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REGULAR ARTICLE

Thermal Insulation Properties of Red Mud as a Functional Filler for Polymer Composites

L. Melnyk[1], O. Donii[1], V. Sviderskyy[1], N. Kharchenko[2], T. Hovorun[2,*], R. Milotskyi[3]

[1] *National Technical University of Ukraine "I. Sikorsky Kyiv Polytechnic Institute", 03056 Kyiv, Ukraine*
[2] *Sumy State University, 40007 Sumy, Ukraine*
[3] *Kanazawa University, Kakuma-machi, 920-1192 Kanazawa, Japan*

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The study focuses on addressing the issue of industrial waste utilization by integrating red mud (RM), a by-product of alumina production, and chamotte (Pa2) into polymer composites with an emphasis on their thermal insulation efficiency. RM and Pa2 were chosen as fillers due to their availability and unique properties. RM with thermal conductivity of 0.2651 W/m·K and Pa2 with thermal conductivity of 0.2643 W/m·K were incorporated into a styrene-butadiene copolymer matrix (Latex 2012) to create composites with filler concentrations of 65-90 wt. %. Thermal conductivity measurements performed using the IT-λ-400 analyzer showed that composites with 90 wt. % RM and Pa2 had thermal conductivities of 0.58 and 0.53 W/m·K, respectively. Modeling conducted using Hashin-Shtrikman and Maxwell-Eucken models confirmed the suitability of these approaches for predicting the thermal conductivity of systems with high filler content. The results highlight the potential for reusing RM as an effective filler for polymer composites, contributing to reduced environmental impact and the development of materials with high functional performance.

Keywords: Waste utilization, Polymer composites, Thermal conductivity.

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1. INTRODUCTION

In recent decades, there has been a rapid development of the global economy, where industry plays a key role in strengthening economic indicators and improving living conditions. However, the rapid expansion of industrial sectors without proper planning has led to significant negative consequences for the ecosystem. Industrial waste, due to its high toxicity and inefficient disposal methods, creates serious environmental and economic challenges [1].

Modern approaches focus on reducing the environmental impact of industrial waste through effective management, which includes increasing costs for storage, recycling, and reuse of materials in various sectors. Special attention is given to the use of industrial waste as reinforcing additives in polymer composites, which not only helps recycle waste but also improves the mechanical, thermal, and electrical properties of polymer materials [2].

Red mud (RM), a by-product of alumina production, accumulates in large volumes (0.8-1.5 tons of RM per ton of alumina), forming over 120-150 million tons annually, with total global reserves exceeding 4 billion tons [3]. In 2021, alumina production reached 135 million tons, resulting in approximately 200 million tons of red mud [4].

Due to its high alkalinity and the presence of toxic elements such as Pb, Zn, Cd, and Cr, RM poses significant environmental risks [5]. Conventional methods of red mud disposal, such as landfill storage or dumping into water bodies, cause groundwater contamination, dust formation, and the release of toxic compounds. Tragic events, such as the 2010 tailings dam failure in Hungary, which resulted in human casualties, evacuation of settlements, and widespread water contamination [6], or a similar disaster in China in 2016 [7], highlight the high risks associated with careless RM disposal.

At the same time, recent studies show the great potential of recycling red mud, which not only reduces environmental risks but also contributes to the development of new functional materials. Therefore, strategies for its safe disposal are intensively being developed, particularly in the production of building materials, the chemical industry, and environmental protection.

Recent research highlights the potential of using RM to create functional materials such as flocculants, adsorbents, catalysts, and soil additives [2] is also widely used in building materials, for example, as a cement replacement or additive in concrete [8], as well as in road construction, particularly as a material for roadbed foundations, soil stabilizers, and embankments [9], and in semi-flexible coatings for high-traffic areas [10].

Polymer composites are also a promising field for integrating RM, as they not only allow for the recycling of waste but also improve the properties of materials. For example, studies on RM in polypropylene,

* Correspondence e-mail: hovorun@pmtkm.sumdu.edu.ua

polyethylene, and epoxy matrices confirm its effectiveness in creating new functional materials [11].

