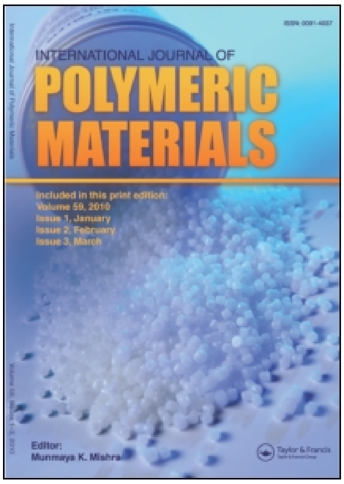

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Effect of Nickel-Cobalt-Zinc Ferrite Filler on Magnetic and Thermal Properties of Thermoplastic Natural Rubber Composites

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A sample of $Ni_{0.25}Co_{0.25}Zn_{0.5}Fe_2O_4$ ferrite was prepared by a double-staged sintering method in air. Thermoplastic natural rubber (TPNR) was prepared by melt blending of natural rubber (NR), liquid natural rubber (LNR), and high density polyethylene (HDPE) in an internal mixer Brabender Plasticorder PL 2000. Magnetic polymer composites were prepared from the ferrite and TPNR matrix using the same melt blending method at 135°C with mixing rate of 50 r.p.m. for 12 min. The fillers were varied from 5 to 30 weight percent. A uniform dispersion of the filler in the matrix was confirmed by thermogravimetric analysis (TGA). The density of the composites was determined using densitometer MD 200S. Magnetic properties were studied using a vibrating sample magnetometer (VSM) at room temperature (25°C). The results show that magnetization (M), saturation magnetization (M_S), remanent magnetization (M_R), initial susceptibility (χ_i) and initial permeability (μ_i) increase with increasing filler content at all compositions. The composites can be classified as soft magnetic materials as their coercivities are in the range of 30–36 Oe. The differential scanning calorimetric (DSC) results indicate that the glass transition temperature (T_g) and the melting point (T_m) of

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all the composites are independent of the filler content. The thermal conductivity of the composites was found to be in the range of 0.26 to 0.52 $W m^{-1} K^{-1}$.

Keywords: coersive force, hysteresis, magnetic polymer, magnetic properties, magnetization curve

INTRODUCTION

In recent years, demand for magnetic materials has increased steadily due to a progressive development in home-use electrical applications, audio equipments, electronic appliances, and communications. Metallic and ceramic magnets are not readily machinable. In order to overcome this disadvantage, polymer magnets are beginning to attract attention by many researchers. Magnetic polymer composites, in which small particles of magnetic materials are suspended in nonmagnetic matrix or binder, are one of the examples that combine the favorable properties of the magnetic materials with those of the polymers [1–2].

Metal powder fillers, which have been frequently used in polymers, were seen to influence the electrical conductivity, magnetic permeability, and thermal conductivity of the composites. The usefulness of metal powder-filled polymers depends on their physical properties, which are subject to the type and percentage of the filler materials. Magnetic polymer composites, which are prepared by traditional methods, offer significant advantages in term of shaping and cost compared to their metallic or ceramic counterparts. The resulting composite materials can be shaped by a conventional molding process such as injection molding, to obtain magnetic parts of complex shapes [3–4].

This study focused on magnetic and thermal properties of some nickel-cobalt-zinc (NiCoZn) ferrite-thermoplastic natural rubber composites as a function of filler content ranging from 5 to 30 wt%.

EXPERIMENTAL METHODS

Filler and Matrix

The ferrite powder with chemical composition of $Ni_{0.25}Co_{0.25}Zn_{0.5}Fe_2O_4$ was prepared by a conventional double sintering technique from high purity powder of NiO (99.998%), CoO, ZnO (99.99%), and Fe_2O_3 (99.99%), which were supplied by Alfa Aesar, A Johnson Matthey Company. The oxides in stoichiometric proportion were weighed, mixed, and ground thoroughly for 2 h. The mixture was then calcined at 1030°C for 6 h in the HTC 14/3 Carbolite furnace. The prereacted mixture was sintered at 1230°C for 15 h before it was slowly cooled to room temperature. The ferrite was then reground to obtain particles of about 3 μm in size.

