DOI: https://doi.org/10.1016/j.clay.2019.105300

Rooj, S., Das, A., Thakur, V., Mahaling, R.N., Bhowmick, A.K., Heinrich, G., 2010. Preparation and Properties of Natural Nanocomposites Based on Natural Rubber and Naturally Occurring Halloysite Nanotubes. Mater. Des. 31, pp. 2151–2156. DOI: 10.1016/j.matdes.2009.11.009

Singh, B., Gilkes, RJ., 1992. An Electron-optical Investigation of the Alteration of Kaolin to Halloysite. Clays Clay Miner,40, pp. 212−229. DOI: https://doi.org/10.1346/CCMN.1996.0440614

Singh, B. and Mackinnon, I.D.R., 1996. Experimental Transformation of Kaolin to Halloysite. Clays and Clay Minerals, 44, pp.825 834. https://doi.org/10.1346/CCMN.1996.0440614

Yuan, P., Tan, D., Annabi-Bergaya,F., 2015. Properties and Applications of Halloysite Nanotubes: Recent Research Advances and Future Prospects. Appl. ClaySci.112–113, pp.75–93. DOI: http://dx.doi.org/10.1016/j.clay.2015.05.001

Zirbstein, B., Tabaka, W., Frasca, D., Schulze, D., Schartel, B., 2018. Graphene/Hydrogenated Acrylonitrile-Butadiene Rubber Nanocomposites: Dispersion, Curing, Mechanical Reinforcement, Multifunctional Filler. Polym. Test. 66, pp. 268–279.