The goal of this work is to explore the potential of using red mud as a functional filler for polymer composites with thermal insulation properties. This approach not only enables the recycling of hazardous waste but also creates materials with unique characteristics for industrial applications.

2. MATERIALS AND METHODS

In this study, the polymer matrix used was the aqueous dispersion Latex 2012, which is a copolymer of styrene and butadiene. The dispersion is characterized by a dry matter content of 51 %, an average particle size of 140 nm, and a viscosity of 200 mPa·s. Red mud (RM) obtained from PJSC "Zaporizhzhia Aluminum Plant" (Ukraine) and chamotte (Pa2) produced by mixing RM with 20 wt. % clay, followed by firing at a temperature up to 900 °C, were used as fillers.

According to the chemical composition analysis [12], RM and chamotte are distinguished by high content of Fe_2O_3 and TiO_2. Significant concentrations of alkaline earth and alkali metal oxides ($RO + R_2O$) were also detected: 8.62 wt. % for RM and 8.08 wt. % for Pa2.

To prepare the composites, a binary system was used, consisting of a polymer binder and a filler. To increase the surface activity of the particles and improve their interaction with the polymer matrix, the fillers were subjected to mechanical activation in a planetary ball mill for 20 minutes.

After activation, the material was sieved to ensure particle uniformity with a size of less than 100 μm. This facilitated the even distribution of the filler in the composite. The further preparation included the following steps:

– the homogenized mixture was distributed into cylindrical molds with a diameter of 15 mm and left to cure at room temperature for 48 hours.

– the curing of the samples was performed by gradual heating to 80 °C and holding at this temperature for 1 hour, ensuring the formation of a stable structure.

– the cooled blanks were pressed under cold pressure of 5-10 MPa to achieve optimal density and mechanical integrity.

The results of previous studies (Table 1) showed that red mud and chamotte have specific physicochemical properties that determine their behavior as fillers in polymer composites. The high concentration of metal oxides, varying levels of porosity, and morphological features allow us to predict their contribution to changes in the thermal and mechanical properties of the composites.

Table 1 – Values of the physical characteristics of metals used in the simulation

Filler	Specific Surface Area, BET, m²/g	Wetting Angle, °	Surface Energy, mJ/m²	Thermal Conductivity, W/m·K	Pycnometric Density, g/cm³
RM	19.63	74	45.02	0.265	2.64
Pa2	17.69	75	40.07	0.264	2.39

The difference in the properties of the studied fillers significantly affects the thermal behavior of the composites created based on them. To assess the impact of these fillers and their structural characteristics on thermal conductivity, polymer composites with varying filler content were fabricated.

Thermal conductivity measurements were conducted using the IT-λ-400 analyzer, which operates based on the principle of dynamic calorimetry and provides research results in the temperature range from 173 to 373 K. The working principle is described in the study [13].

The conducted thermal conductivity studies (Fig. 1) revealed the relationship between the type of filler, its concentration, and the thermal properties of the composites.

3. RESULTS AND DISCUSSION

The conducted thermal conductivity studies (Fig. 1) revealed the relationship between the type of filler, its concentration, and the thermal properties of the composites.

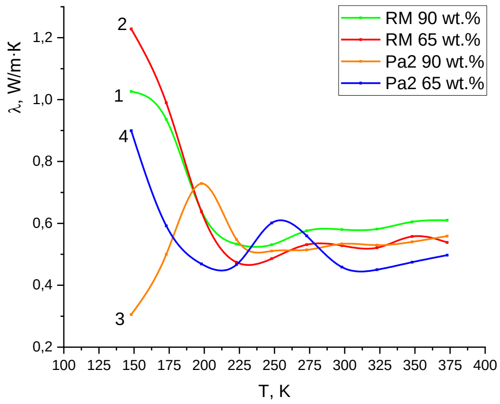

Fig. 1 – Dependence of thermal conductivity on temperature for systems based on Latex 2012 with different fillers: 1 – RM 90 %, 2 – RM 65 %, 3 – Pa2 90 %, 4 – Pa2 65 %

For the RM-based systems at a concentration of 90 wt.% (curve 1), a gradual increase in thermal conductivity is observed at low temperatures (100-200 K), which stabilizes in the range of 200-325 K at approximately 0.8 W/m·K. This indicates significant thermal activity of the material at low temperatures, which may be related to internal structural changes in the filler.