The matrix was prepared from natural rubber (NR), liquid natural rubber (LNR), and high-density polyethylene (HDPE) in the weight ratio of 5:1:4. The NR and HDPE were supplied by Rubber Research Institute Malaysia (RRIM) and Mobil, respectively. The LNR, which is the compatibilizer for the mixture, was prepared by a photochemical oxidation process.

Preparation of the Composite Samples

Magnetic composites were prepared by blending the magnetic filler with the polymeric mixture in a mixer. Thermoplastic natural rubber (TPNR) composites with filler concentration in the range of 5 wt% to 30 wt% were prepared by melt blending in the internal mixer (Brabender Plasticorder P-L 2000). Blending was carried out at mixing speed of 50 r.p.m. at 135°C for 12 min. The ferrite powder was added into the mixer 3 min after the blending started. Once a homogeneous mixture was assumed, the composite was removed and subsequently compressed at 140°C with 8 kN pressure to produce sheets of about 3 mm thickness using a hot press (Carver laboratory). The specimens for magnetic measurements were compression molded into spheres of about 3 mm in diameter.

Measurements

A Shimadzu TGA-50 thermogravimetric analyzer was employed to confirm the uniformity in the dispersion of the NiCoZn filler in the matrix and to investigate the thermal stability of the composites. All the samples were heated under atmospheric pressure from 20°C to 600°C with a heating rate of 20°C min^{-1}.

The density of the composites was determined using an electronic densitometer (Model MD 200 S) based on Archimedes principle in which the determination of relative density is based on the density of water at 4°C (1 g/cm^3).

The magnetic properties of the composites were measured using a vibrating sample magnetometer (VSM model LDJ 9600) at room temperature (25°C). The measurement was carried out in a maximum field of 5 kOe.

Glass transition temperature of the composites were measured using differential scanning calorimeter (DSC model 822^e) under atmospheric conditions. Thermograms were traced from –110°C to 150°C at heating rate of 10°C min^{-1}.

Thermal conductivity of the composites were determined using a modified version of the Lee's Disc Technique. The thermal conductivity of the samples derived from the one-dimentional heat equation for dynamic method is given by Reference [5]:

$$k = \frac{L}{a}\left[\left(\frac{\tau}{C}\right)\left\{1 + \frac{T_C - T_\infty}{T_\infty - T_0}\right\}\right]^{-1}$$

where L is the sample thickness, a (>> L) is the cross-sectional area of the sample, τ is the time taken so that $T_C - T = 1/2(T_C - T_0)$, T_C is the temperature of block B, T is the steady temperature of block A for a given time t, T_0 is the temperature that corresponds to t = 0, T_∞ is the steady temperature of block B and C is the heat capacity of block A.

RESULTS AND DISCUSSION

The percentage of the NiCoZn filler content in the TPNR matrix from TGA is shown in Table 1. The thermograms for all composites are shown in Figure 1. The diagram shows that the samples exhibit good temperature stability below 300°C. It can be seen that the composites show two-step weight loss mechanism [6]. The first degradation occurs at temperatures between 340°C and 440°C corresponding to the NR degradation. The second degradation occurs at temperatures in between 460°C to 520°C corresponding to the HDPE degradation.

The results of the density measurements for the composites are shown in Figure 2. The results indicate that the density of the composites increases with increasing filler content. The magnetization curves for pure NiCoZn ferrite and the composites with different filler contents are shown in Figure 3. The saturation magnetization (M_S) increases with increasing filler content. The Ni–Co–Zn ferrite filler has a strong influence on the magnetization because of the positive magnetic interaction between the dipoles of neighboring atoms. Within the grain structure, a substructure composed of magnetic domains is produced. When magnetic field is first applied, the magnetization initially increases slowly, then more rapidly as the domains begin to grow through domain wall motion. Later, the magnetization is slowly increasing as the domains eventually rotate to reach saturation where the dipoles are optimally oriented [7]. The variation of

TABLE 1 Percentage of NiCoZn Filler in the TPNR Matrix

Nominal NiCoZn content (wt%)	NiCoZn content from TGA (wt.% ± 0.01)	μ_i (±0.01)	χ_i (±0.001)	M_S(emu/cm^3) (±0.05)	M_R(emu/cm^3) (±0.05)	H_C(Oe) (±0.05)	H_S(Oe) (±5)
5	5.79	1.03	0.003	2.89	0.11	36.5	3300
10	11.19	1.08	0.006	5.97	0.22	33.0	3150
15	15.61	1.11	0.008	9.78	0.35	34.5	3050
20	20.36	1.17	0.014	15.28	0.46	34.0	3000
25	26.03	1.19	0.015	19.91	0.68	36.0	2950
30	30.57	1.28	0.023	25.96	0.95	29.7	2900
100		23.15	1.762	342.00	10.80	5.35	1550

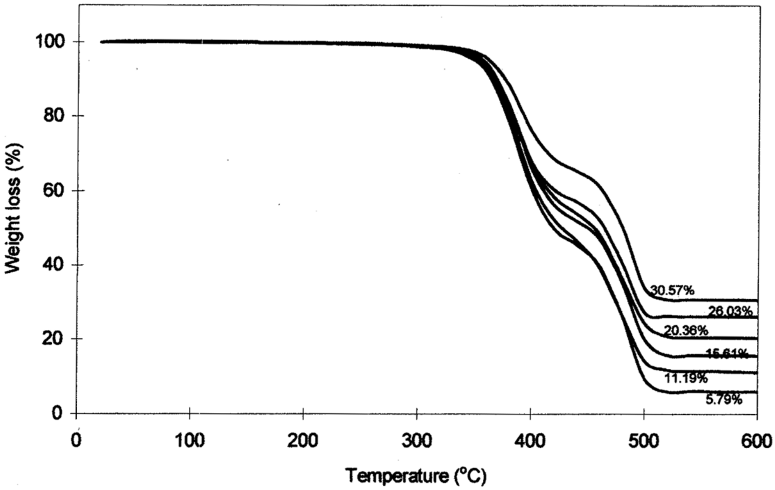

FIGURE 1 TGA termogram of the composites with different filler contents.

the magnetic susceptibility (χ_i) and initial permeability (μ_i) with filler content are shown in Figure 4. A linear increase of χ_i and μ_i for filer content <15 wt% is in according to the relation $\mu(\phi) = 1 + A\phi$, where

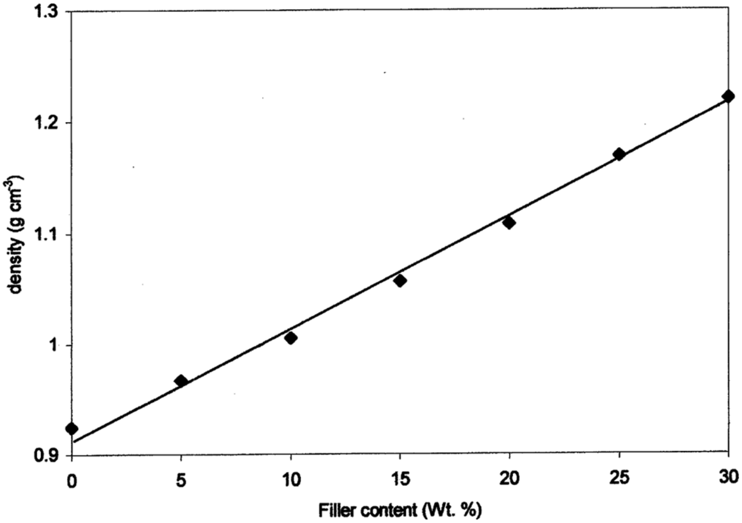

FIGURE 2 The experimental density for the composites with different filler contents.

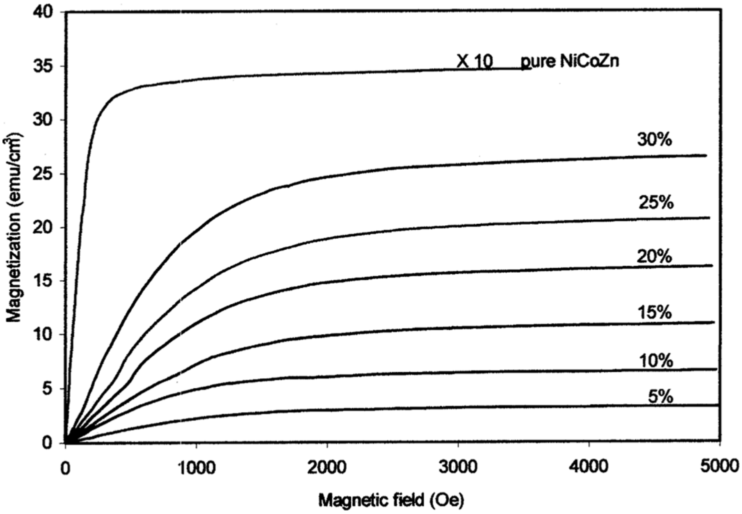

FIGURE 3 Initial magnetization curve for the composites with different filler contents.