The RM-based systems at a concentration of 65 wt. % (curve 2) demonstrate the highest thermal conductivity among all studied systems, reaching 1.2 W/m·K at a temperature of around 150 K. However, as the temperature increases, thermal conductivity decreases sharply, indicating lower stability of thermal characteristics in this temperature range.

The Pa2-based composites at a concentration of 90 wt. % (curve 3) exhibit stable thermal conductivity behavior with a minimum value (~ 0.4 W/m·K) in the 150-200 K range, followed by a gradual increase to 0.6 W/m·K at 300 K. This behavior indicates the formation of a denser material structure, contributing to better thermal stability.

The Pa2-based systems at a concentration of 65 wt. % (curve 4) show the most stable thermal conductivity across the entire temperature range. The λ values remain between 0.4-0.5 W/m·K, emphasizing the uniformity of the composite's thermal characteristics and its suitability for use in stable thermal conditions.

Overall, the results showed that RM-based composites have higher thermal conductivity compared to Pa2, especially at low temperatures, making them less effective for thermal insulation applications. In contrast, Pa2-based composites exhibit better thermal stability and lower thermal conductivity, making them more suitable for use in thermal insulation materials. The impact of filler concentration is more pronounced for RM, while for Pa2, the changes in thermal conductivity are less significant, indicating a denser material structure and more stable properties.

A comparative analysis of the effect of filler concentration on thermal conductivity (Fig. 2) at different temperatures (298 and 373 K) indicates that the overall trend shows that thermal conductivity increases with the increase in filler concentration.

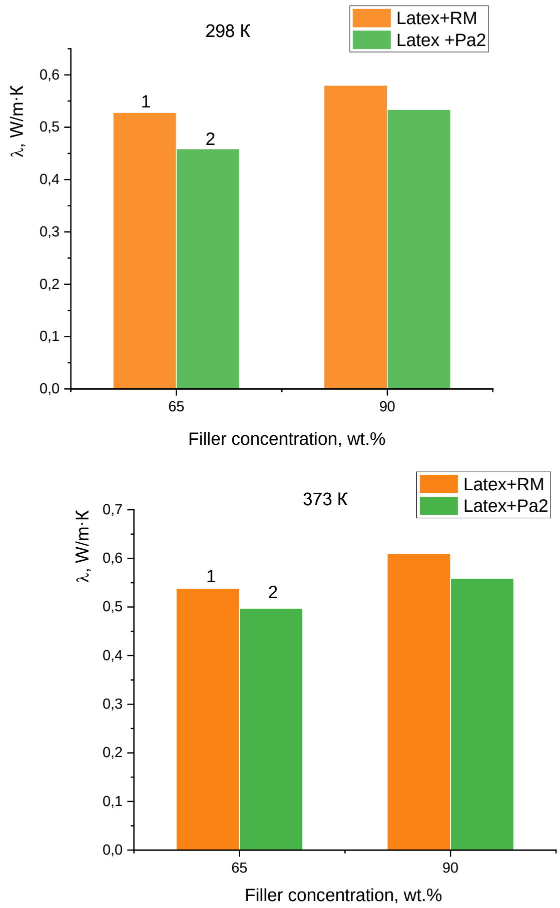

Fig. 2 – Dependence of thermal conductivity on concentration (at different temperatures) for systems based on Latex 2012 with different fillers: 1 – RM, 2 – Pa2

The obtained results (Fig. 2) show that the thermal conductivity of RM-based composites is higher compared to Pa2 across all studied concentrations and temperatures. This is due to the structural characteristics of RM, which promote more intense heat transfer. However, Pa2 demonstrates lower thermal conductivity, making it more suitable for thermal insulation applications. The increase in filler concentration has a more pronounced effect for RM, whereas for Pa2-based composites, the changes in thermal conductivity are less significant, indicating more stable thermal insulation properties of this material.

To gain a deeper understanding of the heat transfer mechanisms and assess the influence of the structural features of the composites on their thermal conductivity, a comparison of experimental data with the results of calculations using the Hashin-Shtrikman model [14] was conducted.