$\mu(\phi)$ is the magnetic permeability of granular composites, ϕ is the volume fraction of the filler, and A is a coefficient dependent on magnetic properties, geometry, and volume of the filler. The results agreed well with other magnetic polymers reported by others researchers [8–10].

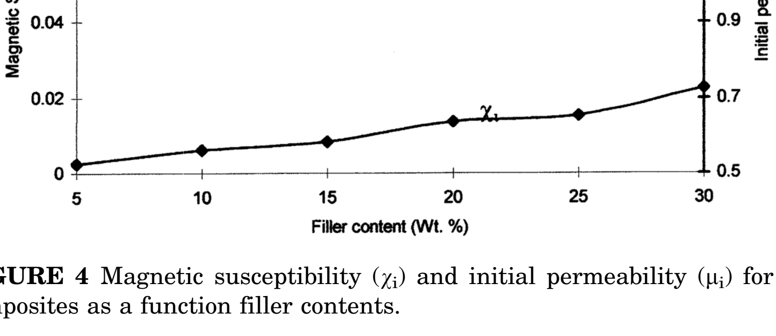

FIGURE 4 Magnetic susceptibility (χ_i) and initial permeability (μ_i) for the composites as a function filler contents.

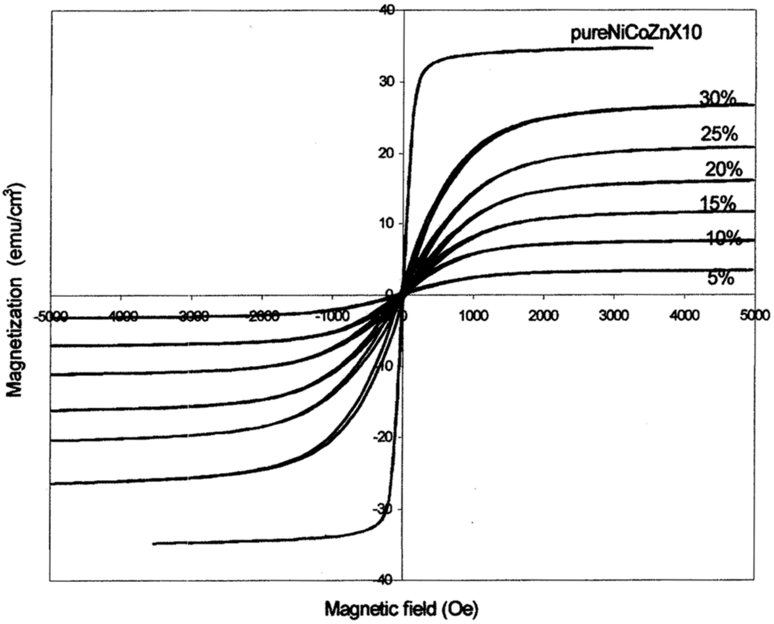

FIGURE 5 Hysteresis curve for the composites with different filler contents.

The coercive force (H_C) and remanent magnetization (M_R) for all the samples were determined from magnetic hysteresis curves, shown in Figure 5. Incorporation of the ferrite into TPNR decreases the coercive force of the composites, as shown in Table 1. Figure 6 shows that M_R and M_S increase with increasing filler content. These results agree with those reported by [11] on barrium ferrite filler in a thermoplastic natural rubber and magnetic silicone rubbers [12]. A slightly higher increment is observed around 15 wt% ferrite content.