The ***Hashin-Shtrikman*** model was chosen for its universality and ability to accurately evaluate the effective thermal conductivity of heterogeneous materials consisting of a matrix and filler. This model sets the theoretical upper and lower bounds of thermal conductivity depending on the properties of the components and their volume fractions. The formula for the upper bound of the Hashin-Shtrikman model is as follows (Equation 1) [11]:

$$\lambda_{HS,upper} = \lambda_m + \varphi \cdot \frac{\lambda_f - \lambda_m}{(1-\varphi)\cdot \frac{\lambda_f}{\lambda_m} + 1}, \quad (1)$$

where $\lambda_{HS,upper}$ – upper bound of the composite's thermal conductivity, λ_m – thermal conductivity of the matrix, λ_f – thermal conductivity of the filler, φ – volume fraction of the filler.

An important parameter that influences thermal conductivity is the porosity of the composite material. Since the proposed model does not take this into account, the possibility of using other models was considered. For calculating the thermal conductivity of a porous material, the following models are commonly used:

Maxwell-Eucken model is used to estimate the effective thermal conductivity of composites, considering porosity [15]. It takes (Equation 2) into account the contribution of the solid phase and pores, treating them as separate components, assuming the pores are uniformly distributed throughout the material and have minimal impact on phase interaction:

$$\lambda_{eff} = \lambda_s \cdot \frac{1-2\varphi}{1+\varphi}, \quad (2)$$

where λ_{eff} – effective thermal conductivity of the composite, λ_s – thermal conductivity of the solid phase (e.g., filler), φ – volume fraction of pores (total porosity).

Lichteneker-Rother model (Equation 3) (logarithmic mixture of components) [16]:

$$ln\left(\lambda_{eff}\right) = (1-\varphi)\cdot ln(\lambda_s) + \varphi \cdot ln\left(\lambda_p\right), \quad (3)$$

where λ_p – thermal conductivity of pores (for air 0.025 W/m·K).

Dependence for open and closed pores [17]. Effect of open porosity (Equation 4):

$$\lambda_{eff} = \lambda_s \cdot \left(1-\varphi_{open}\right). \quad (4)$$

Closed porosity reduces thermal conductivity non-linearly, depending on the distribution and nature of the pores.

In the analysis, two of the most commonly used models were applied to model the thermal conductivity of the developed composites: the Maxwell-Eucken model and the Hashin-Shtrikman model. The initial data for modeling and the results of the calculations are presented in Table 2.

Experimental studies have shown that the thermal conductivity of Latex 2012-based composites with red sludge (RM) and chamotte (Pa2) fillers depends on the filler concentration, structure, and porosity level. The experimental thermal conductivity values for systems with 90 mass. % RM and Pa2 were 0.580 W/m·K and 0.530 W/m·K, respectively, which agrees with previous studies [7, 18].

Table 2 – Experimental initial data and modeling results

PCM Composition	Filler Concentration, C, %	Open Porosity, %	Closed Porosity, %	Total Porosity, %	Thermal Conductivity at 298 K, W/m·K				
					Experimental	Maxwell-Eucken	Hashin-Shtrikman	Lichtenaker-Roter	Dependence for Open and Closed
Latex 2012 + RM	45.2	9.07	1.39	10.46	0.533	0.190	0.159	0.207	0.241
	57.3	15.23	13.94	29.17	0.566	0.086	0.171	0.133	0.225
	69.2	18.38	22.46	40.84	0,570	0.035	0.187	0.101	0.216
	75.3	21.37	26.19	47.56	0.580	0.009	0.198	0.086	0.209
Latex 2012 + Pa 2	47.0	19.49	3.52	23.01	0.460	0.116	0.160	0.154	0.213
	59.0	23.08	5.11	28.19	0.490	0.204	0.173	0.218	0.203
	70.8	31.25	4.53	35.78	0.520	0.055	0.187	0.114	0.182
	76.7	35.26	4.97	40.23	0.530	0037	0.200	0.102	0.171

Comparison with other works confirms that the high thermal conductivity of RM is related to the balanced ratio of open and closed porosity, which promotes efficient heat transfer. Similar effects were observed in the studies of [11] for composites with a high concentration of inorganic fillers, where increasing density reduced thermal resistance.

To compare experimental results with theoretical models, the Maxwell-Eucken and Hashin-Shtrikman models were used. The Maxwell-Eucken model showed significant underestimation of thermal conductivity, especially at high filler concentrations. For example, for the Latex 2012 + RM system (75.3 vol. %), the calculated thermal conductivity by this model was 0.009 W/m·K compared to the experimental value of 0.580 W/m·K. This corresponds to the findings in the study by [16], where this model did not account for phase interactions.

The Hashin-Shtrikman model showed much better agreement with experimental data. For the same conditions, the calculated value using this model was 0.198 W/m·K, which is closer to the experimental result. A similar pattern was observed for the Latex 2012 + Pa2 system, where the calculated value using this model was 0.200 W/m·K compared to the experimental value of 0.530 W/m·K. Similar conclusions were made in the study by [11], where this model was successfully applied to describe the thermal conductivity of composites with high filler content.

The Lichtenaker-Roter model showed average accuracy. For the Latex 2012 + RM system, the thermal conductivity using this model was 0.086 W/m·K for composites with RM at 75.3 vol. %. A similar situation was observed for the Pa2 system, where the thermal conductivity under the same conditions was 0.102 W/m·K. This model better accounts for the effect of porosity, but the logarithmic nature of its formula limits its accuracy for materials with a high filler concentration.

The model for open and closed pores provided results that best agreed with experimental data for systems with low filler concentration. For example, for the Latex 2012 + RM system at a concentration of 45.2 vol. %, the thermal conductivity calculated by this model was 0.241 W/m·K, which is closer to the experimental value of 0.533 W/m·K. For the Latex 2012 + Pa2 system at the same concentration, the thermal conductivity was 0.213 W/m·K compared to the experimentally determined 0.460 W/m·K. However, this model also underestimates thermal conductivity for systems with high filler concentration, as it only considers open porosity, ignoring the contribution of closed porosity, which significantly affects heat transfer in the material.

A comparative analysis of the porosity of the fillers showed that the total porosity of composites at 65 mass. % fillers is higher for RM (47.56 %) compared to Pa2 (40.23 %), but RM has a higher proportion of closed porosity (26.19 % vs. 4.97 % for Pa2). This explains the higher thermal conductivity of RM, as closed porosity contributes to reduced thermal resistance. Similar patterns were described in the study by [17], where closed porosity improved heat transfer efficiency.

In the Pa2 systems, more developed open porosity (35.26 %) creates a thermal barrier and reduces thermal conductivity. However, such a structure may be useful for materials where reduced thermal conductivity is important, such as for thermal insulation applications [19].

The results of this study demonstrate that Latex 2012-based composites with RM and Pa2 can compete with other polymer composites with inorganic fillers. For example, in the study by [11], the thermal conductivity of composites with SiC particles ranged from 0.52 to 0.60 W/m·K, which is close to the values obtained for RM. This confirms that RM is an effective filler for creating thermally conductive composites, while Pa2 provides materials with reduced thermal conductivity for thermal insulation applications.

The analysis showed that the results of calculations using the mentioned theoretical models somewhat diverge from the experimental results. Therefore, it was reasonable to build mathematical models using the obtained experimental results, which are presented in Table 3. These models should account for both the filler content (×1) and the presence of porosity (×2). Considering this, the chosen variable parameters were the volumetric concentration of filler and total porosity. The correlation analysis shows high correlation coefficients between the selected parameters and the thermal conductivity of the composite (y):

Rx1, y = 0.956, Rx2, y = 0.971 for Latex 2012 + RM,

and

Rx1, y = 0.998, Rx2, y = 0.998 for Latex 2012 + Pa2.

This indicates the possibility of building a linear approximation of the obtained experimental results.

Using the multivariate version of the least squares method [20], mathematical models were obtained, which have the form (Equation 5):

$$y = a_0 + a_1 \times x_1 + a_2 \times x_2 \qquad (5)$$

The coefficient values are presented in Table 3, and the approximation results and their errors (Δ) are shown in Table 4.