Figure 7 shows that H_C is almost constant for different filler contents, whereas the saturation magnetic field (H_S) decreases slightly. The average value of H_C is about 34 Oe. A small coercive field indicates that domains can be reoriented with a small magnetic field. A small coercive field allows these composites to be use in low-loss high frequency applications, wherein the dipoles can be aligned at exceptionally rapid rates. A small hysteresis loop causes these composites to minimize power losses by heating if eddy currents are produced [7]. A small remanent magnetization indicates that magnetization diminishes when the external field is removed. These characteristics also lead to a small hysteresis loop, as shown in Figure 5, therefore minimizing energy losses during operation [7].

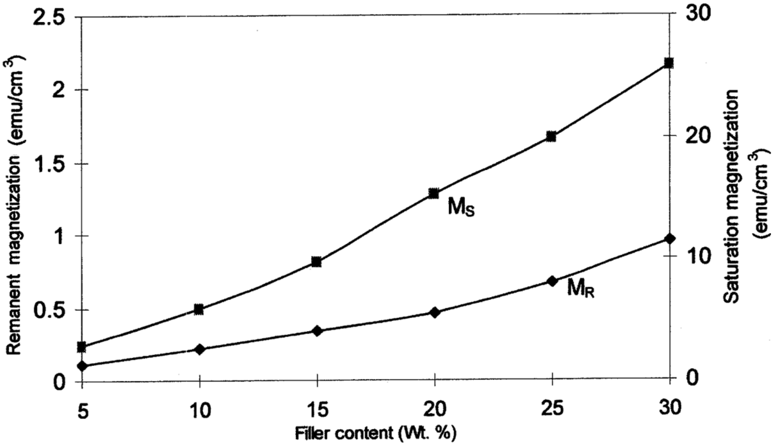

FIGURE 6 Saturation magnetization (M_S) and remanent magnetization (M_R) for the composites as a function of filler contents.

Most semicrystalline polymers are characterized by two transition temperatures. They are T_m, the melting temperature of the crystalline domains and T_g, the temperature at which the amorphous domains of the sample undergo glass transition [13]. The specific heat (C), melting temperature (T_m), and glass transition temperature (T_g) for the composites over the experimental temperature range are shown in

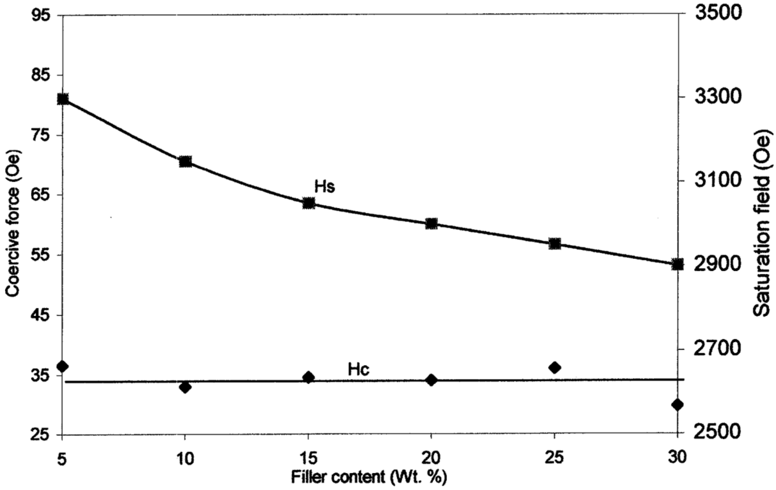

FIGURE 7 Coercive force (H_C) and saturation field (H_S) for the composites as a function of filler contents.

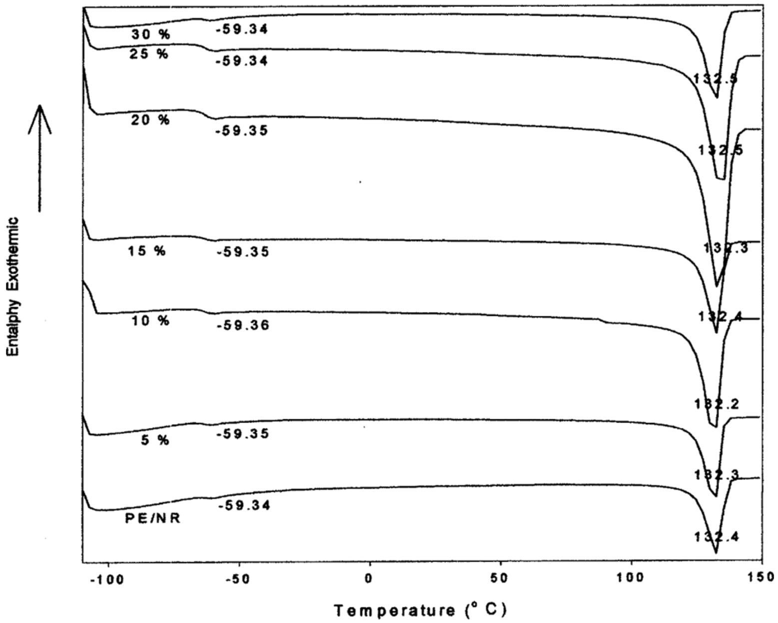

FIGURE 8 DSC termogram of the composites with different filler contents.

Figure 8. The melting process for the composites occurs in between 110°C and 140°C with the endotherm peak at 132°C. A constant T_g and T_m for all samples suggests a poor interaction between the matrix and the magnetic particles [2,7]. T_m and T_g were found to be 132°C and -59°C, respectively, for all samples.

Figure 9 shows the variation of thermal conductivity for the composites. It can be seen that thermal conductivity increases with increasing filler content. The values of thermal conductivities for the composites with low filler contents ($<5\%$) are almost the same as that of the pure TPNR. In these composites the magnetic particles are homogeneously distributed in the matrix and are not interacting with each other [3]. Energy is transferred only by vibrations and movements of the polymer chains. This condition agrees with Maxwell model $k_c = k_m\{k_f + 2.k_m + 2.\phi.(k_f - k_m)/k_f + 2.k_m - \phi.(k_f - k_m)\}$, where k_c, k_m, and k_f are thermal conductivities of composite, matrix, and filler, respectively, and ϕ is the volume fraction of filler. At higher filler contents ($>20\%$) the Agari and Uno model [14], $\log k_c = \phi.C_2.\log k_f + (1 - \phi).\log(C_1.k_m)$ predicts quite well the thermal conductivities in this region where C_1 is a measure of the effect of the particles on secondary structur of the polymer and C_2 measures

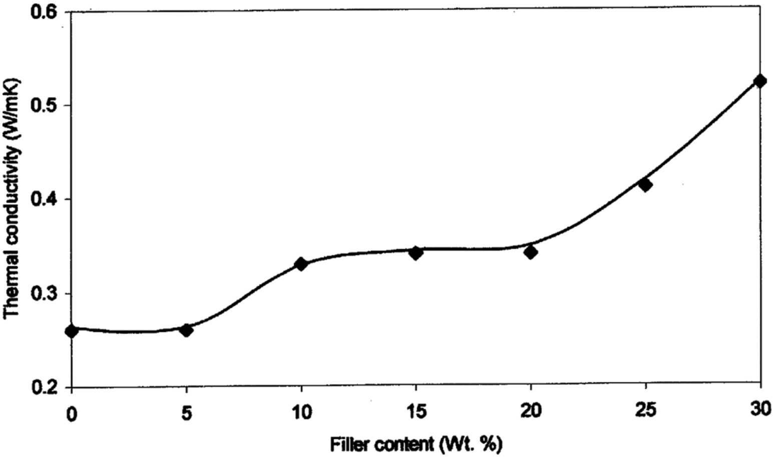

FIGURE 9 Thermal conductivity for the composites with different filler content.

the ease of the particles to form conductive chain. The filler particles begin to touch each other and form agglomerates and conductive chains in the direction of heat flow, resulting in a rapid increase in thermal conductivity of the composites.

CONCLUSIONS

The homogeneity of the NiCoZn filler in the TPNR matrix indicates the suitability of the temperature, time, and rotor speed used in the blending process. The density of the composites increases with increasing filler content. The magnetic properties of the composites were found to depend on the concentration of the magnetic filler. The saturation magnetization, remanent magnetization, initial susceptibility, and initial permeability increase with increasing filler content. The small value of coercive force, H_C ($<10^2$ Oe) and the narrow hysteresis loops indicate that these composites are magnetically soft. The glass transition temperature (T_g) and the melting point (T_m) for all the composites were found to be at -59°C and 132°C, respectively. The thermal conductivity of the composites was found to be in the range of 0.26 to 0.52 $\mathrm{W\,m^{-1}\,K^{-1}}$.

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