Table 3 – Coefficients of Equation (5)

Coefficients	Latex 2012 + RM	Latex 2012 + Pa 2
a_0	0.7074	0.3411
a_1	– 0.0056	0.0032
a_2	0.0062	– 0.0014

Table 4 – Results of the approximation of the dependence of thermal conductivity on filler concentration and total porosity

Composition of PMC	x_1	x_2	y	y^*	Δ,%
Latex 2012 + RM	45.2	10.46	0.533	0.533	0.04
	57.3	29.17	0.566	0.566	0.02
	69.2	40.84	0.570	0.571	– 0.25
	75.3	47.56	0.580	0.579	0.19
	47.0	23.01	0.460	0.459	0.06
Latex 2012 + Pa 2	59.0	28.19	0.490	0.491	– 0.20
	70.8	35.78	0.520	0.518	0.33
	76.7	40.23	0.530	0.531	– 0.19

As seen from Table 4, the agreement between the experimental data and the approximated values is satisfactory, which is also confirmed by the low errors, with a magnitude of less than one percent. However, it should be noted that the constructed mathematical models can only be used for the specified composites, Latex 2012 + RM and Latex 2012 + Pa2.

4. CONCLUSIONS

1. The study confirmed that using RM and Pa2 as fillers in polymer composites is a promising approach for industrial waste recycling. It was established that these materials not only help reduce environmental impact but also allow for the creation of composites with improved functional properties..

2. Experimental studies showed that the thermal conductivity of composites based on RM and Pa2 depends on the filler concentration, their porosity, and structural characteristics. Specifically, the closed porosity of RM (26.19 %) contributes to reducing thermal resistance, resulting in higher thermal conductivity (0.58 W/m·K) compared to Pa2 (0.53 W/m·K).

3. The Hashin-Shtrikman model demonstrated better agreement with experimental data, while the Maxwell-Eucken model significantly underestimated thermal conductivity, especially for composites with high filler concentrations.

4. A mathematical model was proposed for calculating thermal conductivity, which takes into account the volume concentration of the filler and total porosity. The conducted correlation analysis shows high correlation coefficients between the selected parameters and the thermal conductivity of the composites.

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Теплоізоляційні властивості червоного шламу як функціонального наповнювача для полімерних композитів

Л. Мельник[1], О. Доній[1], В. Свідерський[1], Н. Харченко[2], Т. Говорун[2], Р. Мілоцький[3]

[1] *Національний технічний університет України «КПІ ім. І. Сікорського», 03056 Київ, Україна*
[2] *Сумський державний університет, 40007 Суми, Україна*
[3] *Канадзавський університет, 920-1192 Канадзава, Японія*

Дослідження спрямоване на вирішенні проблеми утилізації промислових відходів шляхом використання червоного шламу (ЧШ), побічного продукту виробництва глинозему, та шамоту (Ра2) в полімерних композитах з акцентом на їхню теплоізоляційну ефективність. ЧШ та Ра2 були обрані як наповнювачі завдяки їхній доступності та унікальним властивостям. ЧШ з теплопровідністю 0,2651 Вт/м·К та Ра2 з теплопровідністю 0,2643 Вт/м·К були включені в матрицю стирол-бутадієнового сополімеру (Latex 2012) для створення композитів з концентрацією наповнювача 65-90 % мас. Вимірювання теплопровідності, виконані за допомогою аналізатора ІТ-λ-400, показали, що композити з 90 % мас. ЧШ і Ра2 мали теплопровідність 0,58 та 0,53 Вт/м·К відповідно. Моделювання, проведене за допомогою моделей Хашина-Штрикмана та Максвелла-Еукена, підтвердило придатність цих підходів для прогнозування теплопровідності систем з високим вмістом наповнювача. Отримані результати підкреслюють потенціал повторного використання ЧШ як ефективного наповнювача для полімерних композитів, що сприяє зниженню негативного впливу на навколишнє середовище та розробці матеріалів з високими функціональними характеристиками.

Ключові слова: Утилізація відходів, Полімерні композити, Теплопровідність.